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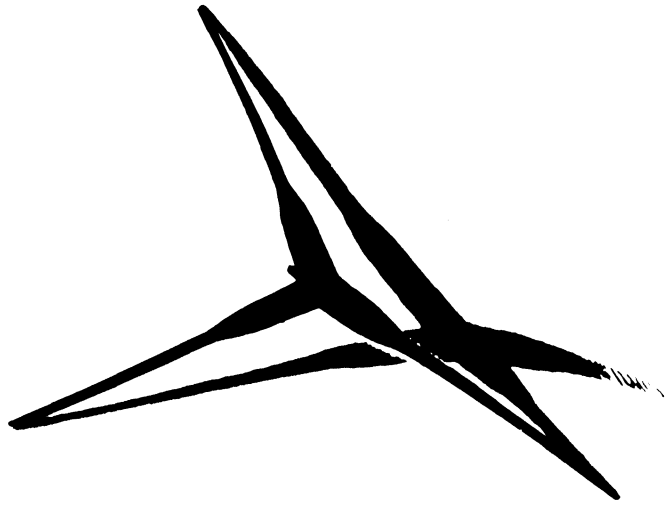
New world chemistry. 1953

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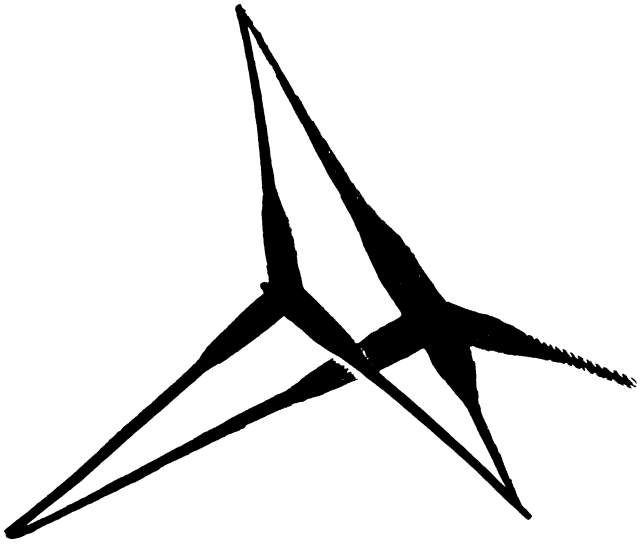
NEW WORLD OF CHEMISTRY

SCIENCE IN THE SERVICE OF MAN

NEW WORLD OF CHEMISTRY



BY
BERNARD JAFFE



SILVER BURDETT COMPANY
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MEN OF SCIENCE IN AMERICA
OUTPOSTS OF SCIENCE
CRUCIBLES
CHEMICAL CALCULATIONS

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NEW WORLD OF CHEMISTRY was first published in 1935 and completely revised in 1942 and 1947. Minor revisions have been made every two or three years to keep the book up-to-date. This 1955 edition is an extensive revision. The text has been largely rewritten, newly designed, newly illustrated.

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TO THE TEACHER:

For success and satisfaction in modern living, the citizen must understand and appreciate the scientific aspects of his environment and the role of science in the development of civilization. He must base his everyday thinking and action on the best information available with a full realization of why the methods of science are superior to other methods of obtaining information. Finally, the citizen must be ready to use scientific knowledge for the good of all. NEW WORLD OF CHEMISTRY is designed to help students achieve these objectives. It is a textbook for young people who are learning to be citizens.

This 1955 edition of NEW WORLD OF CHEMISTRY has been brought abreast of recent chemical developments and discoveries. Striking advances have been made in nuclear energy, petrochemistry, metallurgy, textiles, and plastics. The chapters dealing with these subjects have been thoroughly revised to take these changes into account.

The basic plan of the book, which has been so widely accepted, has not been altered. But within that framework many changes have been made. Diagrams have been completely redrawn and enlarged. New illustrations have been provided. The index has been expanded to make the text an even more effective source book. Despite the addition of new materials, however, the book as a whole has been shortened.

Perhaps most important of all, the chapters dealing with the basic theory and mathematics of chemistry have been rewritten. Formulas, valence, equations, and problems have been given a new and expanded treatment. The chapters presenting the electron theory, ionization, and the study of gases have been rewritten to achieve a maximum of clarity. While the concepts of chemistry themselves cannot be simplified,

they can be made easier to understand by better arrangement and greater clarity of language. Clarity of writing has been a major goal of this substantial revision of NEW WORLD OF CHEMISTRY.

The book has been written with the purpose of *getting ideas across to the student.* With the exception of necessary technical terms, the vocabulary consists of familiar words. The style is direct, the sentences and paragraphs are short. Much of the illustrative material has been drawn from the student's own environment. Consumer aspects of chemistry and the chemistry of common things are stressed at the same time that requirements of modern courses of study and examining boards are fully met.

Selected materials from the history of chemistry arouse interest and enable the student to see how fundamental scientific ideas have developed and expanded. They reveal that chemical theories and principles are descriptive generalizations of man's growing experience in trying to understand his world. Finally, the historic materials help students see how scientific discovery has affected modern civilization and how the needs of society constantly stimulate scientific research.

The author wishes to express his thanks to the many teachers, chemists, and industrial, educational and governmental organizations that have generously made suggestions, checked the accuracy of materials, and provided illustrations and data for this new edition. He also wishes to acknowledge his indebtedness to his son, Dr. Lionel F. Jaffe, and to Lee Deighton and John H. Williamson of Silver Burdett Company whose careful planning, sound judgment, and never-failing enthusiasm have made this cooperative effort extremely pleasant and, it is hoped, effective.

Bernard Jaffe

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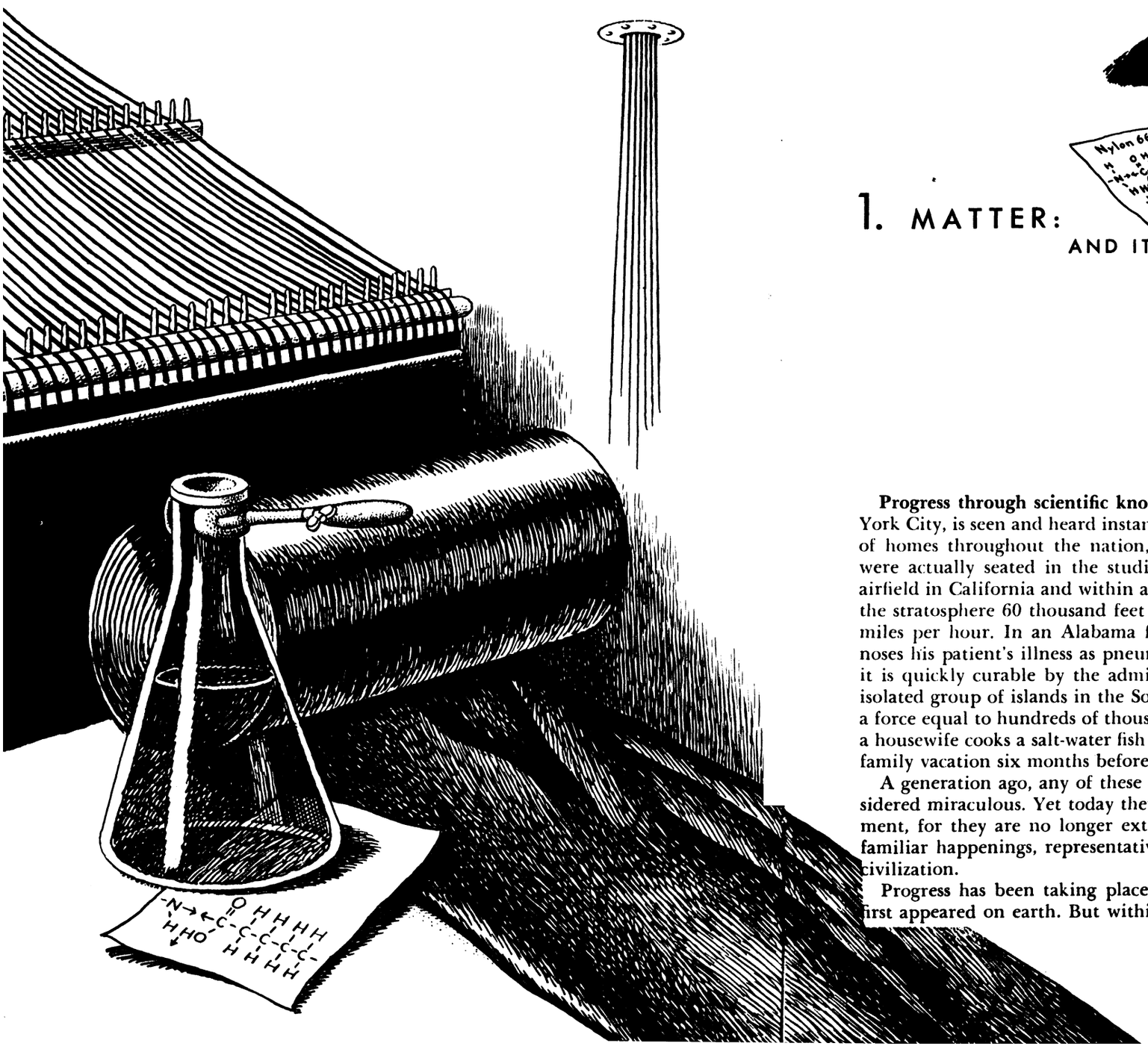
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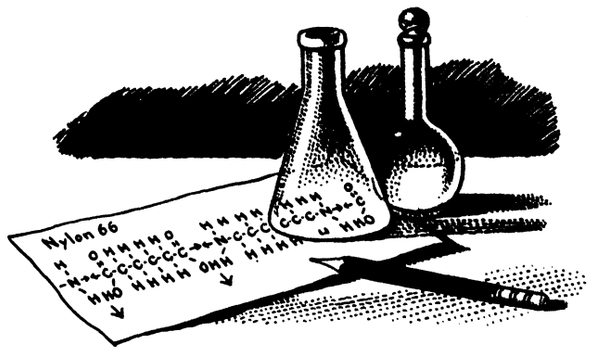
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1. MATTER: AND ITS CHANGES

. . . We must trust in nothing but facts. These are presented to us by nature and cannot deceive. We ought in every instance to submit our reasoning to the test of experiment. It is especially necessary to guard against the extravagances of imagination which incline to step beyond the bounds of truth. Antoine Laurent Lavoisier, 1743–1794

Progress through scientific knowledge. A play, presented in New York City, is seen and heard instantly and simultaneously in millions of homes throughout the nation, as clearly as if its vast audience were actually seated in the studio. An airplane takes off from an airfield in California and within a few minutes is screaming through the stratosphere 60 thousand feet above the earth at more than 700 miles per hour. In an Alabama farmhouse, a country doctor diagnoses his patient's illness as pneumonia, and assures the family that it is quickly curable by the administration of certain drugs. In an isolated group of islands in the South Pacific, a bomb explodes with a force equal to hundreds of thousands of tons of dynamite. In Iowa, a housewife cooks a salt-water fish caught by her husband during the family vacation six months before and two thousand miles away.

A generation ago, any of these occurrences would have been considered miraculous. Yet today they arouse no unusual public excitement, for they are no longer extraordinary events. To us they are familiar happenings, representative of what we call the progress of civilization.

Progress has been taking place in some measure ever since man first appeared on earth. But within the past two or three centuries,

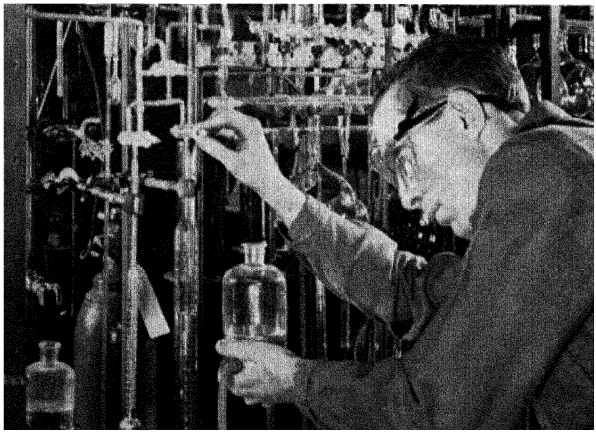
civilization has progressed much more rapidly than in all the previous thousands of years of man's history, with the most radical changes occurring within the past few decades. In the years ahead, civilization will continue to progress. More of the "incurable" diseases will be conquered; methods of transportation and communication will be further improved; the force which gives the atomic and hydrogen bombs their great destructive power will be harnessed for man's welfare; our everyday lives will be made safer and more comfortable.

What enables us to perform acts today which were unheard of just a few short years ago? How may we be certain that the future will bring forth new wonders? The answer to both of these questions lies in the knowledge we now possess concerning the nature and behavior of those things which make up the entire world and all its living creatures. In short, the answer lies in our scientific knowledge.

Scientific knowledge is not something which has been created recently. It has been gathered by many men, known and unknown, during all of man's centuries on earth. Just as a snowball rolling downhill is at first small and slow moving, but in time increases both its size and speed, so it has been with scientific knowledge. In his early days on earth, man knew a limited number of scientific facts, increasing the number with painful slowness as the centuries went by.

But gradually, almost imperceptibly, the number of facts became larger and their rate of discovery quickened. Within the past few hundred years, particularly during the twentieth century, they have been acquired at a prodigious rate. New scientific advances are announced almost daily. A rolling snowball must finally come to rest at the foot of a hill, but there is no indication that scientific knowledge will ever cease to grow. Nor does there appear to be any limit to the progress civilization can make through the application of this knowledge.

Linde Air Products Company



(left) The highly-trained professional chemist makes many important contributions to civilization.

(right) The lessons of the student chemical laboratory find many useful applications in daily life.

Chemistry has helped make a new world. No single science is entirely responsible for our modern civilization. But chemistry ranks high among those which are considered the most important because it is a *basic science*, essential to virtually every scientific study regardless of its nature. In the manufacture of every product of our great industrial civilization, chemistry plays a vital role.

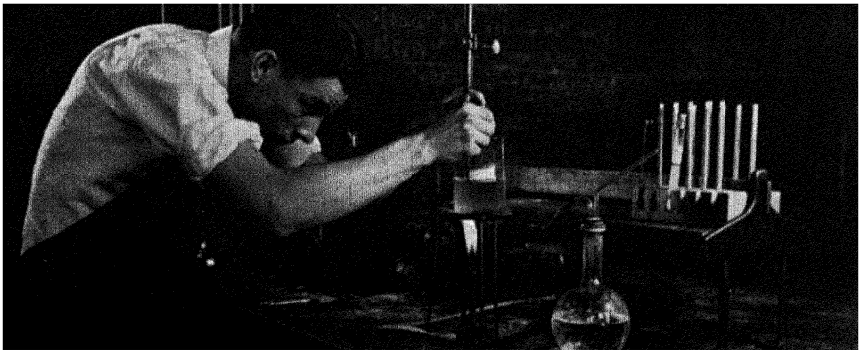
The work of the chemist affects all of us — the physician, the dentist, the engineer, the public health employee, the soldier, the gas station attendant, the clerk, the housewife, the worker of factory, mine, or farm, the schoolboy and the schoolgirl.

While the achievements of modern chemists seem at times to be the result of some kind of magic, nothing could be further from the truth. Chemical "magic" is the result of years of study, hard work, and struggle; of burning the midnight oil when it seems a problem has no solution; and, finally, of a thrilling moment when everything hinges on one more experiment and the world spins 'round in a test tube or flask. Nor are all experiments rewarded with striking success. Sometimes they fail and the chemist must begin, wearily, but with determination, to retrace his weeks or months of work in an attempt to discover where he went astray.

Chemistry is an intensely interesting and rapidly changing field and, like all sciences, its roots extend far back into history. Today's chemist owes a great debt to the men who, over many centuries, added to the knowledge he now uses in performing his "miracles." The lives of those men, how they accumulated information and how that information is applied in modern chemistry is a thrilling story, filled with suspense and drama. It is the story told in NEW WORLD OF CHEMISTRY.

Although we live in the "scientific age," we still see, everywhere in the world, superstitions and prejudices, hunger and disease. To correct these conditions, we must use in the outside world what we learn in the classroom. We must base our actions upon scientific knowledge, always bearing in mind, however, that we know little with absolute finality.

Board of Education, City of New York



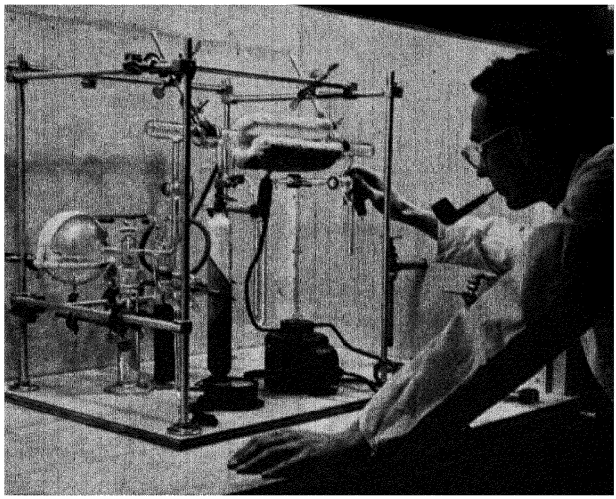
We must also remember that science is a two-edged sword which may be used either to serve man or to destroy both him and his works. Although the spirit of science is essentially democratic and constructive, we alone can prevent its becoming an oppressively tyrannical and horribly destructive weapon. Not many of us may ever become *professional scientists,* the men and women who work in the great laboratories of industry, government, and education. But we can all become scientists in an even broader sense.

We can act on the most dependable information available, using the searching light of science to wipe out prejudices, half truths, and incorrect beliefs. The methods and knowledge of science are in our hands. We can live more fully, more satisfyingly, more comfortably, more humanely, and more intelligently *only* by using them. Look forward to the future with the assurance that, through the efforts of each of us, science *can* and *will* serve mankind.

What is the world made of? For thousands of years, men have tried to find out what the material things of the world are made of. Socrates (sŏk'rȧ-tēz), a learned Greek teacher who lived in the fifth century B.C., believed that he might discover the answer to this question simply by thinking about it. One other Greek teacher is said to have put out his eyes so that his thinking might not be disturbed or influenced by what he could see about him. He wanted to give himself over completely to undisturbed thinking, or *contemplation.*

To be sure these were extreme cases. Not all the ancient teachers relied wholly on pure thought as they tried to find out what the world is made of. Some of them, of course, were influenced by what they could observe. For example, Thales (thā'lēz), who was born in Miletus in Asia Minor in 624 B.C., noticed that water nourishes crops and that it is found in large amounts in the bodies of men and other living things. Hence he *speculated,* or guessed, that water was the basic substance from which all material things were made.

The speculations of Thales were more important to him than his observations. It is said that one day, as he was walking along absorbed in deep thought and looking up at the sky, he fell into a well. Thratte, a housemaid, saw the accident and laughingly said: "In his zeal for things in the sky, he does not see what is at his feet." No doubt, most of you know how easy it is to become so absorbed in trying to solve a problem that you become "blind" to common, everyday things and may even be called "absent-minded." In a similar manner, it is possible to become so engrossed in thinking about a problem that simple methods of solving it do not occur to the thinker. Some of the ancient teachers were victims of this "blindness."

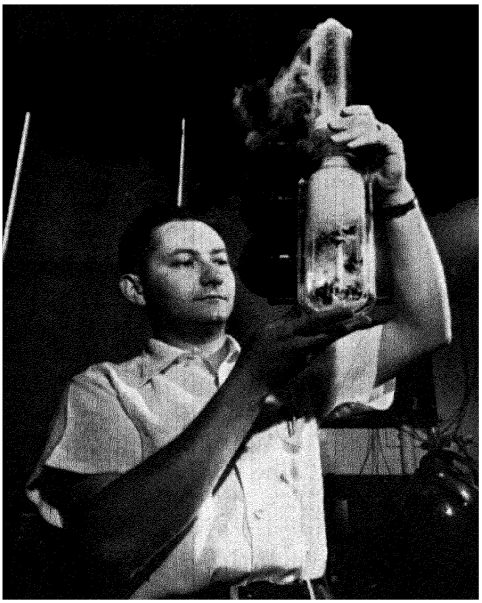


Careful experiments and constant observation are essential to the chemist's study of matter.

Many of Thales' conclusions concerning what the world is made of were wrong. He and other scholars like him depended too much upon what is now called *abstract thought*, and altogether too little upon *careful experimentation* and *observation*. If they had depended less upon abstract thought and more upon observation and experimentation, accurate information would have accumulated much more rapidly. However, even though many of their conclusions were wrong, their work was of value. They were *thinking* about the things that surrounded them, which was more than was being done by most of the people who lived at that time.

Of course, in answering any question, careful thinking is necessary, but it must be thinking based upon *accurate facts*, which can come only from careful observation. Many of the ancient teachers were fine thinkers. They began with what they knew, or thought they knew, and reasoned logically to a conclusion. Many of their conclusions were false, however, because they based their thinking on inaccurate or incomplete information.

Ours is a complex world. This age-old search to find out what the world is made of is not over. Far from it. You, living 2500 years after Thales, know that water is not the basic substance from which the world is made. Yet, if you were asked to name all the different materials that make up the world, you would doubtless think you had been given an impossible task. Imagine listing all the materials that make up the rocks and soil beneath your feet, the vast expanse of water that covers three-quarters of the earth, the multitude of living things, the deep envelope of air that surrounds our globe, and the billions of stars, some so far from the earth that their distances stagger our imagination!



At extremely low temperatures, a gas may become liquid or even solid. This flask contains liquid helium and solid air. Because the frozen air at a temperature of −340° F. is much "hotter" than the liquid helium at −452° F., it is causing the helium to boil and overflow the flask.

Westinghouse Electric Corporation

Matter exists in three states. Even though you could not name all the substances that make up our world, you would at least know that some of them exist as *solids*, others as *liquids*, and still others as *gases*. In fact, probably you know that *matter*, which is *anything that has weight and takes up space*, occurs in one of three conditions — solid, liquid, or gaseous. In which of these conditions, or *states of matter*, any substance exists depends partly on the nature of the substance itself, partly on its temperature, and partly on the pressure.

Many substances exist in all three states, depending on the temperature. For example, water (a liquid) may be changed to ice (a solid) by cooling, or to water vapor (a gas) by heating. Changes from one state of matter to another by heating or cooling are very common. Iron, which we know as a hard gray solid, is melted in foundries and changed to a shimmering, silvery liquid. If its temperature is raised high enough, gaseous iron vapor is boiled off. While iron vapor is something with which most of us are not familiar, astronomers know that iron exists normally in the gaseous state in certain extremely hot stars.

What is a physical change? When water changes to steam or to ice, only its form has been changed. Steam is a form of water; ice is also a form of water. When a piece of limestone is pulverized, only its form has been changed. The small pieces are still limestone, although their form differs from that of the huge chunks in which they came from the quarry. These changes in the water and in the limestone have been in form only. Neither the water nor the limestone

was changed into another substance. *A change in which the original substance does not change into one or more other substances is a physical change.*

Break a piece of wood in two. Heat a piece of iron wire in a vacuum by passing an electric current through it. The heat produced causes the wire to glow, but, after the current is shut off, the wire returns to its original condition. In each case, what kind of change has occurred?

How does a chemical change differ from a physical change? You know that when a piece of paper burns, it is completely and radically changed. The hot gases that are given off and the ash that is left behind do not in any way resemble the original substance. When gasoline is burned in an engine, the resulting substances are entirely different from the liquid gasoline. Animal tissue is totally different from the vegetable substances from which it is made. The dull tarnish on silverware differs completely from the gleaming silver.

In these changes more than the form of the original substance was altered. In each case the composition of the original substance changed. Some form of energy, usually heat, was either liberated or absorbed. *A change in which the original substance disappears (changes) and new substances are formed is a chemical change.*

Place a small quantity of sugar in a beaker or other glass vessel. On the sugar, pour a small quantity of *sulfuric acid* (a liquid which is discussed in detail in Chapter 13). The white sugar changes to a black spongy substance, which cannot be *dissolved,* or absorbed, in water. What kind of change has occurred?

Chemistry is the science that deals with the composition of matter and with the many chemical changes which matter undergoes.

How is a substance identified? Telling one substance from another is called *identifying a substance.* When you try to identify a substance or to find out whether a substance has undergone a chemical or physical change, you need to know its *characteristics* — what the substance is like, and how it acts with other substances.

We find out what a substance is like by asking such questions as: What is its color? its odor? its taste? Is it a solid? a liquid? a gas? At what temperature does it boil? At what temperature does it freeze? How hard is it? Does it conduct electricity? The answers to these questions are characteristics that enable us to describe and identify a substance. These characteristics of a substance are called its *physical properties.*

We find out how a substance acts with other substances by placing it in contact with these substances and observing what occurs. We

ask also how sunlight, electricity, and heat affect it. Our observations and the answers to these and other questions give additional characteristics that enable us to describe and identify a substance. These characteristics are called the *chemical properties* of that substance.

Since two different substances *never* have exactly the same physical and chemical properties, any substance may be identified by determining these properties.

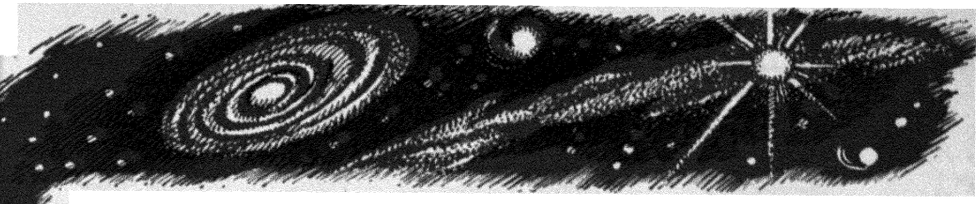
The ancients believed the world made of "four elements." But to return to our original question: What is the world made of? Guesses and speculations would be useless in attempting to answer this question. Because the ancients depended chiefly upon these procedures and also upon inaccurate and uncontrolled experimentation and observation, they made little progress in answering the question.

After Thales had suggested *water,* another man proposed that *air* might be another of the basic substances from which all matter was made. *Fire,* too, was suggested and later *earth.* Pythagoras (pī-thăg'ō-răs), an ancient Greek thinker and mathematician who lived about 600 B.C., is thought to have been the first European to express the idea that all matter was composed of these "four elements."

These conclusions seemed to be proved by the observations of the early investigators. When a stick of green wood was burned, they saw that fire was produced, water was forced out and boiled off at the ends of the stick, a smoky vapor (air) was given off, and an ash (earth) was left behind. They concluded, therefore, that all matter was made up of different amounts of two or more of these four basic, or *elementary,* substances.

The Greek thinkers, however, made a serious mistake. They failed to make enough observations of different substances. They did not make enough experiments. Consequently, their conclusions were wrong. Strangely enough, the idea that all matter is composed of "four elements" (earth, air, fire, and water) persisted until the eighteenth century and was considered correct by many otherwise well-informed persons. Even today speakers and writers often refer to the violent actions of air and water as "the fury of the elements."





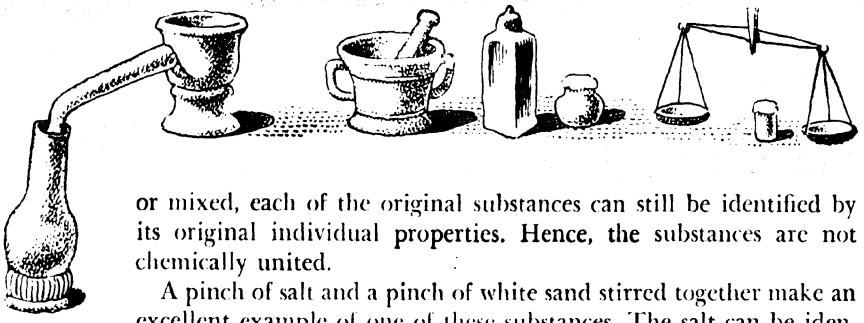
The universe is made of an even 100 chemical elements. Scientists now consider that the mountains, the oceans, the air, all living things, and even the stars and the rest of the universe are composed of simple natural substances that cannot be broken down, or *decomposed,* into simpler substances by the ordinary types of chemical change. *A substance that cannot be broken down, or decomposed, into a simpler substance by the ordinary types of chemical change is an element.*

These natural elements do not all occur on earth in equal amounts. Taken together, 20 of them make up 99.5 percent of the weight of the crust of the earth. All the other elements comprise only 0.5 percent of its weight. In all, there are 100 elements. Eight of these elements have been produced in laboratories by scientists. Probably the elements with which you are most familiar are gold, silver, iron, copper, nickel, tin, aluminum, sulfur, oxygen, carbon, nitrogen, and hydrogen. A list of all the elements is given on page 678.

What is a compound? Most of the substances we see, such as sand, chalk, cotton, table salt, and water, are not elements. Rather, each is composed of two or more elements so combined that (1) only chemical action can tear them apart, and (2) the elements of which each substance is composed can no longer be identified by their original individual properties. *A substance composed of two or more elements so combined that the elements can no longer be identified by their original individual properties is a compound.* The elements of which a compound is composed are said to be *chemically combined,* or *chemically united.*

Marble, for example, is a compound made up of three elements, carbon, calcium, and oxygen, chemically combined. The properties of a compound, such as color, odor, taste, form, and ability to dissolve in water, are nearly always distinctly different from the properties of the elements of which it is composed. For example, pure cane sugar, a sweet, white, crystalline solid which dissolves in water, is completely different from any and all of the three elements of which it is composed.

How does a mixture differ from a compound? In a compound the elements must be chemically united. But there are other kinds of substances made up of two or more elements or compounds. Al-



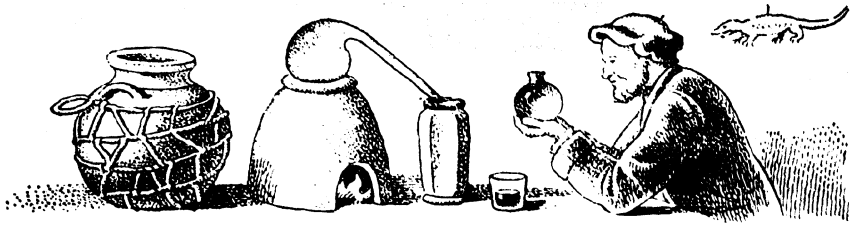
or mixed, each of the original substances can still be identified by its original individual properties. Hence, the substances are not chemically united.

A pinch of salt and a pinch of white sand stirred together make an excellent example of one of these substances. The salt can be identified by its characteristic taste and the sand by its gritty feel on the tongue and teeth. *A substance composed of two or more elements or compounds that still retain their individual properties after they have been thoroughly mixed is a mixture.* Some of the most useful substances in the world, such as soil, air, petroleum, and milk and many other foods, are mixtures.

The properties of a mixture are the same as the properties of the elements or compounds that compose it. A handful of iron powder mixed with a handful of powdered sulfur makes a mixture that resembles both the black iron and the yellow sulfur. If a magnet is passed through it, the iron clings to the magnet. If a liquid called ***carbon disulfide*** is added to the mixture, the sulfur is dissolved. But if the mixture of sulfur and iron is heated, these two elements combine, forming a compound known as *iron sulfide*. Iron sulfide does not look like either sulfur or iron. It is not magnetic and does not dissolve in carbon disulfide. The properties of this compound do not resemble those of either sulfur or iron.

Substances in certain mixtures may be separated mechanically. A mixture of salt and sand may be separated by adding water. The salt dissolves and the sand settles to the bottom. A mixture of iron and sulfur may be separated by passing a magnet through it or by adding carbon disulfide which dissolves the sulfur.

The phlogiston theory, an erroneous explanation of burning. One of man's greatest early achievements was the discovery of the use of fire. So strange did fire appear that for a long time men worshiped it. They considered it the force responsible for all creation. They pondered over its mystery and made many attempts to explain it. Early alchemists thought that fire was the result of some vague "sulfur" which burnable substances contain. But later alchemists felt the need for a better explanation — an explanation which took into account more of the facts that had been observed in burning many different substances. A statement that takes into account and attempts to explain observed facts is known as a ***theory***.



Over many centuries, alchemists, the forerunners of modern chemists, worked in vain with their crude equipment to find the secrets of prolonging life and of making gold from base metal.

About 300 years ago Becher (bĕk'ĕr), a German scientist, advanced the theory that all burnable substances contain *phlogiston* (flŏ-jĭs'tŏn), or "fire stuff." He said that when a substance burned, phlogiston left it in the form of flame. Becher thought that the ash formed when a substance burned was the substance *minus* its phlogiston. According to his theory, substances that burn readily, leaving little ash, contain a great deal of phlogiston, while substances that burn with difficulty and leave much ash contain little. The phlogiston theory was the first great theory in chemistry.

The phlogiston theory *seemed* correct to the alchemists because of certain observations they had made. A rising candle flame seems to tug at the wick. To the alchemists this suggested that phlogiston was escaping from the burning candle. When a small amount of powdered lead is heated in an iron spoon, it melts, burns, and forms a yellow powder. According to the phlogiston theory, this yellow powder is lead ash, or lead minus its phlogiston. Now if some way could be found to add phlogiston to this lead ash, lead should be produced again. Perhaps this could be done by heating the lead ash on some substance that contains a lot of phlogiston, such as charcoal. The charcoal might give up some of its phlogiston to the lead ash. When this experiment is performed, the final product is actually lead.

You can see that this experiment seems to prove the correctness of the phlogiston theory. Why? What mistake did the early scientists make in attempting to prove the phlogiston theory?

For more than two centuries the phlogiston theory was considered to be an accurate explanation of burning, and many of the famous pioneers of modern chemistry, among them Priestley (prēst'lĭ) and Scheele (shā'lĕ) were its ardent supporters.

The first clue to the true explanation of burning. Even though the phlogiston theory seemed to be upheld by experiments similar to the one with lead, other experiments showed it to be false. In these experiments the fact that many substances *increase* in weight when burned could not be explained on the basis of the phlogiston theory, for according to it, all substances *lose* phlogiston when burned, and thereby lose weight.



Lavoisier



Priestley

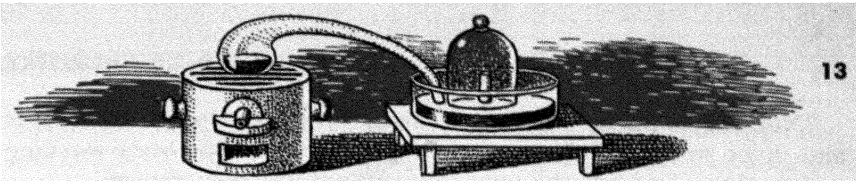
In 1774 Joseph Priestley, an English minister and amateur scientist, led the way toward a true explanation of burning by his discovery of a gas later named *oxygen*. Because of political and religious persecution, he fled from England and spent his last years in Northumberland, Pennsylvania. Priestley showed that the gas he had discovered was present in air and was closely connected with burning. Let us trace the steps that led to the discovery of the true nature of burning.

1) After his discovery of *oxygen*, Priestley, like a true scientist, did not keep his discovery to himself. While he was in Paris later on in 1774, he visited Lavoisier (là-vwà-zyā'), the most eminent chemist in France, and told him about his discovery. Priestley's information was a welcome addition to the many facts which Lavoisier had already collected regarding the nature of burning.

2) Lavoisier examined carefully all the facts that he knew about burning. He pondered over them for months, trying to formulate an accurate theory that would explain burning and be in keeping with *all* the observed facts.

3) Lavoisier was genius enough to use Priestley's work as the basis of a theory which would explain the age-old puzzle of burning. He suspected, and later advanced the theory, that when a substance burned, it increased in weight because it united with something that was present in air. Later this something was shown to be oxygen.

4) Other scientists had noticed this increase in weight when substances were burned in air. However, Lavoisier was the first to formulate a theory based on this fact. He also undertook a series of careful experiments to see whether their results would prove his theory to be correct.



Lavoisier's classic 12-day experiment which explained burning.

"I introduced four ounces of pure mercury into a [sealed] glass vessel," he wrote. "I lighted a fire in the furnace which I kept up continually for twelve days. On the second day, small red particles already had begun to appear on the surface of the mercury." When most of the mercury had been converted into a red powder, he removed the glass vessel and its contents (which he had weighed before the experiment) and weighed them again. There was *no increase* in weight.

Since the glass vessel was sealed, nothing had entered or escaped from it during the heating. Yet when he broke the seal he noticed that air rushed into the vessel. To him this inrush of air indicated that part of the air in the vessel had been used up during the heating, and had left space for more air to enter. After air had entered the vessel, he weighed it once more and determined the increase in weight. He concluded that this increase in weight equaled the weight of something in the air in the vessel that must have combined with the mercury, forming the red powder.

Lavoisier's inquiring spirit was not satisfied. He was a scientist in the most modern sense. He refused to jump to a hasty conclusion on the basis of a single experiment. He withheld drawing a conclusion until he had performed many more experiments. As a further precaution, he reversed his original experiment. He took the red powder of mercury and heated it to a higher temperature. He found that all of the red powder was changed back into mercury and that a gas was given off, which he found by a series of tests to be identical with the oxygen gas that Priestley had discovered. Hence, he concluded that it was the oxygen in the air that was responsible for burning. Of all the substances he tried, he found none that could burn without oxygen.

5) *Burning,* said Lavoisier, *is the chemical union of a burnable substance with oxygen.* Simple enough. No mysterious phlogiston, and the testimony of the most sensitive balance in Europe to support his reasoning. Thus, Lavoisier discovered the true explanation of burning.

6) Lavoisier repeated the original experiment using other substances, including tin and sulfur. He found that the results of these experiments were fully in accord with his theory. In this way his theory was given further support.

"Nothing happens without a cause," said Leucippus 2500 years ago. Ever since man first appeared on earth, he has been working constantly to find out the *why* of many natural occurrences.

What are some of these occurrences that man has tried to explain? Although these are only a few, we might include: Why does a stone fall? What is fire? Why do some substances burn while other substances do not? What makes thunder? Why can birds fly?

In asking ourselves these questions and in answering them, we use several words that probably were not used by primitive man. These words, which appear later on in this paragraph, are words whose meanings have come into rather common use comparatively recently, as scientists measure time, perhaps within the last 25,000 or 50,000 years. Let us examine the first question. Probably we would ask: What *causes* a stone to fall? By this we mean: What force causes a stone to fall, for we know that a stone will not fall unless some force acts on it, producing, we might say, an *effect*. We would answer the question: A stone falls *because* the earth pulls the stone toward its center (the force of *gravity*). As Leucippus (lū-sĭp'ŭs) implied, modern scientists and most modern people believe that every cause has an effect, and every effect has a cause. Such a relationship is known as a *cause-and-effect relationship*.

Establishing a cause-and-effect relationship is not as simple as it might seem. Early man did not have the many tools and instruments which today we use so casually in finding cause-and-effect relationships. Consequently, in attempting to explain the causes of a certain effect, early man relied on what we would now consider magic, mysticism, and superstition, but later on man learned to establish these relationships by other methods. Then, too, it is sometimes difficult to establish a cause, because often several causes taken together produce a single simple effect. Today many cause-and-effect relationships are clearly understood; but on the other hand, the causes of certain effects are not yet known, or even when known, are not thoroughly understood.

The method of deduction compared with induction. In explaining a natural occurrence, Aristotle (ăr'ĭs-tŏt''l), a well-known teacher and philosopher of ancient Greece, often made a bold and sweeping general statement. From this general statement he drew inferences and conclusions, which he thought applied in other similar cases. Aristotle's method is commonly known as the method of *deduction*.

Francis Bacon, who lived almost 20 centuries later, was the first man to make popular another method of reasoning. By a process consisting of observation, collection of facts concerning the problem,

formulation of a theory taking into account and explaining the observed facts, and verification of the theory by actual experiment. he formulated broad *principles,* sometimes called *laws.* Bacon's method is known as the method of *induction,* and today it is used widely. It is the pattern on which scientific method is based. To a great extent, it is responsible for the success of scientific method.

While the method of induction is used very widely, deduction has played its part too in the development of science. The establishment of cause-and-effect relationships, usually by the method of induction, is perhaps the greatest function of science.

What is scientific method? The method that Lavoisier used in reaching the first correct explanation of burning is an example of a pattern of action and thought used by scientists in their work. This pattern is known as *scientific method.*

Scientific method may vary according to the nature of the problem to be solved and the tools available for solving it. In general, however, the steps of the scientific method are represented by the six steps you have just traced. In brief, they may be stated as follows:

1. The collection of all available facts related to a problem
2. The open-minded checking and examination of these facts
3. The formulation of a working theory based upon these facts
4. The testing of this working theory by experiments
5. The formulation of a law, or principle, from the tested theory
6. The use of this law in concrete and specific situations

As you see, a scientific law, or principle, is a descriptive and explanatory statement, or *generalization,* that expresses what men have found to be accurate with respect to natural occurrences.

Triumph of scientific method. Lavoisier's explanation of burning was not at once accepted. Indeed, for some time it met with bitter opposition. Those who believed in the phlogiston theory attempted to adjust their theory to fit the newly discovered facts, but this could not be done. Even so, Lavoisier realized how hard it would be to

convince everyone of the truth of his own theory. He wrote: "I do not expect that my ideas will be accepted at once; the human mind inclines to one way of thinking, and those who have looked at nature from a certain point of view during a part of their lives adopt new ideas only with difficulty; it is for time, therefore, to confirm or reject the opinions that I have advanced. Meanwhile, I see that young men who are beginning to study the science (chemistry) *without prejudice or preconceived notions* no longer believe in phlogiston."

New ideas, discoveries, and new theories as a rule must overcome tradition and prejudice, but this should not discourage those who introduce them. Tradition and prejudice are found not only in the field of the natural sciences — physics, chemistry, astronomy, biology, and others — but also in the social sciences — government, economics, sociology, history, and others — in which they are likely to be even more pronounced.

Lavoisier's theory of burning finally triumphed, however. The accumulated evidence in its favor finally became so overpowering that scientists could believe nothing else. The experimental method of science had won over the strictly logical and theoretical method of the ancients. Twenty years later Lavoisier, who was an aristocrat, was beheaded during the frenzy of the French Revolution. "Until it is realized that the gravest crime of the French Revolution was not the execution of the king, but of Lavoisier, there is no right measure of values, for Lavoisier was one of the greatest three or four men France had produced." This statement, made by an eminent Frenchman, expresses the judgment of thinking men the world over.

There are no *authorities* or *dictators* in science. There are only those persons who know what men up to now have discovered; that is, there are *experts*. In all of science there is no one who can say "This theory is true." But there are many men who can say "On the basis of what we now know, this theory seems to be sound." Scientific method is a democratic method. In most cases, its theories are the outcome of a pooling of facts discovered by many workers, a cooperative effort.

Careful weighing and the law of the conservation of matter. To Lavoisier a balance was absolutely necessary. By carefully weighing all the substances entering into his experiments both before and after each experiment, he found that there was no loss of weight during the burning. The mercury plus the oxygen from the air weighed exactly the same as the red powder of mercury (mercuric oxide). "One may take it for granted," he wrote, "that in every

change there is an equal quantity of matter before and after the operation." In chemical changes we can change the form, the state, or the composition of matter, but we cannot destroy matter itself. In physical changes we can change the form or the state of matter, but we cannot destroy the matter itself.

"But," you might answer, "a candle burns until it is all gone. It becomes smaller and smaller and certainly weighs less and less." And you are right. But if we take the trouble to collect and weigh all the gases formed during the burning of the candle, we find that they weigh more than the original candle. This increase in weight is due to the oxygen with which the burning candle has combined.

"What of an oak tree," you might say. "It grows from a little acorn. Isn't matter created here?" It might seem so, but the fact that many things increase gradually in size and weight does not mean that matter has been or is being created. The oak tree does not come from seed alone. The cells from which the tree is made are built up chiefly from food materials taken out of the air, water, and soil. Parts of the air, water, and soil have been chemically changed and combined, forming living substances.

Matter can be neither created nor destroyed. This fundamental law both of chemistry and of all science, is called the *law of the conservation of matter.*

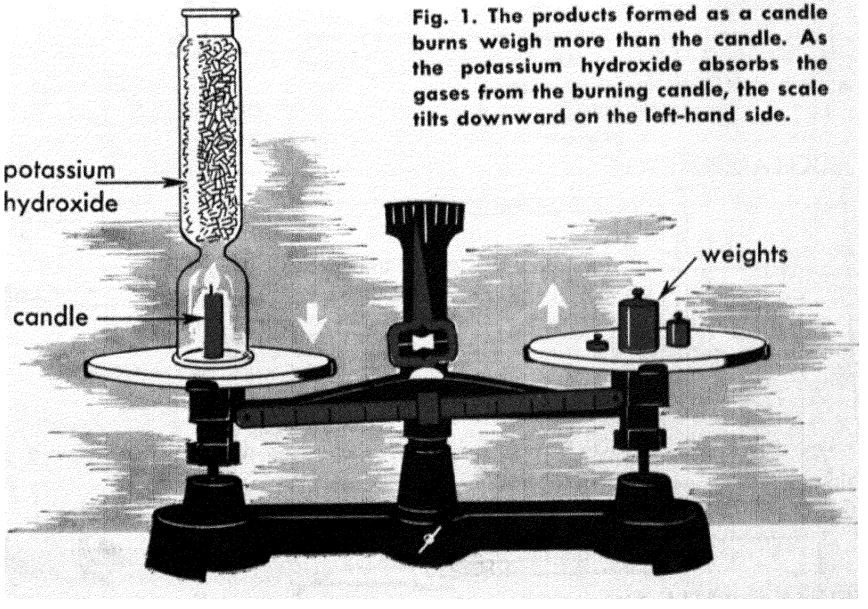


Fig. 1. The products formed as a candle burns weigh more than the candle. As the potassium hydroxide absorbs the gases from the burning candle, the scale tilts downward on the left-hand side.

Energy, too, can be neither created nor destroyed. So far we have considered mainly the changes in matter that take place in burning. But there are other changes that are equally important. When a substance burns, heat is liberated. This heat may be used to convert water in a boiler into steam. The pressure of this steam may then be used to turn a wheel, thus producing rotary motion. By connecting this wheel to a dynamo, electricity may be generated. This electricity may be changed into heat or light or magnetism, depending on whether it is sent through a toaster, a light bulb, or the electromagnet of, let us say, a buzzer or telegraph sounder. Or this electricity may be used to charge a storage battery. In charging the battery, the electricity produces a chemical change, which, on being reversed, yields electricity again.

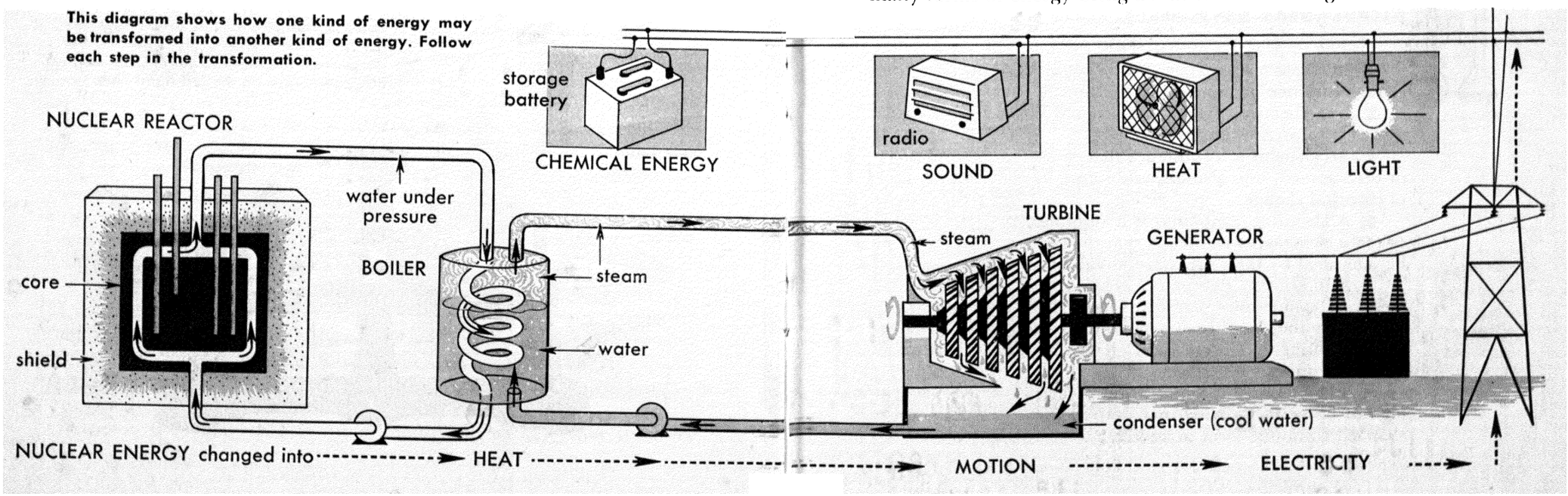
Evidently all these — heat, electricity, the power to produce motion, light, magnetism, and the power to produce a chemical change — can be transformed one into the other. *All are capable of doing work*, and *all* are forms of *energy*. In all energy changes, just as in all changes in matter, there is no loss, only transformation. *Energy can be neither created nor destroyed.* This is a fundamental law both of chemistry and of all science. It is called the *law of the conservation of energy.*

Two laws or one? Researches on the structure of matter and the nature of energy resulted in the atomic bomb. These researches, discussed in Chapter 12, lead definitely to the conclusion that matter and energy are but different forms of the same thing, and that matter can be converted into energy and energy into matter.

As a result, the law of the conservation of matter and the law of the conservation of energy are no longer considered separate and distinct laws. Instead, they may be considered as different phases of a single law. Such a law would state that *matter and energy can be neither created nor destroyed, but that each can be transformed into the other.* In the transformation of matter into energy, matter disappears and becomes energy. In the transformation of energy into matter, energy disappears and becomes matter.

Can any form of energy produce a chemical change? When paper is heated to its *kindling temperature* (see page 28), it burns. Heat, one form of energy, produces a chemical change. When light, another form of energy, strikes a photographic film, it causes a chemical change in the substances that coat the film. Thus, light also can cause a chemical change. When an electric current is passed through water, it splits the water into two gases, neither of which resembles water vapor. Thus electricity, too, is very effective in producing a chemical change. (The energy that was used to split the water appears again as heat energy when the two gases are recombined, forming water.) From these experiments and from others, we know that many forms of energy bring about chemical changes.

This diagram shows how one kind of energy may be transformed into another kind of energy. Follow each step in the transformation.





YOU WILL ENJOY READING

The literature of chemistry is filled with romance. In it you will find stories of human struggle and achievement, stories whose truth makes them all the more worthy to be read and remembered. Even the most interesting and significant parts of this literature cannot all be listed in this book. Nevertheless, they are available, and it will be well worth your while to read as many of them as you can. The following is a selected list of books that deal with some of the topics in this chapter.

Becker, Carl; Painter, Sidney; and Han, Yu-Shan. *The Past that Lives Today,* pp. 22–86. Silver Burdett Co., New York, 1952. A fascinating story of early man, ancient civilizations and the science of the ancients is told here.

Fabre, Jean H. *The Wonder Book of Chemistry,* pp. 6–69. Albert & Charles Boni, New York, 1922. A delightful account of elements, mixtures, and compounds.

Jaffe, Bernard. *Crucibles: The Story of Chemistry,* pp. 34–50. Simon and Schuster, New York, 1948. A simple account of the phlogiston theory.

Somerville, John. *The Way of Science: Its Growth and Method,* pp. 93–113. Henry Schuman, New York, 1953. A very simple illustration of the steps of scientific method.



USEFUL IDEAS DEVELOPED

1. The three states of matter are solid, liquid, and gaseous.

2. In a physical change, the original substance does not change into one or more other substances.

3. In a chemical change, the original substances disappear and new substances are formed.

4. An element is a substance that cannot be broken down, or decomposed, into a simpler substance by the ordinary types of chemical change.

5. A chemical compound is a substance composed of two or more elements so combined that the elements can no longer be identified by their original individual properties.

6. A mixture is a substance composed of two or more elements or compounds that still retain their individual properties after they have been thoroughly mixed.

7. Burning is the chemical change in which a burnable substance unites with oxygen.

8. The law of the conservation of matter states that matter can be neither created nor destroyed. But matter may be changed from one form to another.

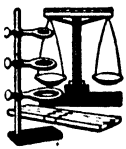
9. The law of the conservation of energy states that energy can be neither created nor destroyed. But energy may be changed from one form to another.

10. Recent researches prove that matter can be transformed into energy, and that energy can be transformed into matter.

11. Establishing accurate cause-and-effect relationships is perhaps the greatest function of science.

12. The steps in the scientific method include (1) the collection of all available facts related to a problem, (2) the open-minded examination of these facts, (3) the formulation of a working theory based upon these facts, (4) the testing of this working theory by experiments, (5) the formulation of a law, or principle, from the tested theory, and (6) the use of the law in specific situations.

13. Blind acceptance of so-called "authorities," prejudices, and personal likes and dislikes have no place in the general pattern of action and thought of the true scientist.



USING WHAT YOU HAVE LEARNED

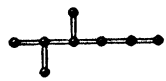
Group A

1. (a) Which of the following are physical changes and which are chemical changes? (b) Give reasons for your answers. Souring of milk, molding of clay, digestion of food, drying of clothes, dissolving sugar in water, decay of fruit, freezing of mercury, photosynthesis (manufacture of starch in the leaves of plants from carbon dioxide gas and water), erosion (the breaking up of rocks and soil by the action of air and water).

2. (a) What were the "four elements" of the ancients? (b) In what respects did their observations seem to support this theory? (c) What was one weakness of the way in which this theory was formulated?

3. What are your reasons for thinking that water is a compound?

4. Classify the following as elements, compounds, or mixtures: table salt, mercury, aluminum, paper, carbon dioxide, gold, silver, iron rust, sugar, sulfur, milk, brass, silver coin.



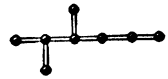
5. Name a compound that contains hydrogen.

6. Explain one method of telling a mixture from a compound.

7. Give briefly the main ideas of the "phlogiston theory."

8. What was Priestley's part in discovering the true nature of burning?

9. (a) Complete the following statement: When red mercuric oxide is heated, it is changed into .... and .... (b) Is the change a physical or a chemical change? (c) Why?



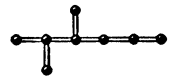
10. Describe Lavoisier's 12-day experiment on burning.

11. Is Lavoisier's explanation the modern explanation of burning?

12. What part did the balance play in the development of chemistry?

13. State the six general steps in the scientific method.

14. Distinguish between the method of science and the method of the ancient teachers and philosophers.



15. (a) What is the law of the conservation of matter? (b) Is the disappearance of camphor balls in clothes an exception to this law? (c) Explain.

16. (a) What is energy? (b) Name three different forms of energy.

17. Give an illustration to show that each of the forms of energy named in your answer to question 16 may produce a chemical change.

18. Assume that coal is the source of energy that lights your home (electric light). Make a list of the transformations of energy that occur, beginning with the burning of coal and ending with the lighted bulb.

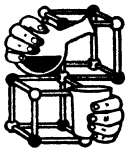
Group B

19. Not many of the chemical elements were discovered by Americans. (a) Which elements are these? (b) Can you suggest a reason why Americans have discovered so few?

20. Aluminum is the most abundant metal in the earth. Tell why only in recent years aluminum has come into common use.

21. (a) Can one use scientific methods in fields other than science? (b) Explain your answer.

22. (a) State four evidences of chemical action, and (b) give one example of each.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Discuss with your teacher of history the problem of prejudice and tradition as obstacles to progress. Write a report on this topic using an illustration from American history or from the history of science.

2. Find an article on some subject such as mental telepathy, communications from the spirit world, extrasensory perception, astrology. Read the article carefully and write your own reaction as to whether you, using the methods of science, would accept the author's conclusions as scientific.

3. Obtain a new photoflash bulb and weigh it on a sensitive balance. Weigh it again after it has been ignited. Do your findings uphold the law of the conservation of matter?

4. Show how you would use the method of science in solving some particular everyday problem which you have had to solve or which you will soon have to solve.

5. With the aid of a medicine dropper, allow a drop of ink to fall into a tall glass of cold water. Observe what happens after approximately 5 minutes, 8 hours, 24 hours, and 2 days. Report to class with reference to physical and chemical changes, and any other conclusion you have drawn.

6. Prepare a brief report on an expert in some field of science. Find out how he became an expert. How does an *expert* differ from an *authority?*

7. On the first page of this chapter, there is a statement made by Lavoisier. Read it carefully. Report to your class on the importance of this statement. What are its implications for everyday living?



2. OXYGEN:

EARTH'S MOST ABUNDANT ELEMENT

. . . I procured a mouse and put it into a glass vessel containing the air (oxygen) from the red powder of mercury. Had it been common air, a full-grown mouse, as this was, would have lived in it about a quarter of an hour. In this air, however, my mouse lived a full half hour.

Joseph Priestley, 1775

A Sunday experiment by an English minister. On Sunday, the first of August, 1774, Priestley was working in his laboratory. He placed a red powder (mercuric oxide) in a bell jar so arranged that any gas which might be formed would pass out of the bell jar through a tube and be collected in a bottle.

Instead of heating the powder over a flame, he used a large burning lens to concentrate the rays of the sun on the powder. "I presently found," he reported, "that *air* was expelled from it readily." But this result was not startling, because others before him had obtained gases by heating solids.

A candle was burning in the laboratory. Wondering what effect this gas would have on a flame, he placed the candle in a bottle of it. Priestley reported in somewhat flowery words: "A candle burned in this air with an amazing strength of flame; and a bit of red-hot wood crackled and burned with a prodigious rapidity exhibiting an appearance something like that of iron glowing with a white heat and throwing out sparks in all directions."

Only natural curiosity or perhaps chance led Priestley to experiment with the gas (or as he called it, air). As Priestley, himself, said later, he had no idea what the outcome might be.

Priestley was unable to explain what had happened. He was such a firm believer in the phlogiston theory that he did not associate this new gas with burning. As we learned in Chapter 1, it was Lavoisier who showed that Priestley's air (later called *oxygen*) is the element necessary for burning, thus solving a mystery that had baffled scientists for centuries.

Half the earth is oxygen! Priestley's discovery of oxygen was a turning point in the development of chemistry. It is one of the strangest facts in history that this element, which surrounds us everywhere and without which life is impossible, was not obtained pure until about 180 years ago. This fact is even more surprising when we realize that this one element, oxygen, is present on earth in quantities equal to the weight of all the other chemical elements put together. Sand and half of the different kinds of rocks on the earth are compounds of oxygen. Water contains almost 99 percent oxygen *by weight,* and air contains about 21 percent oxygen *by volume.*

How oxygen is prepared in the laboratory. Because mercuric oxide, from which Priestley prepared oxygen, costs about one dollar a pound, it is too expensive to use in the laboratory. Instead, we obtain oxygen from a white crystalline solid called *potassium chlorate.* This compound is composed of three elements — potassium, chlorine, and oxygen. By applying heat, the oxygen can be torn away and liberated as free oxygen.

How to express the change by which oxygen is prepared. As potassium chlorate is heated, it yields potassium chloride plus oxygen. This is a *chemical reaction* which produces the chemical change represented by the equation:

Potassium (K) **Chlorine (Cl)** **Oxygen (O)**	→	**potassium** **chlorine**	+	**oxygen**
$2KClO_3$	→	**2KCl**	+	**$3O_2$**
potassium chlorate	→	**potassium chloride**	+	**oxygen**

The chemical shorthand used to express the change will be fully explained later. The forms of energy that take part in the change are, as a rule, omitted from the equation. A chemical change is the result of a chemical reaction.

How the speed of this reaction can be increased. The method of preparing oxygen just described has one serious drawback. Unless a very high temperature is reached, oxygen is liberated very slowly. Someone discovered that if a small amount of powdered *manganese dioxide,* a black solid, is added to the potassium chlorate before

heating, oxygen is liberated more quickly and at a lower temperature.

At the end of the chemical reaction, that is, when oxygen is no longer given off, the same amount of manganese dioxide with which the experiment started remains. The weight of manganese dioxide has not been changed in any way. None of its oxygen has been liberated. Since manganese dioxide remains unchanged at the end of the reaction, it is not included in the equation.

A catalyst changes the speed of a chemical reaction. Chemists have discovered that many chemical reactions can be speeded up or slowed down by placing a small quantity of certain substances in contact with the reacting materials. *A substance that changes the speed of a chemical reaction is called a catalyst, or a catalytic agent.* The catalyst itself may undergo some temporary change, but at the end of the reaction is present in the same state and quantity as at the beginning. Manganese dioxide, as used in the laboratory preparation of oxygen, is a catalyst. However, manganese dioxide does not always act as a catalytic agent. It (see page 137) actually enters into certain reactions in which its composition is changed permanently.

We know little about the reasons that catalysts act as they do. We do know, however, that many vitally important chemical reactions take place too slowly, and hence uneconomically, except in the presence of certain catalysts. Research on the nature of *catalysis* is now being carried on in laboratories throughout the world, and we will know much more about it before very long.

The presence of a catalyst in a reaction is sometimes indicated by writing the catalyst over the arrow in the equation. In the reaction just discussed, the presence of the catalyst, manganese dioxide, might be indicated thus:

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

How oxygen gas is collected. In preparing oxygen, a mixture of potassium chlorate and manganese dioxide is put in a test tube and heated over a bunsen burner (see illustration page 27). Connected to the test tube is a delivery tube which reaches into a bottle that has been filled with water and placed mouth downward in a pan of water. As the potassium chlorate is heated, it is broken down, or decomposed, forming potassium chloride and oxygen.

The potassium chloride is a solid and remains in the test tube. The oxygen is a gas and passes through the delivery tube into the

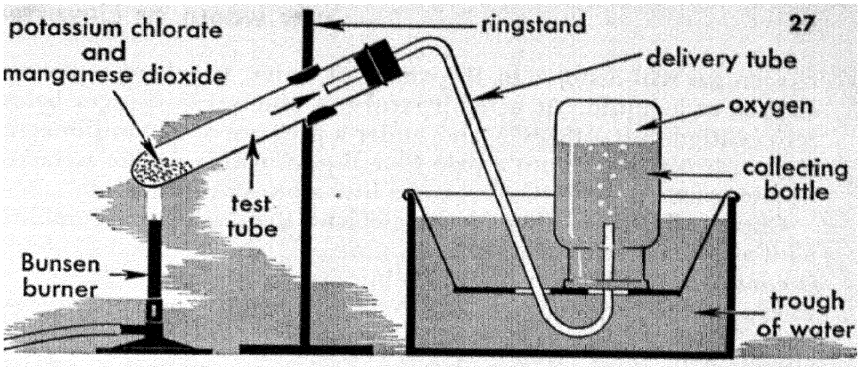


Fig. 2. Laboratory preparation of oxygen. By what method is the oxygen being collected? Why?

water-filled collecting bottle from which it displaces water. This method of collecting gases is called the *displacement of water method,* and was used by Priestley. Priestley also collected gases by the displacement of mercury when such gases dissolved in water but not in mercury. If a gas is collected by the displacement of a liquid, chemists say that the gas is collected *over* the liquid. Thus, Priestley collected oxygen over water.

Physical properties of oxygen. In discussing the physical properties of a gas, we usually consider five characteristics: (1) *color,* (2) *odor,* (3) *weight* compared with the weight of an equal volume of air, (4) *the ease with which it may be changed into a liquid,* and (5) *its absorption by water.* This absorption by water we call its *solubility* in water. Just as solids, such as sugar and salt, disappear as solids when stirred in water and are distributed uniformly throughout the liquid, so gases, such as air and oxygen, when passed through water, may likewise be absorbed by the water. In the case of some gases, *taste* is considered also.

Oxygen is colorless and has no odor. It is slightly heavier than air. It is slightly soluble in water. Under *normal conditions,* that is, at a temperature of 18 degrees centigrade and a pressure of one *atmosphere,* or 760 millimeters of mercury,* about four quarts of

* Scientists often use two terms to describe temperature and pressure, *normal conditions* and *standard conditions.* Standard conditions mean a temperature of 0° C. and a pressure of 760 mm. of mercury, that is, one atmosphere (atm.). Normal conditions mean, in effect, room temperature and the pressure of 1 atmosphere. Throughout this book a pressure of 760 mm. is assumed when stating temperatures at which gases liquefy or liquids solidify. A *millimeter* (mm.) is a small unit of length in the Metric System. Numerically it is equal to 0.001 of a *meter,* a larger unit of length equal to 39.37 inches. For an explanation of metric units and temperature scales, see pages 654 and 644 respectively. Metric units of measurement are used by scientists in all countries.

oxygen gas will dissolve in 100 quarts of water. It is hard to change oxygen to a liquid. At a temperature of about 183 degrees below zero centigrade (−183°C.) and under a pressure of 760 millimeters, oxygen is converted into a pale blue liquid, which can be attracted by a magnet. At −219°C. it changes into a bluish-white solid.

Chemically, oxygen is an active element. Because oxygen combines with almost all other elements, forming compounds called *oxides,* it is considered to be very active chemically. For example, when iron is exposed to oxygen, rust, which is an oxide of iron, is formed.

$$\text{Iron} + \text{oxygen} \rightarrow \text{iron oxide}$$
$$4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$$

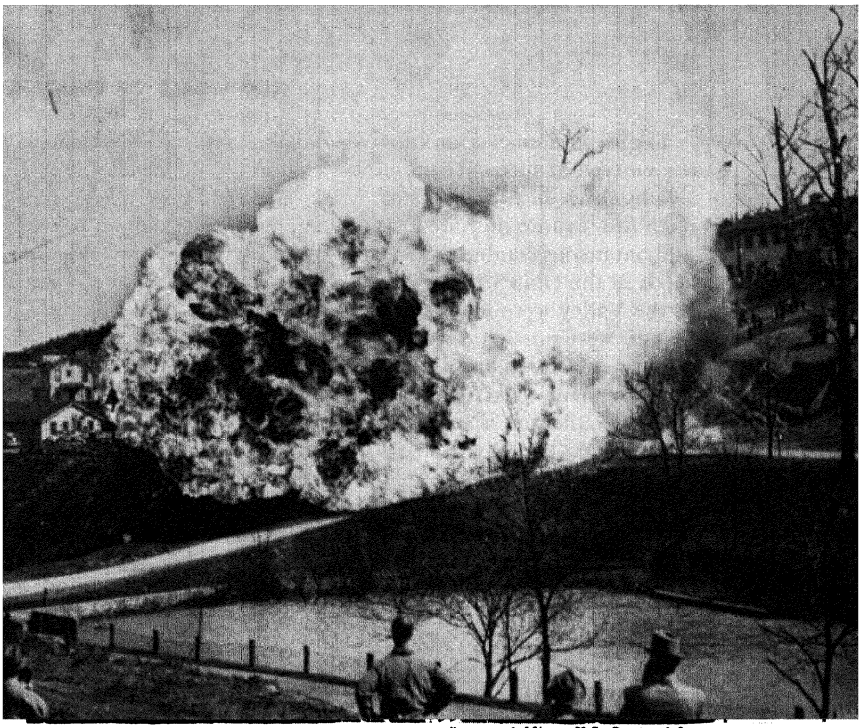
If iron is first heated until it glows and then placed in a bottle of oxygen, the chemical reaction is so vigorous that the iron burns brilliantly, throwing off sparks of glowing iron oxide. This surprising spectacle actually is iron burning in oxygen, just as a piece of paper burns in air!

Differences between slow and rapid oxidation. *When a substance — element or compound — combines with oxygen, new substances are formed. This chemical union of a substance with oxygen is called oxidation.* Rapid oxidation, such as the burning of coal, is accompanied by noticeable heat and light. During slow oxidation, such as the rusting of iron or the decaying of wood, no light is given off nor can we easily detect the heat because it is given off so slowly. Delicate measurements, however, have proved beyond doubt that the amount of heat energy liberated is the same whether the oxidation of a substance takes place slowly or rapidly.

The soft cold light of the firefly, and the glow of some fungi and bacteria are caused by the oxidation of a complex chemical compound, *luciferin,* which they produce.

Why some substances catch fire more easily than others. Some substances catch fire at low temperatures, but others require extremely high temperatures in order to burn. Every substance must be raised to a certain definite temperature before it can combine with oxygen at such a rate that the heat produced is sufficient to keep the substance burning without the addition of more external heat.

In starting a coal fire, we often begin by burning paper, which sets fire to kindling wood, which sets fire to the coal. The heat given off by the burning paper causes the wood to catch fire; the heat given off by the burning wood in turn causes the coal to catch fire. *The lowest temperature at which a substance catches fire and continues to burn is called the kindling temperature of that substance.* We



Bureau of Mines, U.S. Dept. of Interior

A coal-dust explosion issues from the U.S. Bureau of Mines' Experimental Coal Mine in Pennsylvania. Such test explosions are part of the Bureau's safety research program.

say that a substance which is easy to set on fire has a *low* kindling temperature, and a substance which is difficult to set on fire has a *high* kindling temperature.

A substance may have different kindling temperatures, depending upon the size of the particles into which it is divided, that is, upon its state of *subdivision*. A solid piece of iron has a high kindling temperature, but powdered iron, because of the large surface that is exposed to the oxygen of the air, can be made to burn readily in air. Many dust explosions in flour mills, starch factories, grain elevators, and coal mines are caused by the very rapid oxidation of explosive mixtures of air and finely divided materials. A spark resulting from static electricity or friction often sets off the explosion.

Smut dust and air form an explosive mixture which may be ignited by static electricity during threshing operations. Costly fires of this kind have been so widespread that the United States Department of Agriculture has issued a bulletin explaining how to prevent them.

The explosion of a mixture of coal dust and air has been used in one type of internal-combustion engine.

Substances such as asbestos, brick, concrete, and marble never catch fire because they are already completely oxidized.

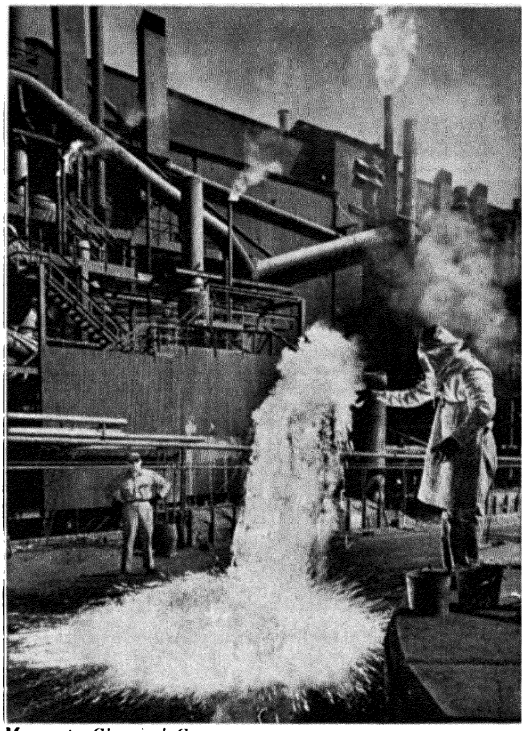
Spontaneous combustion. Several years ago there were widespread floods in the Ohio Valley. The lower parts of thousands of haystacks in the Valley were soaked with water. As the flood waters receded, farmers were puzzled when some of the haystacks began to catch fire.

The explanation of this phenomenon is simple. During respiration of living plant cells, food materials slowly oxidize and heat is given off. This oxidation is speeded up by the presence of a small amount of moisture. The hay itself also slowly oxidizes, liberating heat. As the temperature rises, the rate of oxidation also increases. The heat slowly accumulates, and when the kindling temperature of the hay is finally reached, it bursts into flame. Materials catching fire in this way are said to undergo *spontaneous combustion.* (*Combustion* refers to *any* chemical reaction which produces heat and light. *Burning* is only *one* kind of combustion.)

Fires have also been caused by painters' rags saturated with linseed oil. As the linseed oil slowly oxidizes, heat is given off. Unless there is a free circulation of air to carry away this heat, the oily rags may become hot enough to catch fire. Thus, you see why oily rags should not be kept in poorly ventilated closets. Finely divided coal in the closed hold of a ship, or in a poorly ventilated boiler room must be sprinkled with plenty of water from time to time to prevent the accumulation of heat from slow oxidation.

Phosphorus, an element that burns spontaneously. Ancient alchemists spent most of their time looking for the *philosopher's stone,* which they believed would change lead into gold. In 1669, while searching for the philosopher's stone, Hennig Brand, an alchemist of Hamburg, obtained a new and strange chemical substance from urine. It had so low a kindling temperature that on exposure to air it caught fire immediately and burned, forming a white powder (*phosphorus oxide*). Brand made a famous tour of Europe, exhibiting this unusual substance. Today we know it as white phosphorus, a soft, waxy element, now obtained by a chemical process from bone deposits. At one time it was used in the manufacture of matches (see page 296). This element is sometimes referred to as *yellow* phosphorus.

To keep white phosphorus from catching fire, it must be stored under water. Do not touch it with your bare fingers, for white phosphorus will cause severe burns that heal very slowly.



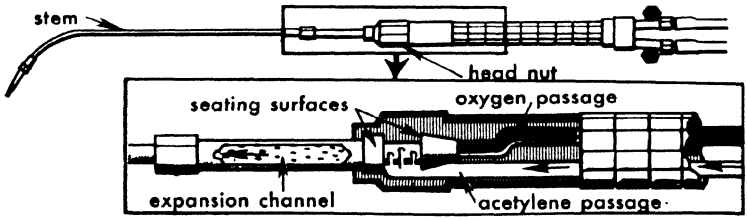
Monsanto Chemical Company

Upon exposure to air, white phosphorus ignites spontaneously in a violent reaction. Note the protective clothing worn by the demonstrator.

You could not live without oxygen! One of the remarkable experiments which Priestley performed showed that a mouse, placed in a bell jar, lived twice as long in pure oxygen as in "common air." This, Priestley was unable to explain; but today we know that the chief chemical change that goes on in the body of any living animal is slow oxidation.

Man obtains his supply of oxygen by breathing. When he inhales, oxygen is taken into his lungs. This oxygen passes through the walls of the lungs and is absorbed by the red cells of the blood, which carry it to all parts of the body. In every living cell or body unit, oxidation takes place, liberating heat and other forms of energy. This slow, steady oxidation is like a tiny flame which keeps life going. Without oxygen, the flame is snuffed out and life is extinguished.

With the exception of a few very low forms of life, all living things take oxygen from the air. This oxygen is in the *free*, or *uncombined*, state. That is, the oxygen is not chemically united with any of the other substances in air. Fish obtain their supply of oxygen from the air that is dissolved in water.



Adapted from drawing by Linde Air Products Company

Fig. 3. Oxyacetylene torch. What is the function of the expansion chamber?

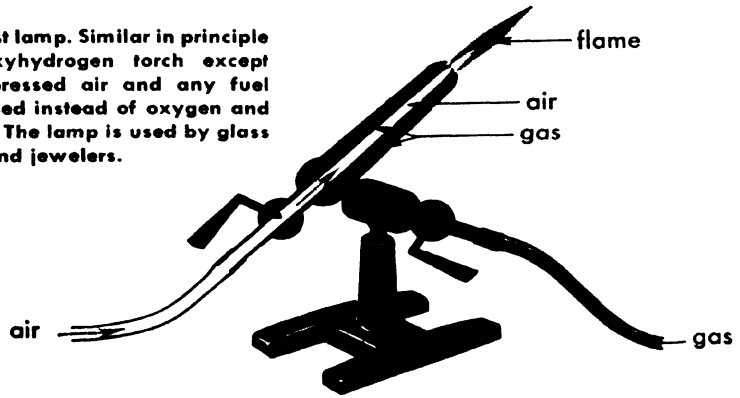
Industry uses great quantities of oxygen. Commercial production of pure oxygen in the United States is more than 25 billion cubic feet a year. Of the oxygen produced, it is estimated that more than 95 percent is used in cutting and processing steel and in welding metals, such as aluminum and steel, by means of *oxyacetylene* and *oxyhydrogen torches.*

It was Priestley who first thought of using oxygen to produce high temperatures. He found that blowing pure oxygen on a piece of glowing wood would cause it to burn furiously. A few years later an American scientist, Robert Hare, of Philadelphia, put this discovery of his friend Priestley to practical use by inventing the oxyhydrogen torch, or *blowpipe.*

The oxyhydrogen torch consists of two tubes, one inside the other. Hydrogen gas passes through the outer tube and is ignited at the tip of the torch. Pure oxygen passes through the inner tube and the mixture of the two gases burns at the tip of the torch with an extremely hot flame, about 2400°C., a temperature much higher than the melting point of iron.

The oxyhydrogen torch was never widely used. Instead, the oxyacetylene torch is used. With the oxyacetylene torch, a flame temperature of over 3300°C. may be easily produced. The oxyacetylene torch is similar in principle to the oxyhydrogen torch, but acetylene

Fig. 4. Blast lamp. Similar in principle to the oxyhydrogen torch except that compressed air and any fuel gas are used instead of oxygen and hydrogen. The lamp is used by glass blowers and jewelers.



gas is used instead of hydrogen (see Fig. 3). The oxygen used in the torch is stored under high pressure in strong steel cylinders. The acetylene, however, is not under high pressure, but is dissolved in a liquid called *acetone*. In almost every automobile service garage, oxyacetylene torches, with their accompanying cylinders of oxygen and acetylene, may be seen ready for use.

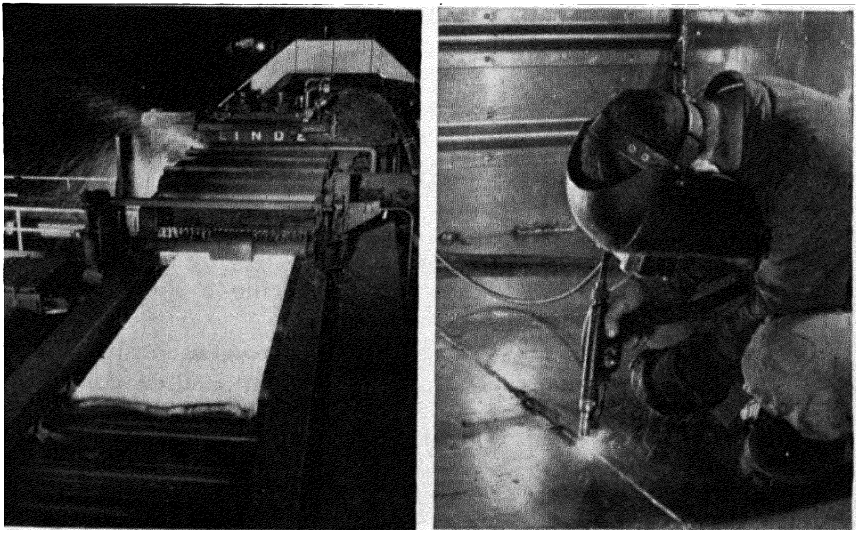
The oxyacetylene torch is an important industrial tool. It is used to weld, cut, and clean metal. It is also used in ***heat treating*** surfaces of metal machine parts to make them more wear resistant.

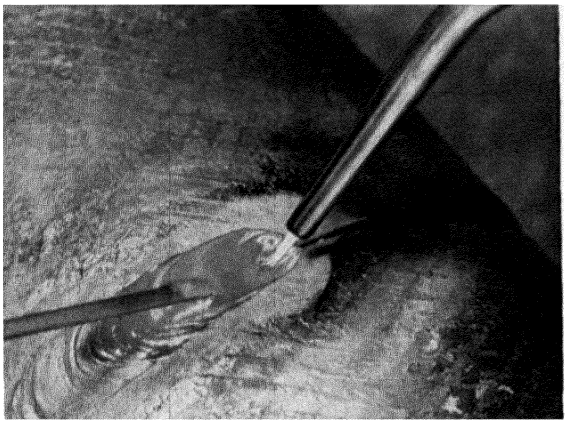
Oxygen rusts and derusts steel. In the presence of air and minute quantities of water vapor, steel rusts. In rusting, oxygen from the air unites slowly with the metal, forming a brown, scaly oxide of iron. At the high temperatures used in the making of steel, rust forms very rapidly and is a serious problem. As red-hot steel is carried to the rolling mills, it becomes covered with seams of iron oxide.

These surface imperfections are removed by a process called *torch-deseaming*, or *scarfing*. In the scarfing operation, the flame of the oxyacetylene torch is directed onto the hot steel. The surface of the steel is quickly oxidized to a depth of about one quarter of an inch. The iron oxide falls off readily, leaving an unblemished surface. Scarfing may be done by hand or by special machines.

(left) Red-hot steel slab passes through scarfing machine in which oxyacetylene torches remove surface defects. (right) Welding metal plates with an oxyacetylene torch.

Linde Air Products Company





Because of the high temperature of the torch, an oxyacetylene weld is smooth and strong.

Linde Air Products Company

Oxygen saves lives. Priestley also discovered another use for oxygen. After inhaling oxygen, he wrote: "My breath felt peculiarly light and easy. It (oxygen) may be peculiarly salutary to the lungs in certain cases where the common air is not sufficient."

Today, pure oxygen is administered to persons with pneumonia and in other cases where the respiratory system cannot function at its normal rate. Usually about two gallons of oxygen are administered per minute. Since air contains only about 20 percent pure oxygen, a patient who is weak, or whose lungs are congested or partially destroyed, can satisfy the oxygen requirements of his body by breathing a much smaller volume of air that is rich in oxygen than he would normally require of ordinary air. Oxygen is usually administered by means of an *oxygen tent*, a canopy which fits over the patient's bed. Pure oxygen is introduced at such a rate that the air inside the canopy always contains from 45 to 60 percent oxygen.

Oxygen in determining basal metabolism. Pure oxygen is used by physicians in determining the rate at which a person's food supply is oxidized while the person is at rest. This is known as his *rate of basal metabolism*. This rate is obtained by measuring the volume of oxygen consumed by the person at rest during a short interval, usually eight minutes.

From these data the number of liters* of oxygen consumed per minute may be calculated easily. This number is then compared with the basal metabolic rate for a normal person of the same age, sex, height, and weight. Persons in normal health use oxygen at a

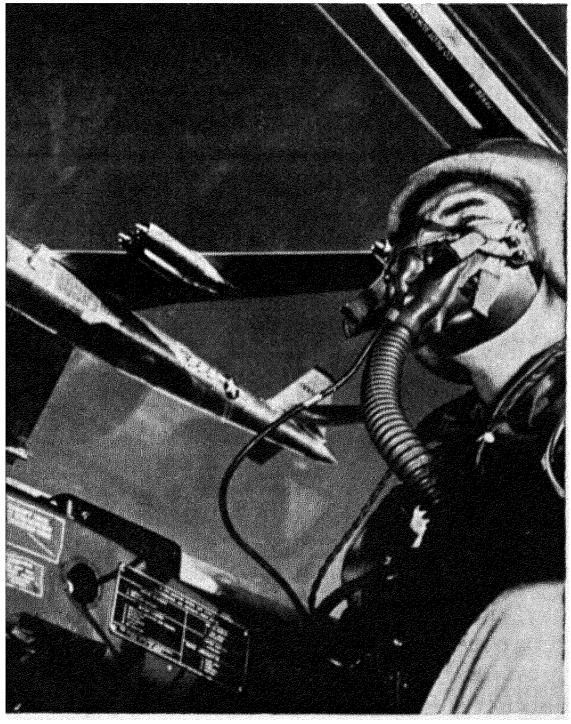
* A *liter* (l.) is a unit of capacity (volume) in the Metric System. It is slightly larger than a U.S. liquid quart.

standard rate. In certain diseases, the patient's rate is higher and in others it is lower than known standards for persons in good health. For example, a high basal metabolic rate always accompanies an overactive thyroid (see pages 147, 581). A low basal metabolic rate may be an indication of an underactive thyroid.

Oxygen flies high. Aviators and mountain climbers who ascend to high altitudes where the atmosphere is very thin must carry supplies of oxygen. Otherwise their senses become dulled and they are likely to lose consciousness. The United States Air Force requires the use of oxygen at altitudes above 10,000 feet in the daytime and from the ground up at nighttime. Airliners flying at altitudes ranging from 15,000 to more than 30,000 feet contain equipment to keep the oxygen concentration inside their cabins only slightly less than that at sea level. The cabins are airtight and are *pressurized* by means of pumps, so that the inside pressure does not become uncomfortably low.

Rescue parties entering mines and buildings in which dangerous gases are present carry oxygen-breathing apparatus.

Air Photographic and Charting Service, U.S. Air Force



High in the stratosphere, this pilot is dependent upon a continuous supply of pure oxygen.

Some other uses of oxygen. Oxygen is used in the photoflash lamps employed in photography. These lamps look like ordinary electric-light bulbs, but they are filled with oxygen and aluminum foil. When an electric current is passed through the filament, the aluminum foil is raised to its kindling temperature. It ignites and oxidizes with a blinding flash. This flash lasts only about $\frac{1}{50}$ of a second.

Pure oxygen has also been introduced in the manufacture of steel, synthetic gasoline, and fuel from underground coal (see pages 335, 360, 417).

How is such a huge amount of oxygen prepared? It is not surprising to find that the two main sources of oxygen are *air,* the most abundant mixture containing oxygen, and *water,* the most abundant compound of oxygen. Nearly all commercial oxygen is obtained from *liquid air* by first lowering the temperature of the air until it is changed to a liquid. The preparation of oxygen from liquid air is discussed on page 100. Less than one percent of the oxygen produced commercially is obtained by decomposing water by means of an electric current. This process, called the *electrolysis of water,* is described on page 62.

How can we test for oxygen? When Priestley prepared oxygen from mercuric oxide, he tested the gas by placing burning and glowing substances in it. In each case, the substance burned more vigorously. This method is still used to identify oxygen. A glowing splint or splinter of wood is thrust into a bottle of the gas. Such a splint placed in a bottle of oxygen bursts into flame at once.

No other odorless gas will cause a glowing splint to burst into flame in this way. Hence, we can distinguish oxygen from any other odorless gas by this simple procedure. We call such a method of identifying a substance a *test* for that substance. Chemists have devised hundreds of tests, which they use in identifying many other pure substances.

Ozone, the active. Ten years after Priestley's discovery of oxygen, another gas which possessed a peculiar odor and which, unlike oxygen, tarnished mercury under normal conditions, was reported. But it was not until 1840 that Schoenbein (shûn'bīn) isolated this gas and called it *ozone,* from the Greek word meaning to *smell.* Its sharp odor is noticeable around electric machines in operation.

Ozone is a pale blue gas, one and one-half times as heavy as oxygen. It is even less soluble in water than oxygen but is more active chemically. It is a strong *oxidizing agent.* That is, it is a substance which readily supplies oxygen for chemical union with another substance.

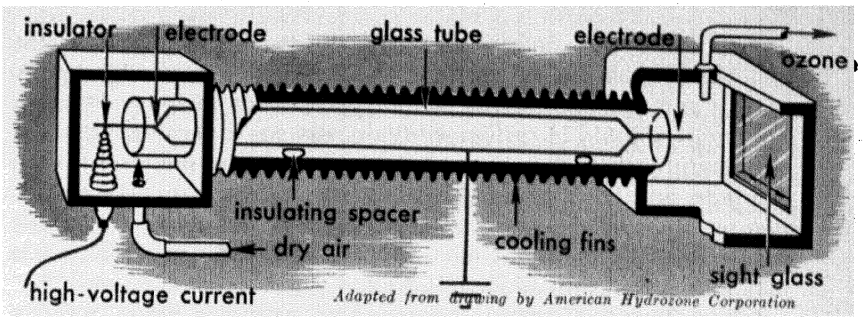


Fig. 5. A continuous-process ozone tube. Dry air enters at lower left, passes through the brush discharge of high-voltage current. Part of the oxygen of the air is converted to ozone which leaves through pipe at right.

Ozone (written O_3) is prepared by passing electric discharges through either dry air or oxygen (written O_2). About eight percent of the oxygen is converted into pure ozone, although slightly larger yields are obtained if the temperature is kept low, or if the process is continuous.

3 volumes of oxygen → 2 volumes of ozone

$$3O_2 \rightarrow 2O_3$$

Ozone is unstable; it changes back to oxygen quickly, two volumes of ozone changing into three volumes of oxygen. It cannot be stored and must be produced at its point of use.

What is allotropy? As we have just learned, oxygen exists in two forms: ordinary oxygen and ozone. The existence in the same physical state (both oxygen and ozone are gases) of two or more forms of the same element is a phenomenon called *allotropy* (ă-lŏt'rô-pĭ). The various allotropic forms of an element have different physical and chemical properties.

The cause of allotropy is not yet completely understood. But we know that it is caused in part by differences in the arrangement of the atoms and in the amount of energy in the various allotropic forms. This can be seen easily by referring to the way in which ozone is produced from oxygen. When an electric current discharges through oxygen, the electric energy changes oxygen into ozone, which, as you would expect, possesses more energy than ordinary oxygen. Ozone, on changing back into oxygen, liberates this energy in the form of heat. During the change from oxygen to ozone, or from ozone to oxygen, no energy is destroyed, nor is any energy created. The change from one allotropic form of oxygen to the other is an excellent example of the law of the conservation of energy.

Allotropy is not confined, of course, to oxygen. For example, the element phosphorus occurs in two allotropic forms: white phosphorus and red phosphorus. White phosphorus melts at 44°C., is poisonous, soluble in carbon disulfide, and has a very low kindling temperature. Red phosphorus is nonpoisonous, insoluble in carbon disulfide, and has a higher kindling temperature than white phosphorus. Red phosphorus is also heavier and less active chemically than white phosphorus. Under proper conditions, red phosphorus may be changed into white phosphorus, and vice versa.

Ozone "burns up" germs. Because of its extreme chemical activity, ozone is used to a limited extent in purifying water. It kills bacteria and other microorganisms in water by oxidizing them, literally burning them up. Other organic materials present are also oxidized. About one gram* of ozone will purify a cubic meter of water.

Ozone destroys odors. Because ozone is an excellent oxidizing agent, it is used also in purifying air in homes, refrigerators, tunnels, and zoos. Small ultraviolet lamps change the oxygen in air to ozone which clears away bad odors. Because of the increasing abundance of low-cost electricity, it seems possible that ozone may be used more widely in the removal of unpleasant tastes and odors from water than it now is.

Ozone helps screen the earth. Ozone is present in the layers of the atmosphere, about 30 miles above the surface of the earth. Scientists believe that this region which is rich in ozone acts as a screen that protects life on earth from the harmful effects of too much ultraviolet light from the sun.

What part does chance play in scientific discoveries? Some years after his discovery of oxygen, Priestley commenting on this memorable occasion said: "I can not at this distance of time recall what it was that I had in view in making this experiment, but I had no expectation of the real issue of it. If I had not happened to have had a lighted candle before me, I should probably never have made the trial, and the whole train of my future experiments relating to this kind of air might have been prevented. More is owing to what we call chance than to any proper design or preconceived theory."

Chance may have played some small part in leading Priestley to make his experiments. It seems likely, though, that he failed to take into account the *consuming natural curiosity,* always present in true scientists, which literally forced him to make his experiments. No

* A *gram* (g.) is a small unit of weight or mass in the Metric System. One thousand grams are equal to a *kilogram*, which weighs slightly more than 2.2 pounds. For a definition of *mass*, see page 157.

doubt one of the tests he would eventually have made on any gas was to see if it would burn. If the lighted candle had not been present at that particular moment, he undoubtedly would have lighted one later on. Probably what Priestley meant by the statement was simply that he had no specific purpose in mind in making the experiment. But *having no specific purpose in mind* and *attributing the results to chance* are not the same. Nevertheless, such confusion exists among scientists even today.

Other men were performing experiments similar to those made by Priestley (among them Scheele), and we might say that the time was ripe for these discoveries. If Priestley had failed to make them, no doubt some other experimenter soon would have made them.

Today carefully planned research has speeded up advances in science. Chance now plays a very slight role in the development of chemistry. Surely we cannot regard as "chance" the keenness of mind to appreciate the significance of, and to follow up by intelligent experiment, a clue furnished by some unforeseen event.

Progress in science and changes in society are closely interrelated. Most of us, although we live in a world of science, have strange notions about what scientists are like. We picture the *research man* as a lone, mysterious genius who locks himself up in his laboratory away from the world, and attempts to solve some abstract scientific problem. We see him emerging triumphant, after weeks or perhaps years, with some great discovery. Most of us have an idea that the efforts of the man of science are influenced very little by the society in which he lives. Nothing could be farther from the truth. The scientist is influenced by society and society in turn is influenced by the scientist.

The steam engine, for example, was developed out of the social needs of the eighteenth century. With the Industrial Revolution, which began in Birmingham, England, came a need for more iron to make the machinery so much in demand. In making iron, wood charcoal had been used, but England's forest reserves had been seriously depleted by the use of timber in the many ships swallowed up in naval wars and commercial ventures. As a result, coal had to be substituted for charcoal, and coal mines, abandoned because they were flooded, had to be reopened. This meant draining mines, and James Watt improved Newcomen's steam engine for this purpose.

At about the same time, the problem of burning was reinvestigated, and Priestley's investigations (which led to his discovery of oxygen) were closely related to society's need for more information concerning the extraction of metals.



YOU WILL ENJOY READING

Becker, Carl. *Modern History,* pp. 581–607. Silver Burdett Co., New York, 1952. "How Science Gave Men Machines to Work for Them, and How the Machines Changed the Conditions under Which Men Had to Live and Labor." Very readable.

Ficklen, Joseph B. "Dust Explosions." *Journal of Chemical Education,* March, 1942, pp. 131–134. Published by the American Chemical Society, Easton, Pa. Editorial office: Metcalf Chemical Laboratory, Brown University, Providence, R.I. An interesting and well-illustrated article.

Friend, J. N. *Man and the Chemical Elements.* Scribners, New York, 1953. The author rambles along into many interesting sidepaths and offers sidelights such as the origin of *gibberish* from the alchemist Geber.

Partington, J. R. *A Short History of Chemistry,* pp. 110–120. The Macmillan Co., London, 1939. The fascinating story of Priestley's discovery of oxygen.



USEFUL IDEAS DEVELOPED

1. A catalyst is a substance that changes the speed of a chemical reaction without being itself permanently changed.

2. Oxidation is the chemical union of a substance with oxygen. In slow oxidation, neither light nor noticeable heat is liberated. In rapid oxidation, light and noticeable heat are evolved. Burning is rapid oxidation.

3. The kindling temperature of a substance is the lowest temperature at which that substance catches fire and continues to burn.

4. Spontaneous combustion is a burning started by the heat accumulated during slow oxidation. Combustion is any chemical action that liberates heat and light.

5. Finely divided powders form explosive mixtures with air because of the extremely large surfaces exposed to oxygen.

6. Elements may occur in two or more varieties, or allotropic forms, in the same physical state. These allotropic forms differ in their properties because of differences in the arrangement of their atoms and differences in the amount of energy possessed by particles of each allotrope.

7. Today carefully planned research has speeded up advances in science, and chance discoveries play a smaller part in the development of chemistry than they once did.

8. Scientific progress and social changes are interrelated.



USING WHAT YOU HAVE LEARNED

Group A

1. Make as large a list as you can of substances containing oxygen combined with other elements.

2. From what chemical compound was O_2 first prepared by Priestley?

3. From what compounds is O_2 usually prepared in the laboratory?

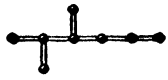
4. (a) What is a catalyst? (b) Illustrate your answer.

5. What assurance have we that the MnO_2 used in the laboratory preparation of O_2 acts as a catalytic agent?

6. What happens to the KCl that is formed by the decomposition of $KClO_3$?

7. Why is it possible to collect O_2 by the displacement of water?

8. Priestley for a time collected gases by the displacement of mercury. Why do we not use this method in collecting O_2?



9. List five physical properties of O_2.

10. Discuss the most important chemical property of O_2.

11. (a) What is slow oxidation? (b) rapid oxidation? (c) Illustrate each.

12. What is the kindling temperature of a substance?

13. Devise an experiment to show that air is necessary for burning.

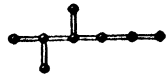
14. Name four substances whose kindling temperatures are lower than that of coal.

15. Why is air removed from an electric-light bulb?

16. It is not as easy to burn a 500-page book whole as it is to burn the same book a page at a time. Explain.

17. Why is asbestos used in making theater curtains?

18. (a) What are the conditions necessary for spontaneous combustion? (b) Show how these conditions work out in the spontaneous combustion of (1) finely divided coal in the enclosed hold of a ship, and (2) moist hay in a hayloft.



19. Why may the presence of dust in the air of a flour mill cause a frightful explosion?

20. Make a list of the uses of O_2.

21. Distinguish between combustion and burning.

22. What is an oxidizing agent?

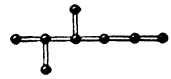
23. Describe the greatest industrial use of O_2.

24. O_2 rusts steel. What part does O_2 play in derusting steel?

25. How do oxygen tents aid patients suffering from pneumonia and other respiratory diseases?

26. (a) What is basal metabolic rate? (b) How is it determined? (c) What is its significance?

27. How does O_2 play an important part in aviation?



28. State the two most important industrial sources of O_2.

29. What three factors must be considered in selecting the method for preparing large quantities of a substance?

30. (a) Describe a test for O_2. (b) What does the word *test* mean to a chemist?

31. O_2 and O_3 can be changed easily from one to the other. (a) How? (b) What great law does this illustrate?

32. How is O_3 prepared?

33. How does O_3 differ from O_2 in physical properties?

34. By means of an illustration, explain the meaning of allotropy.

35. What are the chief uses of O_3?

36. Write word-equations for the burning of (a) coal (carbon), (b) iron, (c) phosphorus, and (d) sulfur.

Group B

37. By using mercury Priestley was able to collect a number of gases that had escaped the attention of other scientists. Explain.

38. Science today depends less upon chance discoveries than it has in the past. Explain.

39. Window curtains behind a fish bowl filled with water caught fire. Was this spontaneous combustion? Explain.

40. Why is O_2 passed through the inner tube of the oxyhydrogen torch rather than through the outer tube?

41. Because of oxidation, linseed oil hardens when exposed to air. How is this chemical reaction speeded up?

42. Fishes die in air, man drowns in the sea. Explain.

43. Blow against a burning candle and it goes out. Blow on the slowly dying embers of a fire and they burn more actively. Explain.

44. Why is green, or moist, hay more susceptible to spontaneous combustion than dry hay?

45. Illustrate the statement "progress in science and changes in society are closely interrelated" by an example not mentioned in this chapter.

46. Coal dust is sometimes shoveled into a burning coal furnace. Why?



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

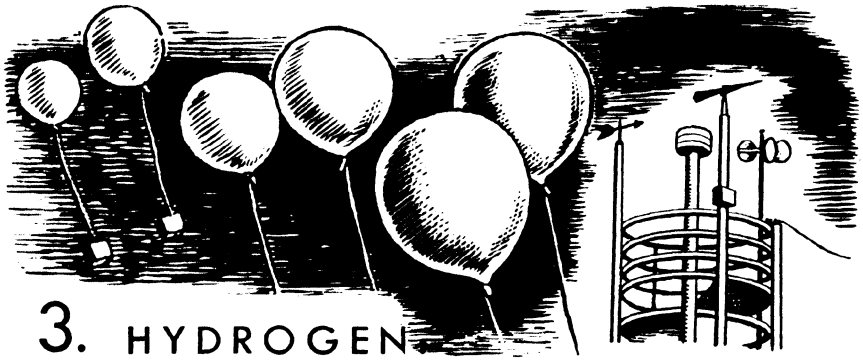
1. Have you ever heard of pure oxygen being administered to athletes before a strenuous game? Consult the football or track coach in your school or in a nearby college. What do you conclude? Explain.

2. Organize a small group in your chemistry class and with the help of your teacher set up apparatus such as Priestley first used when he obtained oxygen. A large burning glass can be borrowed from the physics department. Demonstrate the experiment before your class.

3. Watch your mother put up fruit and jam in jars. Describe her procedure, and explain why the food is heated, and why a layer of paraffin is placed over the food before the jar is sealed.

4. Consult your doctor and a good book on first aid, and write a report on the diagnosis and treatment of first-, second-, and third-degree burns.

5. Read the story of a recent scientific discovery. (a) From the account you read, what part do you conclude that chance plays in scientific discoveries? (b) Why may the scientist himself believe chance plays a more important part than it actually does?



3. HYDROGEN

LIGHTEST OF THE ELEMENTS

. . . Cavendish was almost passionless. An intellectual head thinking, a pair of wonderful acute eyes observing, and a pair of skilful hands experimenting or recording are all that I realize in reading his memoirs. Cavendish did not stand aloof from other men in proud spirit, he did so conscious of his inferiority, not boasting of his excellence.

Dr. George Wilson, 1851

An eccentric man of science. While Priestley was performing his immortal experiments, another Englishman was puttering around in his palace laboratory on the wandering trail of phlogiston. This man was Henry Cavendish, one of the most eccentric persons in the whole history of science. It was said that he was "the richest among the learned and the most learned among the rich." Although the richest man in all England, he shut himself up in his private laboratory and spent more than 60 years tracking down many of the secrets of nature.

In addition to his discoveries in chemistry, Cavendish was interested in physical problems. His work in the fields of heat and electricity was of highest rank; later it was followed up by the work of other eminent scientists such as Joseph Black and Michael Faraday.

The elusive trail of phlogiston. Two hundred and fifty years before the work of Cavendish, Paracelsus (păr-*ă*-sĕl'sŭs) of Switzerland had noticed bubbles of gas rise from an acid into which iron is dropped. Although he found that this gas burns, he carried his investigations no further. Then came Cavendish to whom the search for truth was the ruling motive of life. He too noticed the gas evolved when zinc or iron is dropped into an acid and went to work

to investigate this phenomenon. He collected the gas carefully, and made a thorough study of it. He named it *inflammable air* because it burned. He thought he had obtained phlogiston itself.

Strangely enough, the discovery of this gas, coupled with the discovery of oxygen, paved the way for the complete overthrow of the phlogiston theory and the establishment of Lavoisier's true explanation of burning. Though Priestley died still believing in the phlogiston theory, Cavendish, when the discussion over Lavoisier's new chemistry became very heated, gave up his active interest in chemistry and turned to the problem of determining the weight of the earth. He said that he had no patience with squabbles, that he was interested in experimentation, not controversy.

How is hydrogen produced in the laboratory? Cavendish's laboratory method of preparing hydrogen is still used. Zinc is placed in a generator, as shown in Fig. 6, and dilute hydrochloric or sulfuric acid is poured over it through a thistle tube. Bubbles of hydrogen gas form at once, and heat is generated. The hydrogen is collected in the same way as oxygen, that is, by the displacement of water. Why is hydrogen not collected by the displacement of air?

The chemical change that takes place is represented as follows:

Zinc + hydrochloric acid → zinc chloride + hydrogen

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

Hydrochloric acid is a compound of hydrogen and chlorine. The zinc takes the place of, or *replaces,* the hydrogen of the acid and liberates it as a free gas. Instead of hydrochloric acid, we now have zinc chloride, which remains dissolved in the water in the generator. Zinc chloride is a white solid.

All acids contain hydrogen, which may be replaced by certain metals. Hence, to prepare hydrogen, we may use almost any acid and one of a number of other metals instead of zinc. It is a curious fact that when pure zinc is added to pure hydrochloric acid, the chemical

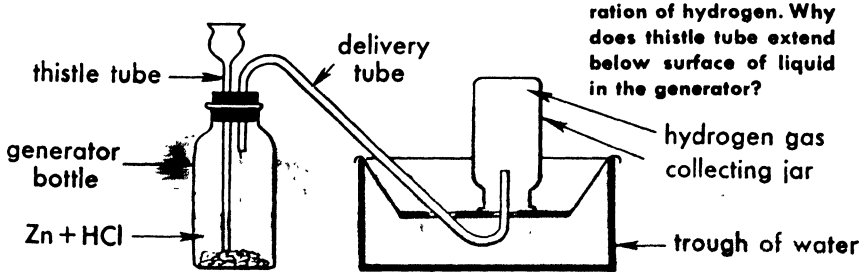


Fig. 6. Laboratory preparation of hydrogen. Why does thistle tube extend below surface of liquid in the generator?

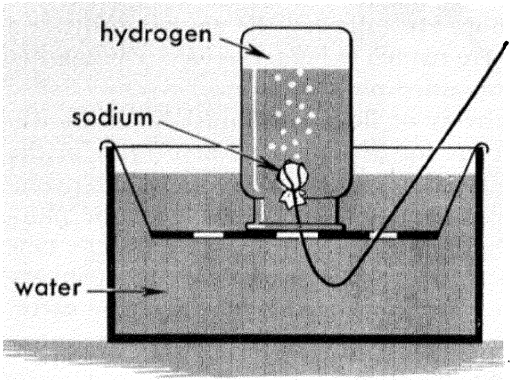


Fig. 7. Preparation of hydrogen by the action of sodium on water. Perform carefully. The reaction may be violent.

action is very slow. However, slightly impure zinc replaces the hydrogen of the acid rapidly. The impurity in the zinc acts as a catalyst.

Can hydrogen also be prepared from water? Perhaps you have been thinking, "If the hydrogen of an acid can be replaced by a metal, can the hydrogen of water also be replaced by a metal?" The answer is *Yes*. Very active metals, such as sodium, potassium, and calcium, possess enough chemical energy to replace the hydrogen of water. This experiment may be tried by filling a bottle with water and inverting it in a dish partly filled with water, as shown in the illustration (Fig. 7). Wrap in filter paper a piece of sodium the size of a pea and put the paper in the coiled end of a wire. Then quickly insert this end of the wire into the bottle. Immediately, a very active evolution of gas is noticed and the bottle becomes filled with a colorless gas. The equation for this reaction is:

Sodium + water → sodium hydroxide + hydrogen

$$2Na + 2HOH \rightarrow 2NaOH + H_2$$

(Water may be represented as H_2O or HOH.)

In the chemical reaction that occurs, sodium replaces half of the hydrogen in water, and forms sodium hydroxide, NaOH. (The OH group is called the *hydroxyl* group.) The sodium hydroxide remains dissolved in the water. The water solution of sodium hydroxide feels soapy, and turns pink *litmus*, a vegetable coloring matter, blue. By evaporating the solution, the sodium hydroxide can be separated from the water as a white solid. Sodium hydroxide belongs to a group of compounds called *bases* (Chapter 14).

Even iron, which is not nearly as active as sodium, will replace the hydrogen of water while the water (as steam) is passed over red-hot

iron in a heated tube. In fact, this method of preparing hydrogen has been used to a slight extent, the products of the reaction being iron oxide and hydrogen.

What is the industrial method of preparing hydrogen? In the order of the quantities of gas produced, hydrogen is obtained for commercial use: (1) by passing steam over hot carbon, (2) by passing steam through natural gas (methane), in the presence of a catalyst, (3) by the electrolysis of water. The equations for these methods are:

1) Steam + carbon → carbon monoxide + hydrogen

$$H_2O + C \rightarrow CO + H_2$$

2) Steam + methane → carbon monoxide + hydrogen

$$H_2O + CH_4 \rightarrow CO + 3H_2$$

3) Water → hydrogen + oxygen

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

In the first two methods, the hydrogen may be separated from the carbon monoxide gas by chilling the mixture of gases. The carbon monoxide, whose freezing point is much higher than that of hydrogen, solidifies, leaving nearly pure hydrogen gas behind. Only a minor part of the total hydrogen production is by electrolysis.

Physical properties of hydrogen. Hydrogen resembles oxygen in most of its physical characteristics. It is a colorless, odorless gas, slightly soluble in water, and very difficult to liquefy, since it changes from a gas to a liquid at −252°C. It differs physically from oxygen chiefly in its weight. It is the lightest element known. It is $\frac{1}{16}$ as heavy as oxygen and $\frac{1}{14.5}$ as heavy as air. One liter of hydrogen weighs approximately 0.09 gram at standard conditions of temperature and pressure.

The metals palladium and platinum absorb large volumes of

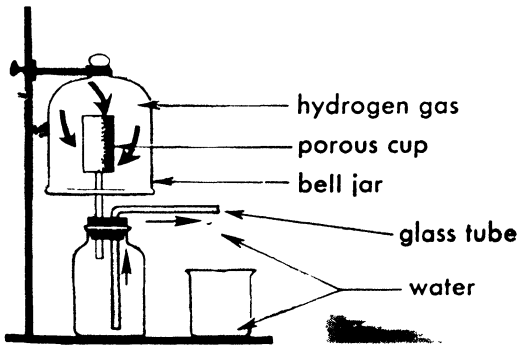


Fig. 8. Passage (diffusion) of hydrogen through a porous cup. Why is water forced through the glass tube?

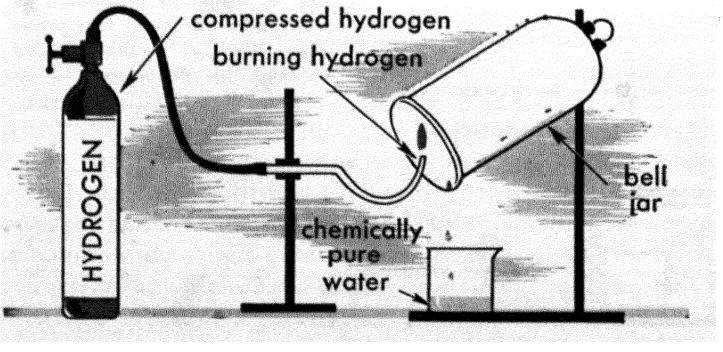
hydrogen. This absorption, or *occlusion,* is accompanied by such an increase in temperature that the metals actually glow. The absorption of hydrogen by these two metals takes place in one type of lighting apparatus sometimes used in lighting the burners of gas stoves. Such a lighter usually consists of a fine wire or wires of one of the two metals strung between two suspension points. The lighter is placed above the burner. When the gas is turned on, hydrogen is absorbed by the wire. This causes the wire to give off heat. In about a second, the kindling temperature of the gas is reached, and the gas is ignited.

If two or more gases are at the same temperature, the particles of the lighter gas move more rapidly than the particles of the heavier gases. Since hydrogen is the lightest gas known, its particles are in very rapid motion, passing through porous substances rapidly, as shown in Fig. 8.

Hydrogen may burn quietly or explode violently. Although pure hydrogen burns quietly in air or in oxygen with a pale blue, almost colorless, flame, a mixture of hydrogen and oxygen may unite with explosive violence. The two gases, when mixed and kept below a temperature of about 800°C., will not unite; but a spark, a flame, or a temperature of above 800°C. will cause them to unite violently. For this reason, great care must be taken while experimenting with hydrogen to keep all flames away from the generator. It is also necessary to wait until the air has been completely expelled from the generator before setting fire to the hydrogen as it escapes from the delivery tube.

When the Frenchman, Pilatre de Rozier, heard of this gas which Cavendish had studied, he tried an unusual and foolish experiment.

Fig. 9. Oxidation of hydrogen to form water. Will water form if bell jar becomes hot? How may bell jar be kept cool?



He inhaled the gas until he had filled his lungs, and then as the gas issued from his mouth he set fire to it. All Paris held its sides with laughter as it watched him spitting fire. However, when he set fire in the same way to a mixture of this gas and air, "the consequence was an explosion so dreadful that he imagined his teeth were all blown out."

The chemical union of hydrogen and oxygen may be written:

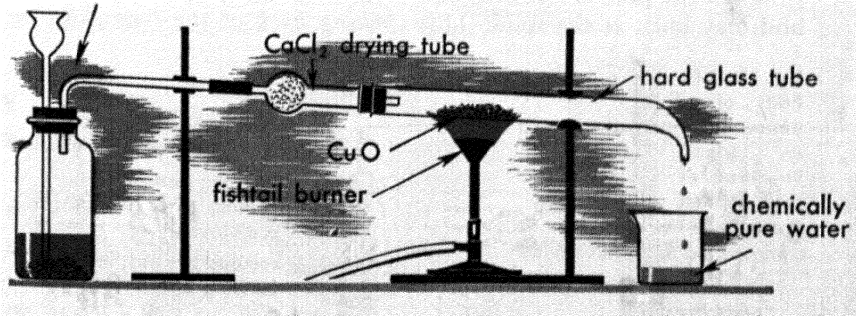
$$2H_2 + O_2 \rightarrow 2H_2O$$

This is an example of the strange behavior of chemical elements. Hydrogen, a highly flammable gas, unites with oxygen, a gas which helps things burn, forming water, a liquid that is one of the greatest enemies of fire.

Experimental proof that water forms. Of course, when hydrogen combines with oxygen, we do not see the formation of a flood of water. We do not because the water that is formed at the temperature of burning hydrogen is invisible since it is in the form of water vapor. However, it is possible to show the actual formation of water by arranging the apparatus shown in the illustration (Fig. 9). As the invisible water vapor strikes the cool surface of the jar, drops of a liquid form. This liquid is pure *synthetic* water. A synthetic compound is a compound built up from simpler substances.

Hydrogen is a powerful reducing agent. Since hydrogen has such a strong attraction, or *affinity,* for oxygen, it is able to tear oxygen away from the other elements of many of its compounds. The removal of oxygen from a compound is a chemical process known as *reduction.* This ability of hydrogen to remove oxygen from the other elements of a compound makes it a *reducing* or *deoxidizing agent.*

Fig. 10. Reduction of copper oxide by hydrogen. The fishtail burner is used to spread the flame, thus heating a larger surface of copper oxide. What is the function of the drying tube? Why is water a product?



For example, if pure hydrogen is passed over black copper oxide brought to a red heat, as shown in Fig. 10, the hydrogen takes the oxygen away from the copper oxide, leaving copper. This change may be represented as follows:

Copper oxide (black) + hydrogen → water + copper (red)

$CuO + H_2 \rightarrow H_2O + Cu$

Although hydrogen is a good reducing agent and is used to reduce the oxides of such metals as wolfram and molybdenum, other reducing agents are of greater commercial use. Perhaps the best example of these is carbon (*coke*), which is used in reducing iron ore (iron oxide) to iron.

The relation of oxidation to reduction. In the experiment just described, the copper oxide, CuO, is reduced to copper. At the same time hydrogen is oxidized to water, H_2O. This illustrates a general principle: namely, that the reducing agent is itself always oxidized. You should remember that whenever one substance is reduced, another is oxidized. Thus oxidation and reduction always occur in the same reaction.

The bunsen burner and how it works. One of the most familiar pieces of apparatus in the chemical laboratory is the *bunsen burner* (named after Robert Bunsen, a German chemist who introduced it in 1855). The function of this burner is to mix a gaseous fuel with air in order to make a nonluminous flame that has a high temperature and will not deposit soot.

The parts of the bunsen burner designed for burning manufactured gas are shown in Fig. 11. Gas enters through the side of the stand, and its speed is increased by passing through the narrow spud. The rapidly moving gas draws in air through the hole in the collar, which may be adjusted to permit the correct volume of air to enter. The mixture of gas and air passes up through the barrel and is ignited at the top.

When the pressure of the gas is low, the flame may be drawn back and may burn at the spud. This *striking back* of the flame can be

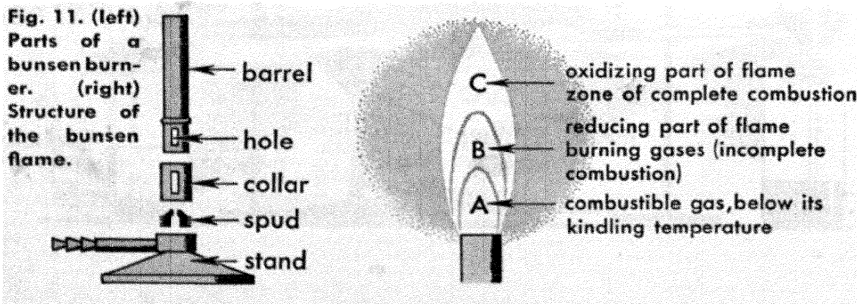


Fig. 11. (left) Parts of a bunsen burner. (right) Structure of the bunsen flame.

dangerous because the stand of the burner becomes hot enough to produce serious burns when touched, and occasionally the hot burner melts the rubber hose and ignites the gas.

In the type of burner for natural gas, the air intake is larger and the hole in the spud is much smaller. It is also supplied with a flame retainer which has 6 small pilot jets fed by gas bled from the main tube. This eliminates the tendency for the flame to blow out.

The burner on a gas range consists of a series of small bunsen burners. Not only is the nonluminous flame of the bunsen burner used in cooking, but it is used also to some extent in illumination by burning the gas inside gas mantles consisting of 99 percent thorium oxide and 1 percent cerium oxide. These oxides, when heated, glow with a rich white flame. They were first made commercially practical by von Welsbach (fŏn vĕls'bäĸ). The widespread use of electricity as an illuminant has made this type of mantle burner all but obsolete.

The nature of a flame. A flame is produced only when combustible vapors reach their kindling temperature in the presence of air, oxygen, or some other substance that supports combustion. When iron is heated gently, it glows, but a flame is not produced, because iron does not vaporize at low temperatures. A candle, on the other hand, burns with a flame, because the candle melts and the heat from the burning wick causes this liquid to change to a vapor that burns in air. It can be shown that the interior of a candle flame consists of a combustible gas by holding one end of a piping hot tube in the innermost part of the flame and then touching the other end with a lighted match (Fig. 12).

The structure of the bunsen flame. Three distinct zones are noticeable in the bunsen burner flame as well as in the candle flame. The innermost zone *A* is composed of combustible gas that has not yet reached its kindling temperature. This fact may be tested by placing a match head in zone *A*. This may be done by piercing a match near the head with a pin. The pin serves as a bridge across

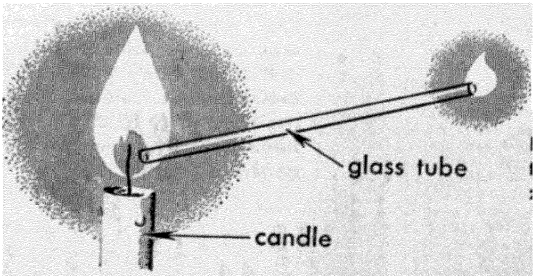


Fig. 12. Experiment showing the nature of the innermost zone of a candle flame.

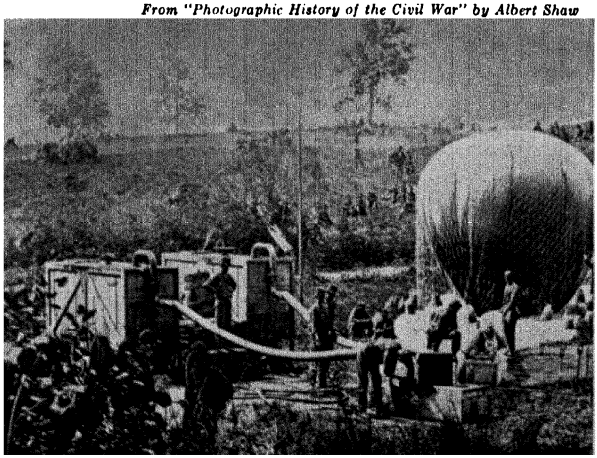
the opening of the burner. If the burner is lighted carefully, the match will not catch fire. Outside zone *A* is zone *B* in which the gas is burning. The light-purple zone *C* is the region of complete combustion, where carbon dioxide and water vapor are formed.

Just below the tip of the flame, plenty of air is available and, therefore, this is the *oxidizing* part of the flame. Zone *B* is the region of somewhat incomplete combustion, where one of the products formed is carbon monoxide, a reducing agent. Hence this zone is the *reducing* part of the flame. This zone of the flame is used in reducing metallic oxides to free metals by means of carbon. The blowpipe directs the flame, as shown in Fig. 71, page 321.

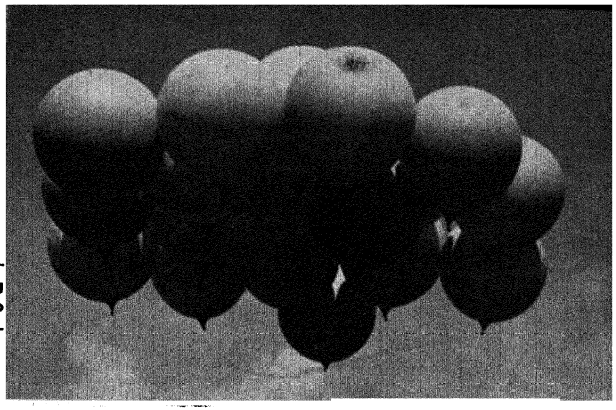
The luminosity of the flame of the bunsen burner, when the collar is closed, is caused by the decomposition by heat of a small amount of the hydrocarbons and the subsequent burning of free carbon. This may be proved by holding a cold dish in the luminous flame. The carbon is reduced below its kindling temperature by contact with the dish and, hence, deposits soot on the dish.

Hydrogen rides the winds. Interesting historically, but of only slight commercial importance today, is the use of hydrogen in filling balloons and other lighter-than-air craft. Soon after the discovery of hydrogen, Dr. Charles (shärl), of Paris, constructed the first large hydrogen-filled balloon, and in the presence of 300,000 spectators, Pilatre de Rozier, who had experimented unwisely with hydrogen before, bravely climbed inside its basket and started on the first aerial voyage ever made by a human being. Since that time, balloons filled with hydrogen have carried men around the world and have lifted explorers of the atmosphere to altitudes of almost 14 miles. The development of the motor-propelled, rigid balloon called a *dirigible* gave us gigantic craft, nearly 1000 feet long and weighing more than 100 tons.

From "Photographic History of the Civil War" by Albert Shaw



The observation balloon was used to advantage by the Union Army in the War Between the States. Here the balloon *Intrepid* is being filled with hydrogen by the generators at the left.



Such helium-filled balloons, carrying recording instruments, are used to determine weather conditions at high altitudes.

Official United States Navy Photograph

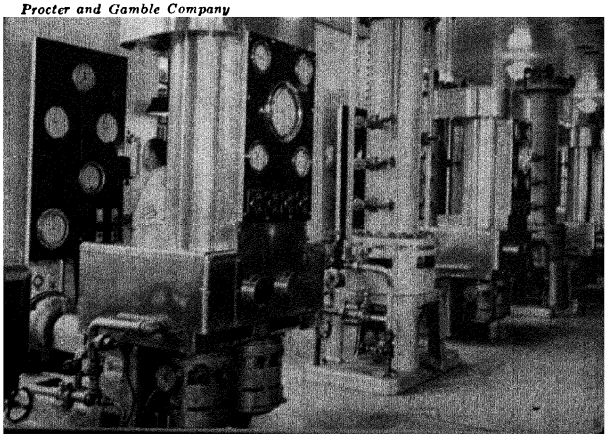
The history of this type of flying machine was filled with tragedy, to a large extent because hydrogen ignites and explodes readily. With the discovery of large sources of a nonflammable gas, *helium*, and its subsequent use, this ever-present danger was removed. There are no dirigibles in existence today, although blimps, which are motor-propelled, nonrigid balloons, are used for military purposes.

Helium, which possesses about 93 percent of the lifting power of hydrogen, may be obtained today at a cost not much greater than that of hydrogen. The United States is fortunate in possessing the largest supply of helium of any nation. As high as seven percent helium is extracted from the natural gas of some western fields.

To conserve our own supplies and prevent other nations from using helium for military purposes, Congress passed a law in 1938 which placed its export under very strict government control. Scientific discoveries often turn out to be two-edged swords, and the careful control of such discoveries should be part of the business of government.

Hydrogen, a gas, helps solidify fats and oils. One of the most important uses of hydrogen is based on the discovery that hydrogen

Procter and Gamble Company



These machines, called "freezers," are used in the hydrogenation of vegetable oils to give the oils creaminess and smooth texture.

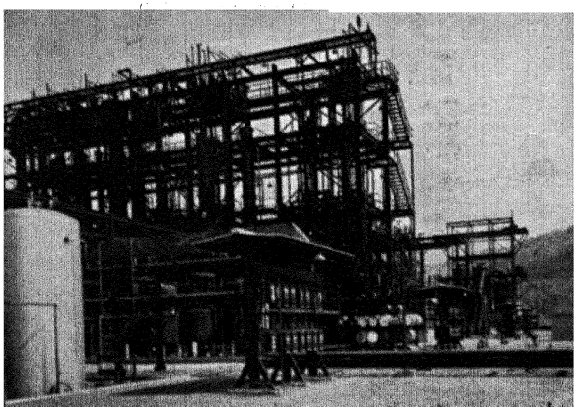
can be chemically combined with other substances to form new products of great value. This process of chemically combining hydrogen with other substances is called *hydrogenation.* In normal times, hydrogenation of fats and oils is the largest use of hydrogen.

Generally, during hydrogenation, liquid oils are changed to semi-solid fats. Thus, cottonseed oil, in the presence of a finely divided nickel catalyst, unites with hydrogen, forming a white fat that is often sold under such trademarks as "Crisco" or "Spry." Fish oils, formerly almost useless, have been hydrogenated similarly and rendered useful. Fats for soap-making and candle-making have been prepared commercially by this process also. Crude oil, coal, and certain waste products of petroleum refining are also hydrogenated and changed in this way into high-quality gasoline. Wood alcohol is another important chemical made with the aid of hydrogen.

Oleomargarine, or *margarine,* a widely used butter substitute, is made of either hydrogenated vegetable oils or animal fats, or mixtures of these substances. Much of the margarine now marketed is of vegetable origin.

The introduction of hydrogenation on a large scale helped the cotton farmers of the South by opening a new market for their cottonseed oil. It has had even greater effects abroad, for it has enabled several European countries to become less dependent upon other nations for their vital supplies of gasoline and edible fats.

Hydrogen for the synthesis of ammonia. Ammonia, a compound of nitrogen and hydrogen, leads a double life. It is an important component of nearly all of the world's most powerful explosives, and it is an important ingredient in fertilizers used all over the world. The most significant industrial process for the preparation of ammonia is one that embodies the direct combination, or *synthesis,* of nitrogen and hydrogen. This process is discussed in detail in Chapter 17. In wartime, production of ammonia probably requires more hydrogen than any other industrial use.



In this plant, bituminous coal is hydrogenated to produce many useful chemicals.



Based on photographs by Mt. Wilson Observatory and the High Altitude Observatory

An illustration of a solar prominence. Solar prominences are great tongues of glowing hydrogen which shoot out of the chromosphere of the sun and extend far into space. The flames often attain lengths of more than 100,000 miles and have been known to reach lengths of more than 1,000,000 miles.

Hydrogen in heating and cooling. Hydrogen has another important use. When it is burned, it gives off four times as much heat as an equal weight of coal. Because of the high temperature produced, hydrogen is used both in the oxyhydrogen torch and as a constituent of certain gaseous fuels such as *water gas*, which contains about 50 percent hydrogen. Hydrogen gas is also used as a cooling agent instead of air. Because of its very low density it cuts down friction in machines such as high speed turbine-generators. When hydrogen is so used, the machine is completely enclosed to shut out air.

The test for hydrogen. Hydrogen is not the only colorless gas that burns with a pale blue, almost invisible flame. But it is the only gas that forms water as the only product of its burning. This fact gives us a simple chemical test for hydrogen.

Where is hydrogen found? Unlike oxygen, only small amounts of hydrogen occur on earth in the free state. However, free hydrogen is the most abundant element in the sun. The immense luminous tongues, or *solar prominences*, some of which extend half a million miles from the sun's surface, consist of glowing hydrogen. It is also the commonest element found in interstellar space, and by far the most abundant material out of which the whole universe is built.

Combined hydrogen is very common on earth. Hydrogen constitutes about 11 percent by weight of all water and is one of the elements in petroleum, all acids, and living cells (protoplasm). In spite of its widespread occurrence, the extreme lightness of hydrogen accounts for the fact that it constitutes only 1 percent by weight of the earth.

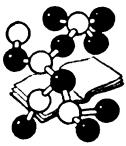


Henry Cavendish (1731–1810), one of the most unusual personalities in the history of science. For the most part, he shunned society of any kind, even instructing his servants to keep out of his sight. Yet, over his long lifetime, he made many important contributions in the fields of chemistry and physics.

Theories lead to great discoveries. In 1932, three Americans headed by Harold C. Urey discovered that ordinary hydrogen could be separated into two distinct forms. They named the heavier of these forms *deuterium*. Two years later, it was proved that there is a third form of hydrogen. This form, the heaviest of the three, has been named *tritium*. The three forms have the same chemical properties, but differ in certain physical properties.

This achievement is remarkable, not so much because ordinary hydrogen was shown to be a mixture of three forms of the same element, but because it afforded a definite example of a great contribution to chemistry made by scientists who forecast these discoveries purely from theory. Their success points to the fact that science needs the man who experiments, the thinker who can put his imagination and reason to work in propounding theories, and the engineer who works to discover how these theories and processes may be used in the service of man.

Another example of how theoretical problems in science may turn out to be of great practical value, was the theorizing of the great mathematician, James Clerk Maxwell. In 1863 he came to the conclusion that just as light results from a wave disturbance in the ether, so electric disturbances from a spark should produce similar waves, invisible, to be sure, but nevertheless existent. Experimental evidence of such waves was found 23 years later by a young physicist, Heinrich Hertz. These *Hertzian waves,* now known as *radio waves,* were later used by Marconi in the transmission of wireless messages. Thus modern radio originated, and out of a purely theoretical investigation came one of the most practical and valuable of modern scientific marvels. Often, even the greatest scientist cannot predict the practical value of theoretical research.



YOU WILL ENJOY READING

Hoyle, Fred. *The Nature of the Universe*. Harper and Brothers, New York, 1950. This is a very small book that gives an exciting picture of the composition of the stars and interstellar space.

Jaffe, Bernard. *Men of Science in America*, pp. 339–355. Simon & Schuster, New York, 1944. Interesting information on early American work in aeronautics.

Watters, Leslie. "Chemistry Exhibits and Projects." *Journal of Chemical Education*, March, 1939, pp. 113–115. An illustrated article on exhibits and projects made by high-school students. Suggestions for what you, too, could do along this line.



USEFUL IDEAS DEVELOPED

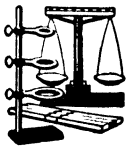
1. A reducing agent removes oxygen from a compound containing oxygen. (This definition will be somewhat expanded later.)

2. Reduction and oxidation always occur in the same reaction.

3. Occlusion is the absorption of gases by metals.

4. Careful control of some scientific discoveries is necessary to prevent their misuse.

5. Chemistry needs the experimental chemist, the scientist able to use creative imagination in formulating theories, and the engineer who works to discover how theories and processes may be used in the service of man.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) Who is credited with the discovery of pure H_2? (b) How was H_2 first prepared?

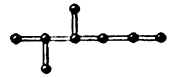
2. (a) What substances are used in the laboratory preparation of H_2? (b) How do we know that the H_2 comes from the acid and not from the metal? (c) Write the word-equation for this reaction.

3. (a) What advantage is there in collecting H_2 by the displacement of H_2O? (b) What kind of gas could not be collected in this manner?

4. (a) Make a labeled diagram of the laboratory preparation of H_2. (b) Why should the thistle tube extend below the surface of the liquid in the generating bottle? (c) What are two reasons for using a thistle tube?

5. (a) When Na displaces H_2 from H_2O, what is the other substance formed? (b) Why can you not see it? (c) How can you obtain it for inspection of its properties?

6. What metals other than Na are so active that they will liberate H_2 from water when the metal is simply placed on H_2O?



7. (a) What metal will liberate H_2 from H_2O under certain special conditions? (b) Describe this method of preparing H_2.

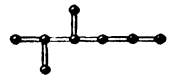
8. (a) In what two ways is H_2 prepared for commercial use? (b) Why were these methods selected in preference to ones used in the laboratory?

9. What precaution must be observed in preparing and handling H_2?

10. (a) List five physical properties of H_2. (b) Describe a simple experiment to illustrate the fact that H_2 is a very light gas.

11. Determine the weight and cost of the H_2 that would be needed to fill a dirigible of seven-million-cubic-foot capacity. Consider that the cost of the H_2 is $2.00 per hundred cubic feet of gas.

12. What element in the air is used in the burning of H_2?



13. How can you show that water is formed when hydrogen burns?

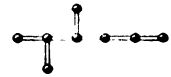
14. What is reduction?

15. In the reduction of CuO by H_2, what substance is oxidized?

16. How can you identify each of the products obtained in the reduction of CuO by H_2?

17. Oxidation and reduction always occur together. Explain.

18. (a) Give an example of reduction carried out on a large scale in industry. (b) What reducing agent is used?



19. (a) What is the function of each part of a bunsen burner? (b) What is meant by the striking back of the flame?

20. (a) What conditions are necessary for a flame? (b) Make a labeled drawing of the flame of a bunsen burner.

21. What formerly useless byproduct is converted into a very useful substance by the use of H_2?

22. How is oleomargarine made?

23. In what special fuels is H_2 chiefly responsible for the high temperatures obtained?

Group B

24. Can you suggest a safe way to test H_2 for its burnability as it emerges from the end of the delivery tube in the laboratory preparation?

25. Helium gas is twice as dense as hydrogen gas and yet can lift about 93% as much weight as hydrogen gas. Explain.

26. (a) Could pure H_2 be used in the gas range at home? (b) Explain.

27. Why does pure H_2 burn quietly in an atmosphere of air, yet burn with explosive violence when the two gases are mixed and ignited?

28. Tightly bound inflated balloons gradually collapse. Explain.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. A student's mother stopped using "Crisco" after her son came home with the news that "Crisco" was not a "natural product" but was manufactured chemically. (a) Was the mother justified? (b) Give reasons for your answer after you have consulted your family physician, the producers of "Crisco," and the U.S. Department of Agriculture.

2. Organize a small discussion group in your chemistry class and discuss the topic, "Synthetic chemistry has helped in the rise of totalitarian states."

3. Prepare a report or organize a class discussion on the topic "Theoretical science has frequently resulted in great practical discoveries."



4. WATER: THE COMMONEST LIQUID COMPOUND

. . . Laboratories are necessary, and, though an artist without a studio or an evangelist without a church might conceivably find under the blue dome of heaven a substitute, a scientific man without a laboratory is a misnomer. Frederick Soddy, 1877–

Water a compound of two gases — impossible! For thousands of years, water was considered an element. Aristotle, one of the wisest of Greeks, included this liquid among the "four elements" of the ancients. No power of man seemed strong enough to break it up into any recognizable components. Although it is true that by 1780 a number of scientists had really decomposed water so that hydrogen was liberated, they were unaware of the real nature of what they had done. They could not believe that hydrogen had actually come from the water.

"It is very extraordinary that this fact should have hitherto been overlooked by chemists. Indeed, it strongly proves that in chemistry it is extremely difficult to overcome prejudices imbibed in early education." These were the words of Lavoisier. Often it is hard to overcome superstition, prejudice, and tradition. However, we must learn to do so in order to think and act scientifically.

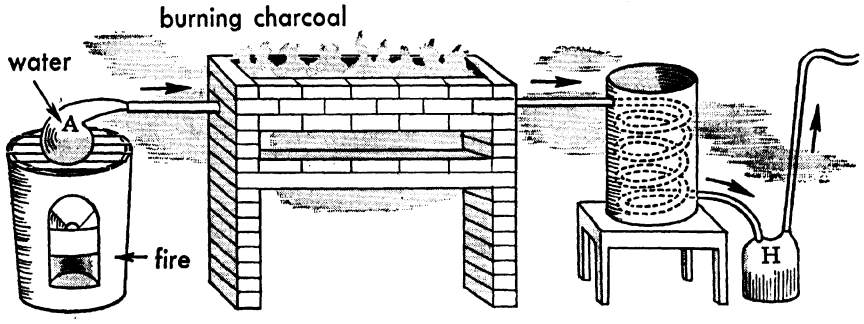
In 1784, Cavendish, who had studied hydrogen, read an exciting paper before the members of the Royal Society of England. This is what he told them: "Water is a compound of oxygen and hydrogen." What a startling announcement! Water a compound of two colorless, tasteless gases? What were his proofs? Cavendish told them

quietly and without emotion. He said that he had placed in a glass flask a mixture composed of about twice as much air as hydrogen. Then he had passed an electric spark through the mixture. "All the hydrogen and about one-fifth of the air condensed into a dew which lined the glass. In short," he continued, "it seemed pure water." His experiments proved conclusively that water is a compound of oxygen and hydrogen, and yet Cavendish said "it seemed." He suspected his listeners would not be convinced. Water a compound of two gases — impossible!

Lavoisier convinces the world that water is a compound. Lavoisier, who had explained the nature of burning, determined to tear apart, or *analyze,* water by an experiment that would convince the world, just as Cavendish had shown the world that he had built up, or *synthesized,* water from oxygen and hydrogen.

He arranged the apparatus shown below. In the retort *A* he heated pure water, so that steam would pass through the tube containing pure charcoal, which, as you see, was heated in a furnace. The gas that escaped passed into the jar *H*. He found carbon dioxide gas dissolved in the water in the jar and identified the gas issuing from *H* as hydrogen. The water (steam) had been broken up into hydrogen, which passed on as a gas, and oxygen, which combined with the carbon, forming carbon dioxide. Lavoisier collected and weighed both gases. The weight of all the resulting products accounted for all changes in the weights of the substances used in the reaction. Thus Lavoisier proved without a doubt that water could be broken up into the two gases of which it is composed — hydrogen and oxygen.

Fig. 13. Apparatus used by Lavoisier to analyze water. Compare this equipment with that used in a modern laboratory.



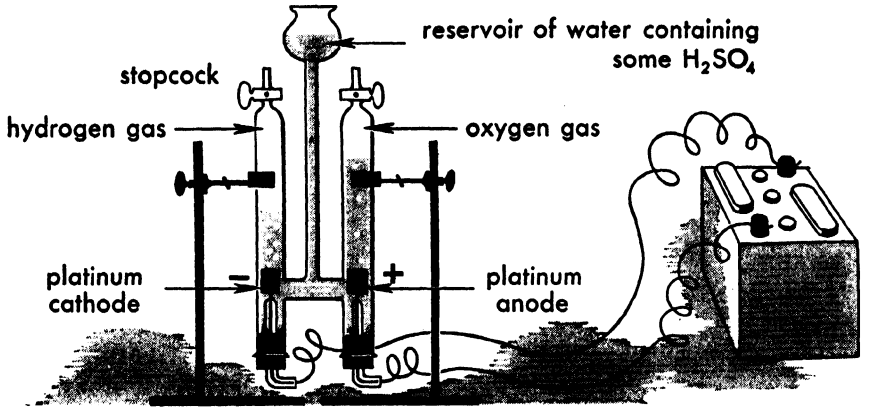


Fig. 14. Electrolysis of water. Why is a reservoir necessary in this apparatus?

The equation for the chemical changes that took place in this experiment is:

$$2H_2O + C \rightarrow 2H_2 + CO_2 \text{ (carbon dioxide)}$$

How water can be broken up by an electric current. In 1800, the invention of the electric battery by Volta put into the hands of scientists a new and powerful tool for determining the composition of compounds. The decomposition of any compound by electricity is called *electrolysis.*

Within a few months following Volta's invention, an apparatus had been devised for the electrolysis of water. This special piece of apparatus is used in the laboratory in determining the composition of water by volume. Water is poured into the center glass tube, which acts as a reservoir, and fills the other two tubes, as shown in Fig. 14. Since pure water is an extremely poor *conductor* of electricity, that is, will not allow electricity to pass through it readily, a small amount of sulfuric acid is added. (At the close of the chemical action, the amount of sulfuric acid is unchanged.)

The electric current enters the apparatus through one of the platinum electrodes, passes through the mixture of water and sulfuric acid, and leaves the apparatus at the second platinum electrode. The source of current may be any source of direct current, such as a storage battery or dry cells. As soon as the circuit is closed, bubbles of gas collect on the surface of the electrodes, rise through the water, and collect at the top of the two outside tubes. The gas that collects at the negative electrode, or *cathode,* is hydrogen; the gas that collects at the positive electrode, or *anode,* is oxygen.

The composition of water by volume. No matter when we stop the action of the current in the electrolysis of water, we discover a singular fact. The volume of the gas at the cathode is twice the volume of the gas at the anode. In other words, water always consists of 2 parts of hydrogen to 1 part of oxygen by volume.

If the gases hydrogen and oxygen are mixed in a closed chamber and then exploded by an electric spark, water vapor is formed, and the ratio in which these gases unite, forming water vapor, is always 2 volumes of hydrogen to 1 of oxygen. Any excess of either gas is left uncombined.

The composition of water by weight. If pure water is thus decomposed, forming two gases in a definite ratio by volume (*volumetric ratio*), and if water is formed by combining these gases in the same volumetric ratio, it ought to be possible to find in this combination a constant ratio by weight. This is what Cavendish did in 1784 when he formed water by combining these two gases. He actually weighed both the gases and the water. Today we know that if we combine 1 gram of hydrogen (11 liters) with 8 grams of oxygen (5.5 liters), we obtain 9 grams of water. Thus, *the composition of water by weight is 1 part of hydrogen to 8 parts of oxygen.*

The composition of water by weight may be tested in the laboratory by making use of the fact that pure hydrogen passed over heated copper oxide reduces the copper oxide, yielding free copper, by uniting with the oxygen of the copper oxide, thus forming water (see page 50). The weight of the water formed is always found to be exactly the same as the weight of the hydrogen used *plus* the weight of the oxygen lost by the copper oxide. The following data are the results of such an experiment:

Weight of copper oxide before experiment	80 grams
Weight of copper left after experiment	64 grams
Weight of oxygen that combined with hydrogen	16 grams
Weight of water produced	18 grams
Weight of hydrogen used	2 grams

Result: 16 parts by weight of oxygen combined with two parts of hydrogen (or 8 parts of oxygen combined with one part of hydrogen), forming water.

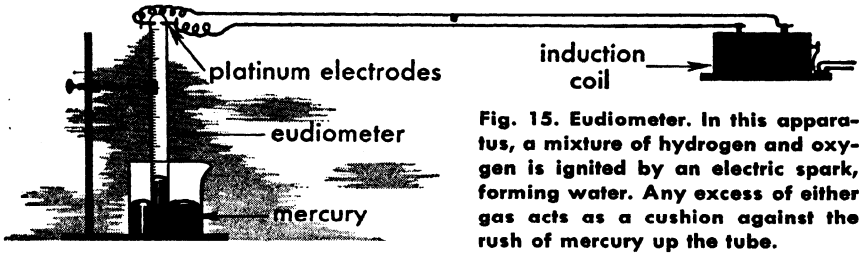


Fig. 15. Eudiometer. In this apparatus, a mixture of hydrogen and oxygen is ignited by an electric spark, forming water. Any excess of either gas acts as a cushion against the rush of mercury up the tube.

Accuracy and satisfaction in scientific investigations. An exact determination of the relative combining weights of oxygen and hydrogen was essential to the mathematics of chemistry. Hundreds of men performed thousands of experiments to determine these values as accurately as human ingenuity could devise. Many eminent Americans were among them. Edward Morley (1838–1923), a professor at Western Reserve University, spent more than ten years of his life on such experiments. Finally he arrived at a number which still stands as the basis for chemical calculations. He found that 1.008 parts of hydrogen by weight combine with eight parts of oxygen by weight, forming water.

Morley and the others did not receive monetary rewards from these experiments. Theirs was a labor of love, a work of pure scientific research. Their sole reward was the satisfaction of knowing that they were helping to increase scientific knowledge which might be of use to all humanity. The world needs such unselfish men.

The law of definite proportions. You have learned that the composition of water is always the same. Perhaps you have wondered if this is a property of all chemical compounds. It is one of the fundamental laws of chemistry that, in forming compounds, elements combine in exact proportions. In fact, constancy of composition is the most valid test used in deciding whether a substance is a compound or a mixture. In other words, *the composition of a pure compound never varies.* This is the *law of definite proportions.*.

"The stones and soil beneath our feet and the ponderous mountains are not mere confused masses of matter; they are pervaded throughout their innermost constitution by the harmony of numbers." This is indeed fortunate, for if the composition of pure compounds ever changed, instead of being always the same, the exact measurements that we use in chemistry would not be possible. Particularly is this true of *quantitative* chemistry, for if the composition of compounds varied, we should have no reliable standard chemicals. Standards are necessary, not only as a means of judging the purity of a substance which we plan to use, but also as a reliable basis for comparison.

What is a "pure" chemical? Absolutely pure chemicals are almost impossible to make or buy. Chemicals that have no appreciable trace of impurities are called *C.P.*, that is, *chemically pure.* The designation *U.S.P.* refers to standards of purity of chemicals to be used in medicines listed in the *United States Pharmacopoeia.* Such chemicals contain no *harmful* impurities. *Reagent* grade chemicals conform to the standards of the American Chemical Society. *Tech* chemicals do not meet any definite, or fixed, standards of purity but are suitable for many uses in which slight impurities are of little importance.

Patent medicines, other remedies, and drugs, such as aspirin, are frequently advertised and sold under trademarks. The purchaser should always carefully examine the label on the package in order to be sure of the purity of the contents. The chemical composition of the contents will also serve as a guide to the fair price of the article. Occasionally, simple and inexpensive C.P. chemicals, such as bicarbonate of soda, are masked behind trademarks and sold at exorbitant prices. The consumer can help to guard against such practices by insisting that accurate and complete statements of composition be printed on labels of all packaged goods.

Some physical properties of water. As you know, water is an odorless, tasteless liquid that is colorless, except in very thick layers, when it appears blue. Pure water freezes at 0°C. or 32°F. and boils at 100°C. or 212°F., at standard conditions. In general, impure water has a higher boiling point and a lower freezing point than pure water.

The fact that water is so universally distributed has led to its use in the devising of scientific standards of measure. Thus a gram, the metric unit of weight, is, by definition, the weight of a milliliter * of chemically pure water at 4°C. This temperature is chosen because, when water cools, it contracts until the temperature reaches 4°C. Below that temperature it begins to expand again. Hence, 4°C. is the temperature at which a unit volume of water weighs the most. *The weight of a unit volume of a substance is known as its density.* Thus at 4°C. water has its greatest density. Since we use the gram and the cubic centimeter or the milliliter as our units of weight and volume, we may redefine the density of a substance as the weight in grams of 1 cubic centimeter or 1 milliliter of that substance.

* A *milliliter* (ml.) is a small unit of capacity (volume) in the Metric System. Numerically it is equal to 0.001 of a liter and is used in measuring the volume of fluids. The cubic centimeter (cc.) is also used in measuring volumes, particularly of solids.

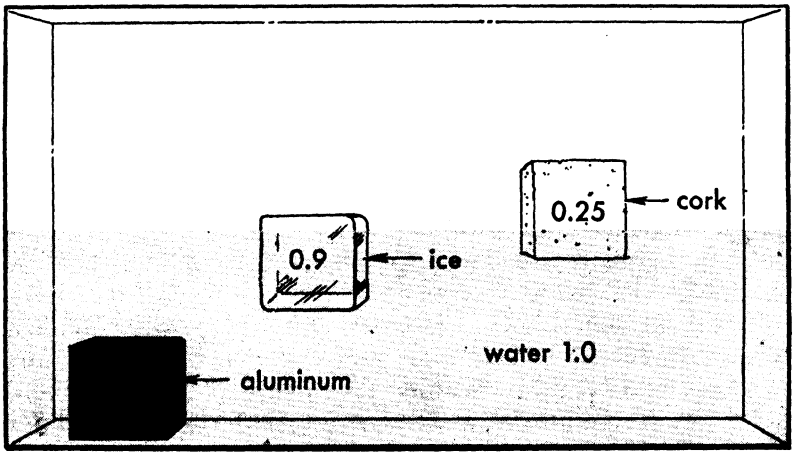


Fig. 16. The relationship of specific gravity and buoyancy. Aluminum has a specific gravity greater than that of water and does not float. Ice has a specific gravity slightly less than that of water and floats largely submerged. Cork has a low specific gravity and floats with most of its mass above water.

Since water has a density of *1*, that is, 1 milliliter of water weighs 1 gram at 4°C., the density of any substance is also the *ratio of the weight of a given volume of that substance to the weight of an equal volume of water.* We call this ratio the *specific gravity* (sp. gr.) of the substance. It shows the comparison between the weight of the substance and the weight of an equal volume of water. For example, when we say that concentrated sulfuric acid has a specific gravity of 1.84, we mean that it is 1.84 times as heavy as water, volume for volume. Since below 4°C. water expands, ice is lighter than water and floats on it. Ice, of course, has a specific gravity less than that of water.

TABLE 1. DENSITIES OF COMMON SUBSTANCES

(In grams per cubic centimeter or per milliliter)

Sodium	0.97	Iron (pure)	7.86	Lead	11.37
Water	1	Gold	19.3	Platinum	21.5

The high specific heat of water. The amount of heat necessary to raise the temperature of 1 gram of water 1 degree centigrade is called a *calory*. The number of calories necessary to raise the temperature of 1 gram of a substance 1 degree centigrade is known as the *specific heat* (sp. ht.) of that substance. Because it takes 1 calory to raise the temperature of 1 gram of water 1 degree centigrade, the specific heat of water is *1*.

Since it takes only one-thirtieth as much heat to raise the temperature of 1 gram of mercury 1 degree centigrade as it does to raise 1 gram of water 1 degree centigrade, the specific heat of mercury is one-thirtieth of 1, or $\frac{1}{30}$.

Water has a higher specific heat than most other substances. Since it requires so much heat to raise its temperature, it warms up slowly. Conversely, upon cooling it gives up a larger amount of heat for the same fall in temperature than most other substances do. It is partly because of the high specific heat of water that it is used in home heating systems and in the cooling systems of automobiles.*

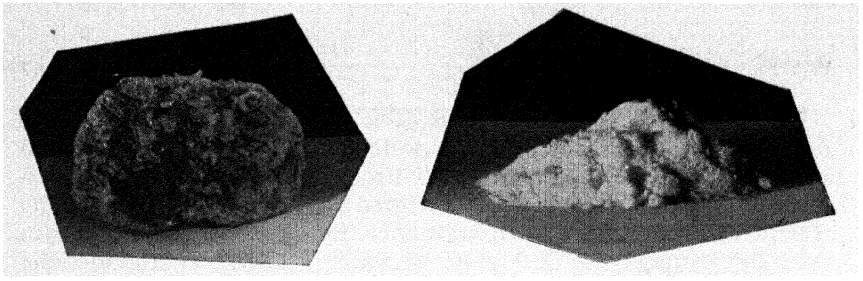
The chemical properties of water. Water is a *stable compound,* that is, it cannot be decomposed easily. It does not even begin to decompose into hydrogen and oxygen until a temperature of 1000°C. is reached. Even at 2500°C. only two percent of it is decomposed. However, electricity, in the presence of a catalyst, tears it apart easily (see page 62).

At ordinary temperatures, water is decomposed by the more active *metals,* such as sodium and potassium, and at higher temperatures by the less active metals, such as iron. In these cases the gas liberated is hydrogen. Water is also decomposed by the more active *nonmetals,* such as chlorine and bromine, but these liberate oxygen from water instead of hydrogen.

Water acts as a catalyst in many chemical reactions. For example, perfectly dry oxygen and hydrogen do not unite when a spark is passed through them, yet the faintest trace of water causes such a mixture to explode. Phosphorus does not burn in perfectly dry air, but burns readily if even a trace of water vapor is present.

* Although the temperatures of boiling water and steam are the same, it takes about 540 calories to change 1 gram of water from its boiling point of 100°C. to steam at 100°C. This amount of heat is called the *heat of vaporization* of water. Real steam, or water vapor, the gaseous form of water, is invisible. The visible cloud commonly called *steam* is water vapor after it has condensed into tiny liquid droplets.

In ice water the temperatures of the freezing water and the melting ice are both 0°C. Yet it requires about 80 calories to change 1 gram of ice at 0°C. to 1 gram of water at 0°C. This amount of heat is called the *heat of fusion* of ice.



(left) Photomicrograph of a crystal of sodium carbonate. (right) The same crystal after a few hours of exposure to air. What has occurred?

Water of crystallization. A *crystal* is a solid mass having a well-defined and angular form. The word is derived from a Greek word meaning *clear ice.* Most elements and compounds are capable of assuming the crystalline form, showing sharp edges and flat surfaces. Such a substance is crystalline washing soda, or sodium carbonate.

When a crystal of washing soda is heated or even exposed to air, it gives off water and crumbles to a white powder which is not crystalline. The weight of water liberated bears a fixed ratio to the weight of the crystal and is united chemically with the compound of which the crystal is composed. Water which is thus *chemically* united with a substance and gives that substance its crystalline form is called *water of crystallization.* Such water is rather loosely held in chemical combination and may be easily expelled. The water of crystallization is separated from the rest of the formula by a centered dot, which means *plus* (+) and is not a multiplication sign. A substance that contains water of crystallization is sometimes called a *hydrate.*

Another common hydrate is crystallized copper sulfate once commonly known as *blue vitriol.* When this compound is heated, its water of crystallization is liberated and it crumbles to a white powder.

$CuSO_4 \cdot 5H_2O$	$\rightarrow$	$CuSO_4$	+	$5H_2O$
crystallized copper sulfate		copper sulfate (anhydrous)		water of crystallization

This change in color is further evidence that the water of crystallization is chemically united with the copper sulfate. Use is made of the difference in color between white anhydrous copper sulfate and the blue hydrated copper sulfate as a test for water. Water will change anhydrous copper sulfate to the blue hydrate.

The ability to form crystals is not always dependent upon the presence of water. Many crystalline substances, such as table salt (sodium chloride) and sugar, do not contain water of crystallization. They are said to be *anhydrous,* meaning *without water.* Crystals that have lost their water of crystallization are also said to be anhydrous.

Efflorescent substances give up water. Crystallized washing soda, on exposure to air, loses its water of crystallization and crumbles to a powder. Such a substance is said to be *efflorescent,* which means that it gives up its water of crystallization on exposure to air. The drier the air, the faster the loss of water of crystallization.

Deliquescent substances take up water. Dry sodium hydroxide, when left exposed to air, soon absorbs enough water from the atmosphere to dissolve itself in this water. Such a substance is said to be *deliquescent.* The higher the percentage of water vapor in the air, the faster the process of deliquescence.

Calcium chloride, a white solid, is deliquescent and is often used to sprinkle dry roads and tennis courts. It absorbs moisture from the air and, in this way, helps to keep the dust down. Magnesium chloride, an impurity found in common table salt, is also deliquescent. Removal of the magnesium chloride causes pure table salt to remain dry in damp weather, to pour easily, and not to cake. (What substance does your mother put in a salt shaker to keep the salt from becoming lumpy?)

Deliquescent substances may be used as *drying,* or *dehydrating, agents.* For example, concentrated sulfuric acid absorbs moisture from the air and, therefore, is used in drying gases. When used in the laboratory, these dehydrating agents (the most common of which are sodium hydroxide, sulfuric acid, and calcium chloride) are often placed in the lower compartment of a vessel known as a *desiccator;* the upper compartment, only partially separated from the lower, contains the substance to be dried.

Our lives depend on water. Water is essential to life. Almost 70 percent of the total weight of the human body is water, and plants contain even more. Lettuce, for example, contains as much as 95 percent water by weight.

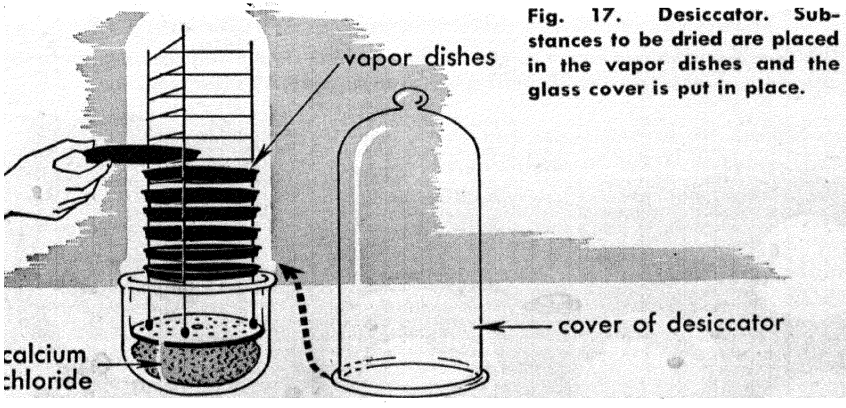


Fig. 17. Desiccator. Substances to be dried are placed in the vapor dishes and the glass cover is put in place.

Immense tracts of land in our own country, such as the hitherto arid Columbia Basin of the Northwest, have been or will be turned into rich farmland by irrigation. Federal government projects have included construction of huge dams such as the Norris Dam, the Hoover Dam, the Fort Peck Dam, and the Grand Coulee Dam. Behind mountainous walls of earth and concrete are stored huge reservoirs of water which are changing more wasteland into fertile plains and are helping to solve the problem of the frequent recurrence of disastrous floods in certain areas.

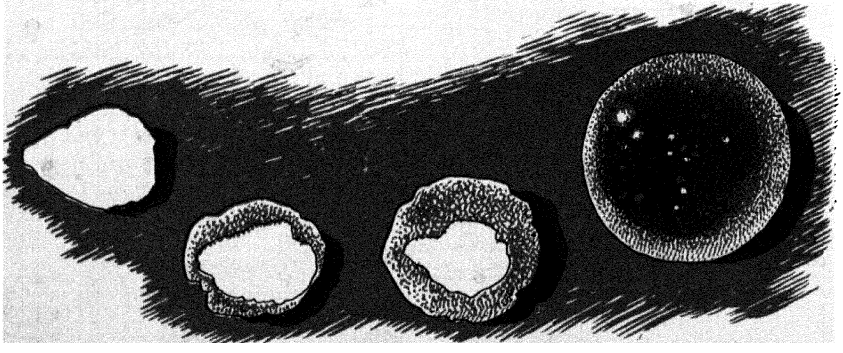
Water is found in rocks, paper, fibers, and other substances generally thought of as "dry." The pages of this book may contain as much as 10 percent water by weight. The importance of water, the most common solvent in nature, is discussed in detail in Chapter 15.

Water and health. Water is a major component of all body tissues and fluids. It plays a major role in the preparation of foods we eat and in the processes of digestion and assimilation. Both nutrients and oxygen are carried to the cells of the body in fluids composed chiefly of water, and many of the waste products of the body are carried away and eliminated in a similar manner. Water, in the form of perspiration, aids in regulating the temperature of the body.

To maintain normal body processes, rather large quantities of water are necessary. The amount of water a person should drink each day to enable these processes to be carried on varies with the kind and amount of activity, the temperature, and various other factors. However, 6 glasses each day should be considered a minimum for good health.

The idea that water should not be drunk with meals is without foundation. Digestion proceeds normally even when large quantities of water are present in the stomach. However, it is very important not to substitute the drinking of water with meals for proper and complete chewing.

This illustration shows how a single calcium chloride crystal deliquesces, gradually absorbing water from the air until it becomes completely dissolved.





YOU WILL ENJOY READING

Holmes, Harry N. *Out of the Test Tube* (4th ed.), Chap. VII. Emerson Books, New York, 1945. "The Elixir of Life," of course, refers to water.

Read the Label on Foods, Drugs, Devices, Cosmetics. Catalogue No. FS 13.111:3/2, 1953. Supt. of Documents, Govt. Printing Office, Washington, D.C. Revision No. 1 of a 35-page illustrated pamphlet containing valuable information. 15¢

Thorpe, T. E. *Essays on Historical Chemistry,* pp. 98–122. The Macmillan Co., London, 1923. A description of the famous controversy (the Water Controversy) over the priority of the discovery of the composition of water, involving Cavendish, Watt, Priestley, and Lavoisier.



USEFUL IDEAS DEVELOPED

1. Analysis is the breaking down of a compound into simpler substances.

2. Synthesis is the building up of a more complex compound from simpler substances.

3. The decomposition of any compound by electricity is called *electrolysis.*

4. Edward Morley spent more than ten years of his life in determining the exact ratio in which oxygen and hydrogen unite in forming water. His work is a fine example of accuracy and patience in scientific research.

5. Every pure chemical compound has a definite composition. This is the law of definite proportions. *C.P.* refers to a chemically pure substance.

6. The density of any substance is the weight of a unit volume of that substance.

7. A calory is the amount of heat necessary to raise the temperature of one gram of water one degree centigrade.

8. The specific heat of a substance is the number of calories necessary to raise the temperature of one gram of that substance one degree centigrade.

9. The specific gravity of any substance is the weight of one cubic centimeter or one milliliter of that substance compared with the weight of an equal volume of water.

10. Water of crystallization is the water chemically present in certain crystalline substances.

11. An efflorescent substance loses water of crystallization on exposure to air; a deliquescent substance absorbs water from the air.



USING WHAT YOU HAVE LEARNED

Group A

1. Why is water considered a compound?

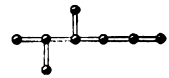
2. How did Cavendish synthesize H_2O?

3. What is the difference between analysis and synthesis?

4. Briefly describe how Lavoisier analyzed H_2O.

5. What is electrolysis?

6. (a) Make a labeled diagram of the apparatus for the laboratory electrolysis of H_2O. Indicate the direction of the current, the cathode, and the anode. (b) At which electrode is the H_2 given off? (c) the O_2?



7. What part does sulfuric acid (H_2SO_4) play in the electrolysis of H_2O?

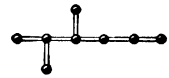
8. Write the word-equation for the electrolysis of H_2O.

9. How would you test to find out which of the gases present in the two outer tubes of the electrolysis apparatus is H_2?

10. (a) What is the composition of H_2O by volume? (b) by weight?

11. What are the differences between *C.P.*, *U.S.P.*, *Tech*, and *Reagent* chemicals?

12. In connection with the study of H_2O, cite an example of the accuracy and patience of men of science.



13. State and illustrate the law of definite proportions.

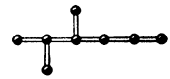
14. (a) Does vigorously boiling H_2O have a higher temperature than slowly boiling H_2O? (b) Explain.

15. What are five physical properties of H_2O?

16. How does steam differ from water vapor?

17. Why is it sometimes unsafe to purchase drugs or medicines by trade-mark alone?

18. Explain why water pipes often burst in cold weather.



19. (a) Which would you prefer to heat your feet on a cold night — a hot flatiron or a bottle of hot H_2O? (b) Explain.

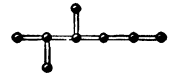
20. If H_2O were less stable than it is, what disaster might occur?

21. Describe two chemical properties of H_2O.

22. Give an example of the part that a trace of H_2O may play in bringing about a chemical change.

23. Illustrate what is meant by water of crystallization.

24. Transparent crystals of washing soda change to a white powder. Is this a physical or a chemical change?



25. Why is an unstoppered bottle of calcium chloride ($CaCl_2$) sometimes left in large clocks?

26. When crystals of table salt (NaCl) are heated, some H_2O is liberated. Is this water of crystallization? Explain.

27. Examine some pellets of NaOH that have been exposed to air. What property does NaOH have?

28. (a) Which gives a more severe burn, boiling H_2O or steam? (b) Why?

29. Explain the importance of H_2O to health.

Group B

30. If H_2O did not expand on freezing, how would it affect us?

31. A spark is passed through a mixture of 60 ml. of O_2 and 50 ml. of H_2 in the presence of water vapor. What substances, and how much of each, will be found in the tube after the explosion?

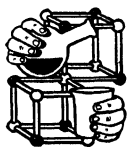
32. Devise an experiment to show the composition of H_2O by weight. Mention actual weights.

33. How would you determine the percentage of H_2O present in a sample of "dry" wood?

34. A liter of H_2 weighs 0.09 g. and a liter of O_2 weighs 1.43 g. Show how you could find the composition of H_2O by weight from these facts (data).

35. What weight of oxygen can be obtained from the electrolysis of 50 pounds of water?

36. Ice is purer than water. Would it be safe to use ice from a polluted pond in your iced tea? Explain.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

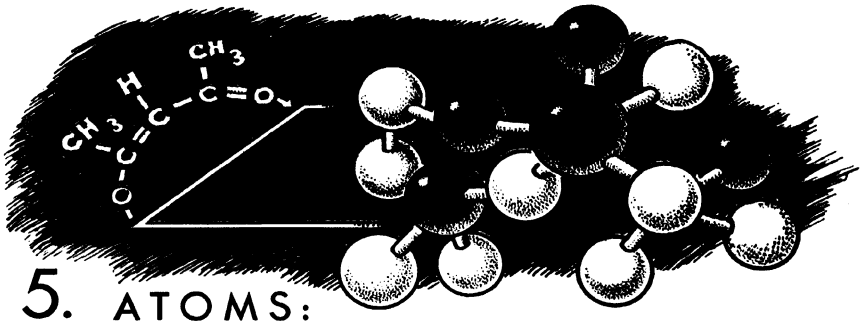
1. Find out from your mother or grocer the cost of pound packages of powdered washing soda and crystallized washing

soda. The water of crystallization present in crystallized washing soda is equal to approximately 63 percent of the weight of the crystal. On this basis, calculate which is less expensive, the crystallized washing soda containing water of crystallization or the powdered washing soda containing no water of crystallization. Make a report of your problem in class.

2. A student came to his chemistry teacher very excited about his invention of a system that would run an airplane indefinitely on a small amount of H_2O. He planned to decompose H_2O by electricity, use the O_2 and H_2 thus produced to supply an oxyhydrogen torch which, when ignited, would boil H_2O for a steam engine. The steam engine in operation would give power to the plane's propeller and, at the same time, to an electric generator. The electricity thus produced would be harnessed to decompose more H_2O, which would be constantly renewed as a product of the burning of the O_2 and H_2 in the oxyhydrogen torch. What do you think of this invention? Your answer should be complete with scientific reasons.

3. Benjamin Thompson, one of the greatest of early American scientists and who later became Count Rumford, made classic contributions in the field of specific heat. "It is a strange coincidence," wrote Albert Einstein, "that nearly all the fundamental work concerned with the nature of heat was done not by professional scientists but by men who regarded science as their great hobby." Mention two other scientific contributions made by men who were not professional scientists.

4. Get some anhydrous copper sulfate and with it determine whether certain "dry substances" really contain water. Report your results.



5. ATOMS:

THE BRICKS OF THE UNIVERSE

The bodies which time and nature add to things little by little, . . . no exertion of the eyesight can behold; and so, too, wherever things grow old by age and decay, and when rocks hanging over the sea are eaten away by the gnawing salt spray, you cannot see what they lose at any given moment. Nature, therefore, works by unseen bodies.

Lucretius, 99–55 B.C.

The origin of the idea of atoms. The most fruitful scientific speculation that came out of ancient Greece 2500 years ago was that matter is made up of small, eternal particles in continual motion. Leucippus and his pupil Democritus (dē mŏk′rĭ tŭs), taught that all matter was composed of invisible, indivisible, indestructible particles, or *atoms.* During the seventeenth century, Newton had similar ideas about the nature of matter. "It seems probable to me," wrote Newton, "that God in the beginning formed matter in solid, massy, hard, impenetrable, moveable particles, so very hard as never to wear or break into pieces." The gradual development of the idea of the atom is an interesting story.

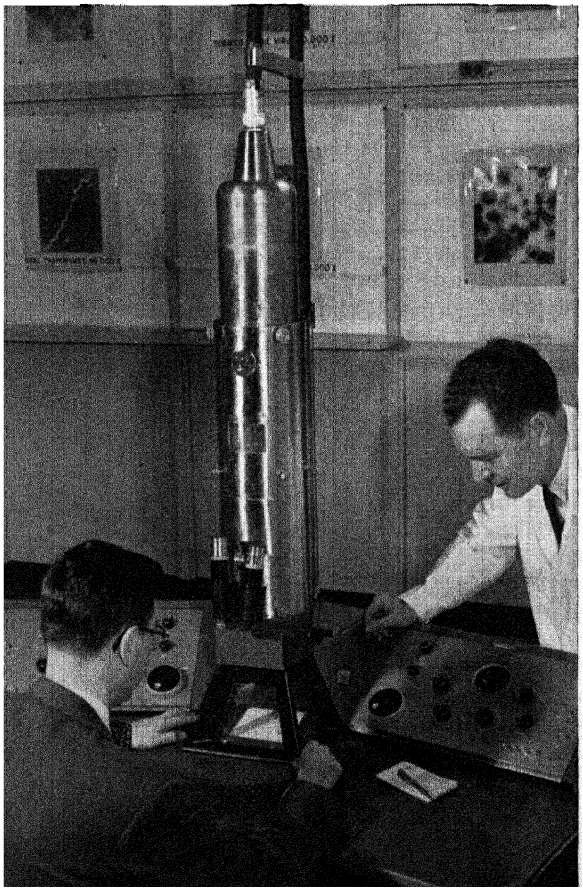
How Dalton's approach to the nature of matter differed from that of the Greeks. Early in the nineteenth century, an English scientist, John Dalton, became interested in the idea of atoms. Newton's idea was a beautiful one, thought Dalton, but did it check with the known facts? Would it help explain some of the physical properties of gases, which had so puzzled him?

It is interesting to note the difference in the way the Greek teachers had come to their ideas and the way in which Dalton formulated his theory. The Greek teachers made a few observations, followed

some logical reasoning, and then ventured an opinion. For example, they noticed that a lump of salt could be broken down into bits of salt, which could then be further reduced to tiny crystals of salt. It was inconceivable, they reasoned, to continue this division forever. There must come a time, therefore, when one would finally reach the smallest piece of salt, that is, an indivisible atom of salt. Dalton did more. He also experimented. He tried to find out why the gases of the atmosphere remained mixed, how gases dissolve in water, and whether the composition of pure compounds varies or is constant.

On the basis of some not too accurate observations in these experiments and some indirect evidence from facts known in his day, he formulated the atomic theory. In 1803 he announced it suddenly without waiting to test all of it by experiment. Since that time a great many additional experiments have proved that Dalton's theory was substantially correct.

Radio Corporation of America



With this electron microscope, scientists may study molecules and other infinitesimal particles. Typical photomicrographs may be seen in the background.

Dalton's atomic theory. Dalton's atomic theory was based on the following ideas:

1) That all matter consists of extremely small particles, called atoms.

2) That all the atoms of any one element are alike in size, shape, and weight.

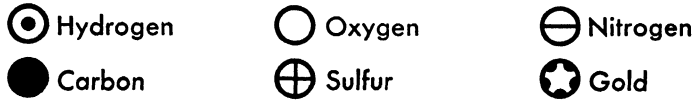
3) That the atoms of one element differ from those of all other elements in size, shape, and weight.

4) That chemical changes are changes in the combination of atoms with each other.

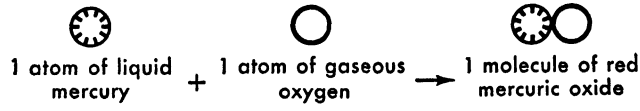
5) That even in the most violent chemical change, the indivisible atoms do not break into pieces.

The diameter of the hydrogen atom is about 1/250,000,000 inches. This is several hundred times smaller than the average-sized bacterium.

To explain his theory, Dalton drew pictures of atoms. Each atom was represented by a circle. Since the atoms of elements are unlike, he varied the pictures of the circles as follows:



Dalton pictured chemical change as the union of one or more atoms of one element with atoms of other elements. He believed that when mercury is heated in air, one atom of mercury unites with one atom of oxygen, forming a particle of the compound, mercuric oxide. To demonstrate this union of atoms, Dalton constructed model spheres, bringing them into contact with each other:



According to Dalton, atoms preserve their individuality in all chemical changes. Hence, Dalton described an *atom* as the *smallest part of an element that takes part in a chemical change without itself being altered.* Atoms combine to form molecules. Two or more atoms may combine into a molecule of an element or into a molecule of a compound. *A molecule is the smallest part of a compound or element that has the chemical properties of that compound or element.*

Inertia in scientific thinking. Dalton's theory was strongly attacked by the leading scientists of his day. One of the most eminent of them said he could not understand "how any man of sense or science would be taken in by such a tissue of absurdities." Dalton's theory was the result of creative imagination and the boldness of a great thinker. Dalton had never seen nor weighed an atom. Yet his theory was of practical value and was accepted gradually by the scientific world as a useful working hypothesis by which chemical changes could be explained.

The newer electron theory of matter (see Chapter 11) has expanded Dalton's theory. It has been modified in details, but its general applications still hold.

The use of Dalton's theory. One of the questions that scientists of Dalton's time were studying was whether the composition of a compound is always the same or whether it varies. Some believed that compounds are always formed from fixed amounts of elements. They believed therefore, that the composition of a compound is always the same.

The French chemist, Claude Berthollet (bĕr'tô'lĕ') ran some experiments to test this question. On the basis of his experiments he believed that the composition of compounds might vary to some extent.

Joseph Proust (prōōst), another Frenchman, set out to settle this difference of opinion. He repeated Berthollet's experiments, using the purest of chemicals and the most delicate apparatus available. Taking every precaution to prevent error, he found mistakes in Berthollet's work. He found that his fellow-scientist had used impure compounds and substances such as glass and mixtures of metals (alloys) and mixtures of liquids, which were not pure compounds.

For eight long years, the difference of opinion persisted. Never, however, did it become anything but an honest, truth-seeking discussion. Personal whims and prejudices did not decide the matter. When Berthollet considered Proust's evidence and discovered his own errors, he accepted Proust's verdict and agreed that the composition of compounds is always the same.

The law of definite proportions. This law states that *the elements in a compound always occur in a definite proportion by weight.* This is another way of saying that the composition of compounds is always the same.

Dalton's little circles very neatly explained the law. The weight of atoms of any element is always the same. Compounds are composed of these minute and unchangeable atoms. Therefore the composition of compounds by weight must be definite and uniform.

Dalton discovers the law of multiple proportions. Dalton knew that one atom of carbon ● unites with one atom of oxygen O to produce the deadly gas, carbon monoxide ●O. In this compound the carbon weighs $\frac{3}{4}$ as much as the oxygen. This fraction can be expressed as the ratio of 3 to 4.

Carbon also combines with oxygen to form carbon dioxide. Dalton wrote this combination as ●OO. In this compound the carbon weighs only $\frac{3}{8}$ as much as the oxygen. The ratio is three parts of carbon to eight parts of oxygen: 3 to 8. From observing this and other similar combinations, Dalton formulated another fundamental law of chemistry, the law of multiple proportions.

You note that in both carbon monoxide, CO, and in carbon dioxide, CO_2, the weight of the carbon is the same. But the weight of the *oxygen* in carbon monoxide is 4, and in carbon dioxide is 8. Thus three parts of carbon combine with either 4 parts or 8 parts of oxygen.

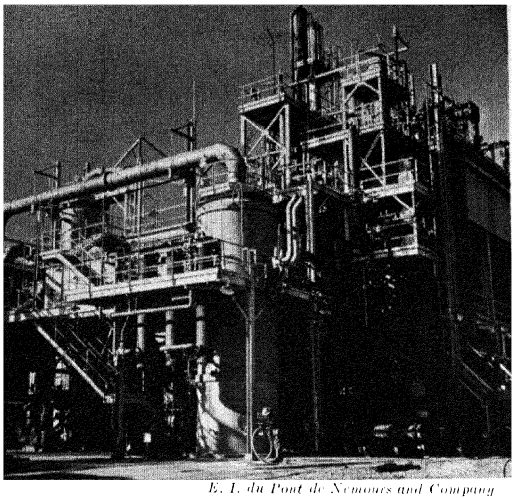
When two elements combine to form more than one compound, with the weight of one element remaining fixed, the ratios of the weights of the other elements are small whole numbers.

Thus the amounts of oxygen that unite with three parts of carbon are in the ratio of 4 to 8, or 1 to 2.

How the discovery of hydrogen peroxide helped to uphold the law of multiple proportions. In 1818, Louis Thenard (tā nàr′), a French teacher of chemistry, discovered a compound, which upon analysis was shown to be made up of equal volumes of oxygen and hydrogen. This compound is hydrogen peroxide.

Hydrogen and oxygen combine to form two different compounds. Water is composed of one part hydrogen and eight parts oxygen by weight. Hydrogen peroxide is composed of one part hydrogen and sixteen parts oxygen. Thus the ratio of the weights of oxygen that combine with a fixed weight of hydrogen is 8 to 16, or 1 to 2.

COMPOUND	ELEMENTS BY WEIGHT		RATIO
Water H_2O	1 H	8 O	1 to 2
Hydrogen peroxide H_2O_2	1 H	16 O	
Carbon monoxide CO	3 C	4 O	1 to 2
Carbon dioxide CO_2	3 C	8 O	



E. I. du Pont de Nemours and Company

This maze of tanks and pipes is required for the commercial preparation of hydrogen peroxide.

Properties and uses of hydrogen peroxide, H_2O_2. Since water and hydrogen peroxide have different chemical compositions, they have different physical and chemical properties. Hydrogen peroxide is a colorless liquid, about one and one-half times as heavy as water. It is odorless and mixes with water, alcohol, or ether. It is useful commercially because it is unstable. That is, heat or light decomposes it easily into water and oxygen:

$$H_2O_2 \rightarrow H_2O + O\uparrow$$

The oxygen atom that is liberated is in a very active state, ready to combine with another atom of oxygen or with any other substance at the instant of liberation. This very active atomic oxygen is sometimes called *nascent* (newborn). Nascent oxygen is written as O, ordinary oxygen as O_2. The arrow pointing upwards represents a gas.

Some colored compounds lose their color when they are oxidized. Fibers containing compounds which give them their color can be bleached by exposing them to nascent oxygen. Hydrogen peroxide is used as an oxidizing agent to bleach, or decolorize, cotton goods, wool, wood pulp, wood used for furniture, as well as silk, hair, feathers, glue, and other animal substances.

Some bacteria are destroyed when exposed to oxygen. Hydrogen peroxide is therefore used as a household antiseptic. The household product actually is mainly water with a small amount (usually 3 per cent) of hydrogen peroxide dissolved in it. It also contains some substance such as *acetanilid*, which retards the decomposition of the hydrogen peroxide. As an antiseptic, hydrogen peroxide is not very effective since the oxygen it releases does not reach enough of the bacteria.

Commercial preparation of hydrogen peroxide. If barium peroxide, a white solid, is treated with dilute sulfuric acid at a temperature below 15°C., hydrogen peroxide and barium sulfate are formed. Barium sulfate is a white *insoluble* solid which settles out.

Sulfuric acid + barium peroxide → hydrogen peroxide + barium sulfate

$$H_2SO_4 + BaO_2 \rightarrow H_2O_2 + BaSO_4\downarrow$$

This type of reaction is called *double replacement* — barium replaces hydrogen. The arrow pointing downward after $BaSO_4$ indicates that this compound is insoluble and separates out, or *precipitates*. The insoluble substance that separates out is called a *precipitate*.

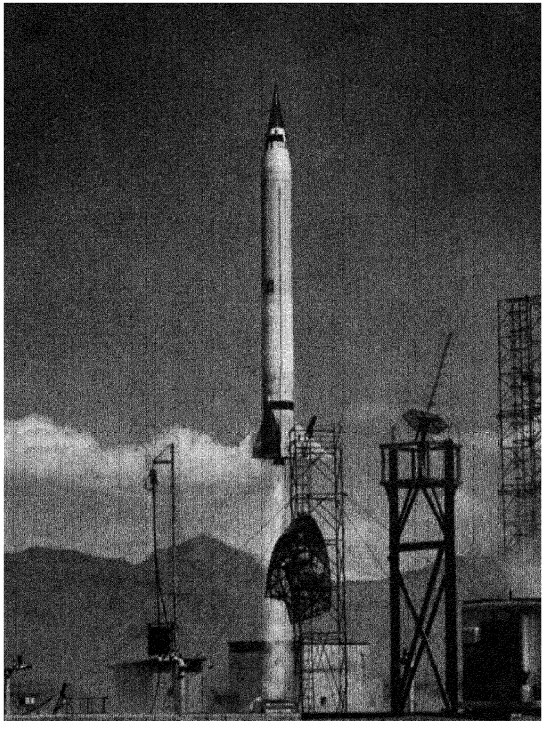
Most of the hydrogen peroxide produced commercially is made by gently heating persulfuric acid, $H_2S_2O_8$, which reacts with water:

Persulfuric acid + water → sulfuric acid + hydrogen peroxide

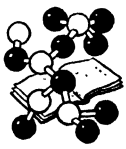
$$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$$

In this process the hydrogen peroxide is distilled out. *Superoxol* is a 30% H_2O_2 solution. A 90% solution of this substance is used as a rocket fuel.

The Glenn Martin Company



Off to an altitude of 160 miles roars the Navy's Viking No. 11 rocket. In flight this rocket will attain a speed of 4300 miles per hour. Rocket development depends greatly upon fuel research carried on in chemical laboratories.



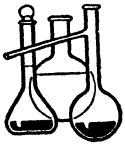
YOU WILL ENJOY READING

Harrow, Benjamin. *The Romance of the Atom,* pp. 27–33. Boni & Liveright, New York, 1927. Origin and development of ideas about atoms.

Langdon-Davies, John. *Inside the Atom.* Harper & Bros., New York, 1933. Amusing, popular introduction to science and the nature of matter.

Leicester, H. M. and Klickstein, H. S. *Source Book in Chemistry,* pp. 215–220. McGraw-Hill Book Company, New York, 1952. Gives John Dalton's observations on the constitution of bodies.

Thomson, J. Arthur. *The Outline of Science,* pp. 245–253. G. P. Putnam's Sons, New York, 1937. "Foundations of the Universe." In "The World of Atoms" the size and energy of these tiny particles are very simply discussed.



USEFUL IDEAS DEVELOPED

1. The idea of individual indivisible particles of matter originated with the ancient Greek teachers. Dalton used this idea and developed the atomic theory in 1803.

2. The chief assumptions of Dalton's theory were: a) That all matter consists of extremely small particles, called atoms. b) That all the atoms of any one element are alike in size, shape, and weight. c) That the atoms of one element differ from those of all other elements in size, shape, and weight. d) That chemical changes are changes in the combination of atoms with each other. e) That even in the most violent chemical changes, the indivisible atoms do not break into pieces.

3. An atom is the smallest part of an element that takes part in a chemical change without itself being altered.

4. A molecule is composed of two or more atoms and is the smallest part of a compound or element that has the properties of that compound or element.

5. Personal whims, prejudices, or prestige should play no part in settling scientific problems.

6. The law of definite proportions states that the elements in a compound always occur in a definite proportion by weight.

7. The law of multiple proportions states: When any two elements combine to form more than one compound, with the weight of one element remaining fixed, the ratios of the weights of the other element are small whole numbers.



USING WHAT YOU HAVE LEARNED

Group A

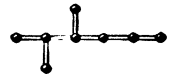
1. When did John Dalton advance his atomic theory?

2. Was the idea of atoms new in Dalton's time? Explain.

3. How did Dalton's approach to the study of the nature of matter differ from that of the Greeks?

4. State the five essentials of Dalton's atomic theory.

5. How did Dalton distinguish between atoms of different elements?



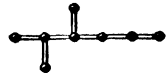
6. According to Dalton, what happens when elements unite?

7. How did the scientific world receive Dalton's theory?

8. Describe the difference of opinion between Berthollet and Proust.

9. (a) State the fundamental law of chemistry that Dalton discovered.

(b) Show how it applies to the composition of CO and CO_2.



10. (a) When and (b) by whom was H_2O_2 prepared for the first time?

11. Compare the physical properties of H_2O and H_2O_2.

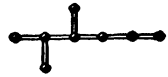
12. Contrast the chemical properties of H_2O and H_2O_2.

13. Compare the compositions of H_2O and H_2O_2 by volume and weight.

14. State two ways in which the decomposition of H_2O_2 may be retarded.

15. Write the word-equation for the decomposition of H_2O_2.

16. What is the difference between O_2 and nascent oxygen?



17. Describe the two most useful properties of H_2O_2.

18. What is the great advantage of H_2O_2 as a bleaching agent?

19. What is an antiseptic?

20. State a commercial method of preparing H_2O_2.

21. Write the equation for the preparation of H_2O_2 from BaO_2.

22. What is a precipitate?

23. Compare the chemical properties of O_2, O_3, and O.

Group B

24. Explain how the law of multiple proportions is based on Dalton's atomic theory.

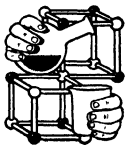
25. Two oxides of nitrogen, nitrous oxide (N_2O) and nitrogen dioxide (NO_2), show the following ratios by weight: In nitrous oxide, the ratio by weight of nitrogen to oxygen is 7 to 4; in nitrogen dioxide, the ratio by weight of nitrogen to oxygen is 14 to 32. With what fundamental law of chemistry are these figures in accord?

26. Do we still believe that all atoms of the same element weigh the same?

27. (a) Is Dalton's atomic theory still a theory or has it been proved experimentally? (b) Explain your answer.

28. Dalton's hobby of recording weather conditions was greatly responsible for the atomic theory. Can you cite another example in science where a hobby has resulted in a great advance?

29. Write a 2- or 3-page report on the life of John Dalton.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

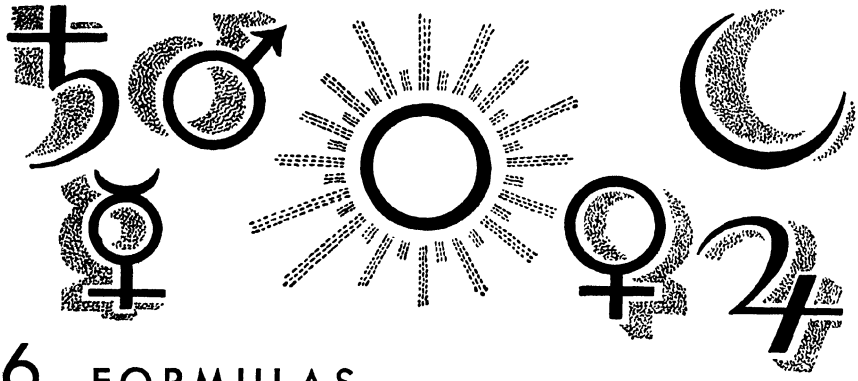
1. Dalton's atomic theory is a beautiful example of creative imagination in pure science. Until very recently America, although it excelled Europe in inventions and applied science, has lagged behind the Old World in the kind of creative imagination represented by Dalton's theory and the germ theory of disease which Pasteur gave humanity. Can you give reasons for this state of affairs? What of the future?

2. Add a pinch of manganese dioxide to one-third of a test tube of hydrogen peroxide from your medicine cabinet. Insert a glowing splint. Prepare a brief report on the reaction which takes place.

3. Prepare a debate or a class discussion on the topic, "If prejudices and superstitions did not exist, social change would proceed more rapidly."

4. Form a committee to investigate and report on prejudices and superstitions common to your community. Do any of these have a scientific foundation?

5. Make models of the atoms of hydrogen, carbon, sulfur, gold, mercury, and nitrogen as Dalton constructed them, using marbles or some other suitable spheres.



6. FORMULAS: THE CHEMIST'S ABBREVIATIONS

The mysterious symbols of alchemy. Ancient alchemists feared that they would lose their unique social position if anyone could understand their work. Consequently they used strange symbols, both to conceal the true nature of their writings and also to give themselves an added air of mystery and magic. They represented sand by  , glass by  , soap by  , and salt by  . To them the symbol for perfection and also for the sun was the circle  . Hence it was used to represent sun-colored gold, which they considered the perfect metal.

Many of their symbols were derived from ancient mythology. The lance and shield of Mars, god of war,  , represented, appropriately enough, iron. The looking glass of Venus,  , was their symbol for copper because, according to legend, Venus had first appeared on the shores of the island of Cyprus, long famous for its copper mines.

Often an alchemist would develop a set of symbols for his own special use and would reveal the meaning to no one, not even to his brother alchemists. In one Italian manuscript written in the seventeenth century, the element mercury was represented by 20 different symbols and 35 different names. As long as alchemy was a purely personal practice carried on for selfish ends, the confusing symbolism presented no problem. However, when the universal science of modern chemistry began to emerge, it was essential to develop a system of symbols which could be understood easily in every country of the world. Dalton, and a few others before him, had attempted to substitute some reasonable system for the jungle of weird signs and strange names used by the alchemists. However, these attempts failed — largely because they were unwieldy and inconvenient.

Berzelius helps bring order out of chaos. Jöns Berzelius (bĕr-zē'lĭ-ŭs) was a Swedish orphan who became, in the words of Sir Humphry Davy, "one of the great ornaments of his age." Berzelius invented a simple system of chemical notation which he introduced in 1814. Today it is used in every country of the world.

Berzelius said very logically: "It is easier to write an abbreviated word than to draw a figure. The chemical signs ought to be letters for the greater ease of writing and not to disfigure a printed book. I shall therefore take for the chemical sign the initial letter of the Latin name of each chemical element, thus, C, H, N, O, S, and P. If the first letter be common to two metals, I shall use both the initial letter and another letter they have not in common, as gold (*aurum*), Au; silver (*argentum*), Ag; antimony (*stibium*), Sb; tin (*stannum*), Sn." The first letter of the symbol is always capitalized; the second, if there is a second, is not.

How a compound is represented by a formula. When we are dealing with a compound rather than an element, we write its abbreviated form, or *formula,* by placing side by side the symbols of the elements that compose the compound. For example, the formula of zinc oxide, a compound of zinc and oxygen, is ZnO; the formula of hydrochloric acid, a compound of hydrogen and chlorine, is HCl. A formula not only represents the *name* of a compound, but also one *molecule* of that compound. Similarly a symbol represents both the *name* of an element, and one *atom* of that element.

The use of the subscript. Berzelius used a *subscript,* a small number placed below and to the right of a symbol, to indicate *the number of atoms of the element represented by that symbol.* Thus, H_2O represents one molecule of water containing two atoms of hydrogen and one atom of oxygen. The subscript *1* is never written.

As you use Berzelius' system, you will see its remarkable simplicity and great value. However, it was not accepted without a struggle. Even Dalton protested against it saying, "Berzelius' symbols are horrifying. A young student might as soon learn Hebrew as make himself acquainted with them." Evidently, Dalton must have forgotten his own very complex pictures of various compounds.

How is the proper subscript determined? You may have already wondered how it is possible to tell what subscript to use. Why Al_2O_3 and $ZnCl_2$ and not AlO and ZnCl? Must we memorize all formulas or are there definite rules to guide us?

Fortunately, it is possible to write formulas without first memorizing them. To do so, however, we must have a thorough understanding of *valence.*

What is valence? The law of definite proportions tells us that atoms occur in compounds in fixed ratios. The following table shows the ratio in which hydrogen combines with other elements to form four common compounds.

COMPOUND	NUMBER OF HYDROGEN ATOMS IN COMPOUND	NUMBER OF ATOMS OF SECOND ELEMENT IN COMPOUND
HCl (hydrogen chloride)	1	1 chlorine atom
H_2O (water)	2	1 oxygen atom
NH_3 (ammonia)	3	1 nitrogen atom
CH_4 (methane)	4	1 carbon atom

In this table, note the difference in the number of hydrogen atoms with which one atom of the other elements combines. *The valence of an element is the number that tells us how many atoms of hydrogen normally combine with one atom of that element.* This is a simplified definition, but will serve us for the present.

From the table we see that one atom of chlorine combines with one atom of hydrogen to form HCl. Thus, we say that chlorine has a valence of one, or as chemists put it, is *monovalent.* One atom of oxygen combines with two atoms of hydrogen. So we say that oxygen has a valence of two, or is *divalent.* Nitrogen has a valence of three, or is *trivalent.* Carbon has a valence of four, or is *tetravalent.*

The idea of valence was introduced in 1852 by Edward Frankland, an English chemist. Hydrogen is used as the standard, because its atom never combines with more than one atom of any other element. Hence, if its valence is considered to be one, the valence of every other element must be a whole number.

Learning valences. There is no "royal road" to the study of valence. You will find that memorizing the valences of the more common elements will save you a tremendous amount of work and will give you a better understanding of the material to follow. Table 2 lists the valences which are considered essential.

Notice that in the table, the symbols of the metals are followed by plus (+) signs and the nonmetals and radicals followed by minus signs (−). These signs represent electric charges, for reasons which you will learn in Chapter 16. The number of these electric charges correspond to the valences of the element or radical. Group-

ing elements as metals and nonmetals is not a completely satisfactory means of classification because some elements behave at times as metals and at other times as nonmetals.

Binary compounds. *A binary compound* is composed either of two elements, two radicals, or one element and one radical. If you keep in mind the following rules, you will find writing the formulas for binary compounds is a simple process. Practice is essential.

TABLE 2. IMPORTANT VALENCES

	MONOVALENT		DIVALENT		TRIVALENT	
METALS	*Ammonium	NH_4^+	Barium	Ba^{++}	Aluminum	Al^{+++}
	Copper (cuprous)	Cu^+	Calcium	Ca^{++}	Antimony	Sb^{+++}
	Lithium	Li^+	Copper (cupric)	Cu^{++}	Arsenic	As^{+++}
	Mercury (ous)	Hg^+	Iron (ferrous)	Fe^{++}	Chromium	Cr^{+++}
	Potassium	K^+	Magnesium	Mg^{++}	Iron (ferric)	Fe^{+++}
	Silver	Ag^+	Mercury (ic)	Hg^{++}		
	Sodium	Na^+	Zinc	Zn^{++}		
NONMETALS	Bromine (bromide)	Br^-	Oxygen (oxide)	O^{--}	Nitrogen (nitride)	N^{---}
	Chlorine (chloride)	Cl^-	Sulfur (sulfide)	S^{--}	Phosphorus (phosphide)	P^{---}
	Fluorine (fluoride)	F^-				
	Iodine (iodide)	I^-				
RADICALS	*Acetate	$C_2H_3O_2^-$	Carbonate	CO_3^{--}	Phosphate	PO_4^{---}
	Bicarbonate	HCO_3^-	Sulfate	SO_4^{--}		
	Chlorate	ClO_3^-	Sulfite	SO_3^{--}		
	Hydroxide	OH^-				
	Nitrate	NO_3^-				
	Nitrite	NO_2^-				

*Radicals: *A radical is a group of atoms acting as a single atom and having its own individual valence. The ammonium radical, NH_4, has a valence of 1.*

HOW TO USE VALENCE IN WRITING FORMULAS OF BINARY COMPOUNDS

1) *Write the symbol with a positive valence first, followed by the symbol with a negative valence.* Add plus and minus signs to the upper right of the symbols, that is, in *superscripts,* to show the valence for each symbol.

2) *If the valences of the symbols are equal* no subscripts are added. This rule is followed *unless* the subscripts represent the actual structure of the compound. Thus, the formula of hydrogen peroxide is H_2O_2 and not HO, since a molecule of hydrogen peroxide actually contains two atoms of hydrogen and two atoms of oxygen.

3) Since every compound is electrically neutral, the number of positive charges must be the same as the number of its negative charges. Therefore, *if the valences are not equal in numerical value, subscripts must be added to equalize them.* Add to each symbol a subscript of the same numerical value as the valence of the *other* symbol. The subscript *1* is never written.

4) *A radical acts like an element, that is, it usually passes through a chemical reaction unchanged. It should be placed in parentheses only if it is followed by a subscript greater than one.*

EXAMPLE A: Write the formula for the compound, zinc oxide.

1) Zinc is written Zn and has a valence of plus two; oxygen is written O and has a valence of minus two. The symbol for zinc appears first in the formula since zinc is a metal and oxygen is a nonmetal. Indicate valences by plus and minus signs.

$$Zn^{++}O^{--}$$

2) Since the valences are equal no subscripts are written, and the subscript for each symbol is understood to be one.

3) The proper formula for zinc oxide therefore is ZnO.

EXAMPLE B: Write the formula for the compound, cupric chloride.

1) Copper is written Cu and has a positive valence of two; chlorine is written Cl and has a negative valence of one. Write the symbol for copper first because it has the positive valence. Indicate the valence of each element by using plus or minus signs. (Note that the *cupric* valence of copper should be used. See Table 2.)

$$Cu^{++}Cl^{-}$$

2) The subscript of each symbol must be equal to the valence of the *other* symbol. Since Cu has a valence of plus two, give Cl the subscript two. Since Cl has a valence of minus one, the subscript for Cu is understood to be one. The crossed arrows show these relationships.



The negative and positive valences are equal because there is one atom of copper with a valence of plus two, and two atoms of chlorine each with a valence of minus one.

3) The proper formula for cupric chloride is therefore $CuCl_2$.

EXAMPLE C: Write the formula for the compound, magnesium sulfate.

1) Magnesium (Mg) has a valence of plus two. The sulfate radical (SO_4) has a valence of minus two. Therefore, Mg appears first in the formula. Indicate the valences by using plus and minus signs.

$$Mg^{++}SO_4^{--}$$

2) The valences of the two symbols are equal. Therefore, the subscript of each is understood to be one, and no subscripts are written.

3) The proper formula for magnesium sulfate is $MgSO_4$.

EXAMPLE D: Write the formula for the compound, zinc nitrate.

1) Zinc (Zn) has a valence of plus two. The nitrate radical (NO_3) has a valence of minus one. Therefore, Zn appears first in the formula. Indicate the valences by using plus and minus signs.

$$Zn^{++}NO_3^{-}$$

2) Since Zn has a valence of plus two, we give NO_3 the subscript two and enclose it in parentheses. NO_3 has a valence of minus one and we consider Zn to have the subscript one. The crossed arrows show these relationships.

$$Zn^{++}(NO_3)_2^{-}$$

3) The proper formula for zinc nitrate is $Zn(NO_3)_2$.

Some elements have more than one valence. Iron is divalent in *ferrous* compounds and trivalent in *ferric* compounds. Ferrous chloride provides an example of divalent iron: $Fe^{++}Cl_2^{-}$. Ferric chloride provides an example of trivalent iron: $Fe^{+++}Cl_3^{-}$.

Mercury is monovalent in *mercurous* compounds and divalent in *mercuric* compounds; copper is monovalent in *cuprous* compounds and divalent in *cupric* compounds. What is the meaning of *-ous* and *-ic* as related to valence?

In the formula Fe_3O_4 (Magnetic oxide of iron) you might think that iron has a valence of four and oxygen a valence of three. However, the real explanation is that this compound is a combination of $Fe^{++}O^{--}$, in which Fe is divalent, and $Fe_2^{+++}O_3^{--}$, in which Fe is trivalent. Oxygen is always divalent. Or, Fe_3O_4 may be thought of as $FeO \cdot Fe_2O_3$. From these formulas it is apparent that some elements may exhibit two or more valences. The electron theory offers an interesting

explanation of the fact that certain elements have more than one valence (see Chapter 11).

PRACTICE IN WRITING FORMULAS

1. Write the formulas for the following compounds showing the + and − signs and the arrows pointing toward the subscripts: (a) sodium chloride, (b) calcium bromide, (c) ferric iodide, (d) potassium fluoride, (e) barium oxide.

2. Write the formulas of: (a) magnesium chloride, (b) zinc oxide, (c) aluminum nitride, (d) potassium sulfide, (e) cuprous chloride.

3. Write the formulas of: (a) aluminum chloride, (b) arsenic oxide, (c) calcium phosphide.

4. Write the formulas of: (a) sodium hydroxide, (b) potassium sulfate, (c) mercurous phosphate.

5. Write the formulas of: (a) calcium bicarbonate, (b) cuprous carbonate, (c) magnesium phosphate.

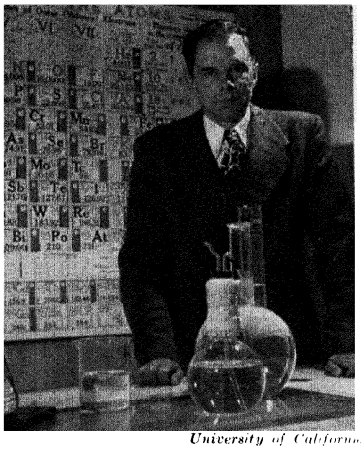
6. Write the formulas of: (a) aluminum nitrate, (b) ferric sulfate, (c) chromium phosphate.

7. Carbon (C^{++++}) and silicon (Si^{++++}) are tetravalent. Write the formulas of: (a) carbon tetrachloride and (b) silicon dioxide.

8. Write the formulas of: (a) mercuric nitrate, (b) sodium nitrate, (c) mercuric chlorate, (d) mercuric hydroxide, (e) mercuric carbonate, (f) mercurous sulfate, (g) calcium sulfite, (h) mercuric phosphate, (i) mercurous chloride.

How to determine valence in compounds of more than two elements. Remembering that in every compound the number of positive charges must equal the number of negative charges, let us find the valence of Cr in K_2CrO_4. There are four oxygen atoms each with two negative charges making a total of eight negative charges. To balance these, the compound has two potassium atoms each having one positive charge or a total of two positive charges. The compound must therefore have six more positive charges which must come from the metal chromium. Hence the valence of Cr in this compound is plus six.

Chemistry has a language and nomenclature of its own. Lavoisier realized the importance of language to a science. In 1789, the year in which the Bastille was stormed, he published a book written in the new language of chemistry. It did not contain the obscure words, the mystic symbols, and the pompous phrases of alchemy.



University of California

An outstanding nuclear scientist is Dr. Glenn T. Seaborg of the Radiation Laboratory, University of California, Berkeley, California. He has played an important role in the discovery of the trans-uranium elements, numbers 93–100. What names have been given elements 93–98? Can you suggest their derivation?

In naming the elements, several methods were used. Some, including bromine, meaning *stench*, were named after a physical property. Some, including argon, meaning *idle*, were named after a chemical property. Some, including *polon*ium, *german*ium, *gall*ium, and *americ*ium, were named after countries or other geographic regions. Some were named after the city or state connected with their discovery. Thus *hafn*ium was christened after the Latin name for the city of Copenhagen, where it was discovered. Radioactive *cur*ium was named after the Curies, who were the earliest investigators in the field of radioactivity. *Thor*ium and *tantal*um were named after figures in mythology. The origins of the names of the earliest known elements have been lost in the darkness of antiquity.

Names of metals and metallic radicals usually end in either *-ium* or *-um,* as sodium, potassium, platinum, curium, hafnium, aluminum, calcium, and the ammonium radical.

Names of nonmetals and nonmetallic radicals usually end in *-ine* or *-gen,* as chlorine, bromine, iodine, oxygen, and nitrogen.

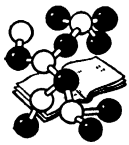
The most common suffixes used in naming compounds are *-ide, -ate, -ite, -ous,* and *-ic.* The suffix *-ide* represents a *binary* compound.

The suffixes *-ate* and *-ite* indicate, as a rule, compounds of three elements, one of which is oxygen. The *-ite* compound contains fewer oxygen atoms than the corresponding *-ate* compound. Thus sodium sulfate, Na_2SO_4, contains four atoms of oxygen, and sodium sulfite, Na_2SO_3, three atoms of oxygen. The *-ate* compounds are salts (see page 197) of *-ic* acids, and *-ite* compounds are salts of *-ous* acids.

The suffixes *-ous* and *-ic* indicate compounds in which the metal has a lower valence in the case of *-ous* and a higher valence in the case of *-ic.* An *-ous* acid contains fewer oxygen atoms than an *-ic* acid; thus sulfurous acid is H_2SO_3 and sulfuric acid is H_2SO_4; chlorous acid is $HClO_2$ and chloric acid is $HClO_3$.

Some commonly used prefixes in chemistry are *mono-* (or *uni-*), *di-* (or *bi-*), *tri-*, *tetra-*, and *pent-*. *Mono-* (or *uni-*), *di-* (or *bi-*), *tri-*, *tetra-*, and *pent-* stand for one, two, three, four, and five atoms. Thus, CO is carbon monoxide, and CO_2 is carbon dioxide. P_2O_3 is phosphorus trioxide and P_2O_5 is phosphorus pentoxide. The prefix *per-* means *more* atoms of an element than are found in a more common compound, and the prefix *hypo-* means *less* atoms. Thus chloric acid is $HClO_3$, perchloric acid is $HClO_4$; chlorous acid is $HClO_2$, and hypochlorous acid is HClO.

In *organic chemistry,* a branch of chemistry which deals with the more than 650,000 compounds of carbon, a more comprehensive nomenclature has been carefully worked out. We shall learn more about organic chemistry later.



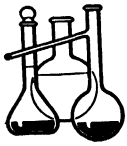
YOU WILL ENJOY READING

Caven, Robert M. and Cranston, John A. *Symbols and Formulae in Chemistry,* pp. 1–29. Blackie & Son, London, 1928. Development and use of symbols and formulas are traced with great clearness and interest in this valuable work.

Jaffe, Bernard. *Crucibles: The Story of Chemistry,* pp. 136–156. Simon and Schuster, New York, 1948. "A Swede Tears Up a Picture Book" deals with Berzelius' life and his contributions to the development of chemistry.

Kendall, James. *At Home among the Atoms.* D. Appleton-Century Co., New York, 1932. This eminent chemist introduces in novel form the problem of valences. He calls the chapter "Valencia."

Oesper, Ralph E. "The Birth of Modern Chemical Nomenclature." *Journal of Chemical Education,* June, 1945, pp. 290–292. An interesting story.



USEFUL IDEAS DEVELOPED

1. Each element has a symbol that stands for one atom of the element.

2. Each chemical compound may be written in abbreviated form as a formula by placing the symbols of the elements that compose the compound side by side.

3. A radical is a group of elements that act as a single element.

4. Subscripts are used in a chemical formula to indicate the number of atoms of any element which occur in a molecule of

any substance. Subscripts are also used following the parentheses around radical groups to indicate how many radicals are present in one molecule.

5. The valence of an element is a number that represents the number of atoms of hydrogen with which one atom of that element normally combines in forming a compound.

6. Names of metals and metallic radicals usually end in *-ium* or *-um;* names of nonmetals often end in *-ine* or *-gen.*



USING WHAT YOU HAVE LEARNED

Group A

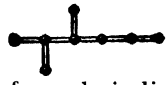
1. What is a symbol?

2. Who introduced the modern symbols and formulas of chemistry?

3. Why was it necessary to replace the old alchemical symbols with a new system of symbols?

4. Write the symbols of three gaseous, one liquid, and three solid elements.

5. Several elements have the same initial letter. How do we indicate these elements by symbols?



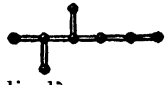
6. What does a formula indicate?

7. (a) Define valence. (b) Who introduced valence into chemistry?

8. What element having a valence of one is used in determining the valence of other elements?

9. What kind of element would have a valence of zero?

10. Of what importance to you is a knowledge of valence?



11. What is a radical?

12. Copy and complete the following statements: Metals have ... valences; nonmetals have ... valences. The most common radical with a plus valence is ....

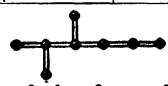
13. Copy and complete the following statements: Three metals with a valence of one are ..., ..., and .... Three divalent metals are ..., ..., and .... Three monovalent nonmetals are ..., ..., and .... The bicarbonate radical has a valence of .... A radical with a valence of three is ....

14. State four rules for writing formulas. Illustrate each.

15. Give two examples of elements that have more than one valence.

16. Copy and complete the following table. Do not write in this book.

	Bromide	Sulfide	Chlorate	Sulfate	Phosphate	Oxide	Hydroxide
Silver	AgBr						
Chromium							
Mercuric							
Ammonium							



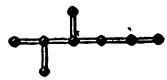
17. Make a list of the formulas of the phosphates of eight different metals.

18. Make a list of the formulas of the carbonates of eight different metals.

19. Make a list of the formulas of five ammonium compounds.

20. Correct the following: FeCl, CuS_2, $Ag(NO_3)_2$, KSO_4, Na_2ClO_3, and $NH_4(OH)$.

21. Write the names and formulas of five compounds of zinc.

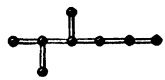


22. Name five elements and tell how their names were derived.

23. How can you tell whether the element ruthenium is a metal or a nonmetal?

24. Give the formulas and names of two acids that illustrate the difference in the use of the suffixes *-ous* and *-ic*.

25. Give the formulas and names of two compounds other than acids that illustrate the difference in the use of *-ous* and *-ic*.



26. How would you name the two compounds, BaO and BaO_2?

27. Explain the meaning of each letter and subscript in these formulas: HNO_3, $FePO_4$, Na_2CO_3.

28. Mark the valences of the elements and radicals in these compounds, using + and − signs. $CuSO_4$, $HgCl_2$, $NaClO_3$, $Ca(HCO_3)_2$, $X_3(PO_4)_2$, $(NH_4)_3Y$, MnO_2.

29. Determine the valence of: (a) sulfur in H_2SO_4, (b) manganese in $KMnO_4$, and (c) chromium in $K_2Cr_2O_7$.

Group B

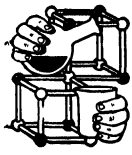
30. An unknown element *X* has a valence of three. Write the formula for its oxide.

31. The metal *Y* has a valence of two and the nonmetal *Z* has a valence of two. Write the formula for their compound.

32. The nomenclature of chemistry is still not completely organized. Can you give any reasons for this state of affairs?

33. What element was named after a Finnish chemist? (Read the chapter on the rare-earth elements in Weeks' *Discovery of the Elements.*)

34. Write a two- or three-page report on the life of Berzelius. See list of additional reading material.

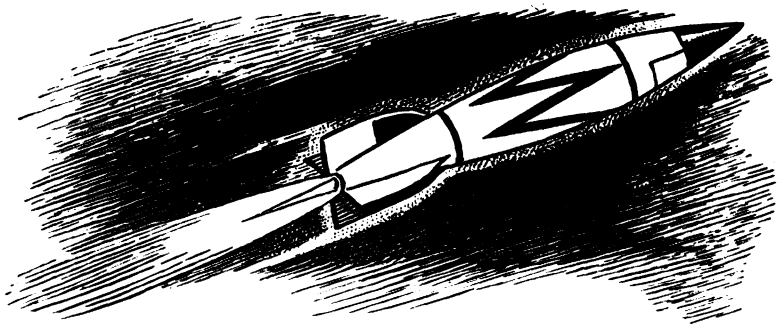


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make a chart and, with the help of your teacher of art, include as many alchemical symbols as you can and their modern equivalents.

2. The old alchemists wanted to keep their knowledge hidden from the rest of the world, and so used strange symbols and mysterious language. (a) Name two groups of people who are modern equivalents of the alchemists. (b) Tell how they keep their knowledge to themselves and clothe their activities with a veil of mystery. (c) What are the reasons for their secrecy?

3. Form a committee to make a report on the trades, professions, and businesses in your community that have "languages of their own." (a) What reasons have they for these languages? (b) What, after all, is the function of language?



7. ATMOSPHERE: THE OCEAN OF AIR

> . . . *It ought to be esteemed much less disgraceful to quit an error for a truth than to be guilty of the vanity and perverseness of believing a thing still, because we once believed it.* Robert Boyle, 1627–1691

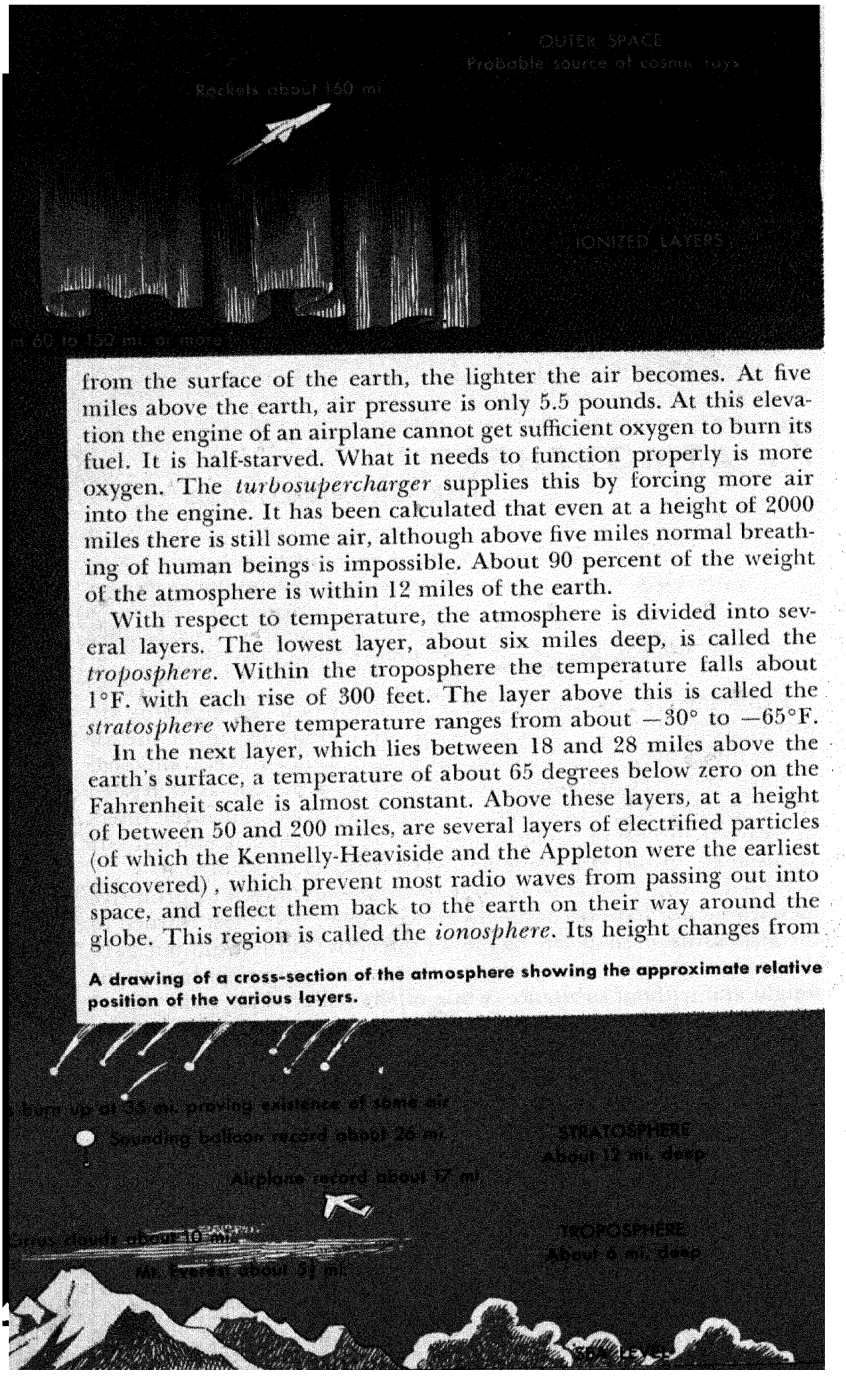
Exploring the atmosphere. Every day many of us see gleaming airplanes flying swiftly overhead. What are conditions up in the air where they travel? Of what is the air in which they travel composed?

Have you ever seen the glowing trail of a meteor as it flashed across the sky? Why did it burn? Have you ever examined the fused, fire-scarred surface of a meteorite? Was it hot when it entered our atmosphere, or did it become heated as it traveled through it?

Probably you know the answers to these questions, but primitive men would not have been able to answer them. The most learned of the alchemists, even as late as the seventeenth century, did not have the answers. Some of them believed that air was empty space without weight and without substance, while others believed air to be one of the "four elements."

It was not until 1643 that Torricelli (tôr-rē-chĕl'lē) invented the mercury *barometer,* which shows that air has weight and exerts pressure. We know today that approximately 15 pounds (14.7 lb.) of air rest upon every square inch of the surface of the earth. Upon every square foot rests a column of air weighing more than one ton!

The density of the atmosphere is not the same throughout its entire extent. It is densest at the surface of the earth, and the farther



from the surface of the earth, the lighter the air becomes. At five miles above the earth, air pressure is only 5.5 pounds. At this elevation the engine of an airplane cannot get sufficient oxygen to burn its fuel. It is half-starved. What it needs to function properly is more oxygen. The *turbosupercharger* supplies this by forcing more air into the engine. It has been calculated that even at a height of 2000 miles there is still some air, although above five miles normal breathing of human beings is impossible. About 90 percent of the weight of the atmosphere is within 12 miles of the earth.

With respect to temperature, the atmosphere is divided into several layers. The lowest layer, about six miles deep, is called the *troposphere*. Within the troposphere the temperature falls about 1°F. with each rise of 300 feet. The layer above this is called the *stratosphere* where temperature ranges from about −30° to −65°F.

In the next layer, which lies between 18 and 28 miles above the earth's surface, a temperature of about 65 degrees below zero on the Fahrenheit scale is almost constant. Above these layers, at a height of between 50 and 200 miles, are several layers of electrified particles (of which the Kennelly-Heaviside and the Appleton were the earliest discovered), which prevent most radio waves from passing out into space, and reflect them back to the earth on their way around the globe. This region is called the *ionosphere*. Its height changes from

A drawing of a cross-section of the atmosphere showing the approximate relative position of the various layers.

morning to night and varies with the seasons. The temperature in these ionized bands rises with elevation.

Extremely short radio waves of sufficient energy can penetrate these electrified layers, as was proved in 1946 by Army Signal Corps scientists, who succeeded in sending *radar* impulses to the moon. Reflections from the moon were received. The round trip, 477,714 miles, was made in 2.4 seconds.

What is air? Air is made up of a number of different gases. During the eighteenth century three of these — nitrogen, oxygen, and carbon dioxide — were *isolated,* or obtained separately, from it. Indications were noted that still other gases, less easily obtained in a pure state, might possibly be present in small quantities. These gases were actually found later on.

Is air a mixture or a compound? How are the gases of the air held together? Are they chemically united or are they merely mixed, just as sand might be mixed with clay? To answer these questions, scientists made use of the law of definite proportions. If air is a compound, they reasoned, then the composition of air must be constant.

To determine whether or not the composition of air is constant, Dalton and others collected and analyzed samples of air taken from thousands of different places — from the tops of mountains, over lakes, in valleys, in sparsely settled regions, and in congested areas. Gay-Lussac (gā-lü-sȧk′) ascended over Paris in a hydrogen-filled balloon to a height of 4 miles to get samples of air. Much more recently, rockets carrying self-sealing bottles brought down air from heights as much as 36 miles.

Although these analyses showed that all the samples of air varied only slightly in composition, enough difference was noted to indicate that the composition of air is not constant. Hence, air could not be a compound. Air, they decided, is a mixture of gases.

Some other proofs that air is a mixture. The conclusion reached by the early investigators that air is a mixture was strengthened by further evidence. For example, rain water contains air that has been dissolved from the atmosphere. By boiling rain water, this air can be driven out and collected. Analysis shows that this air contains almost twice as much oxygen as common air.

If air were a compound, dissolving it in water would not cause any change in its composition. But because air is a mixture, each substance of which it is composed dissolves in water in proportion to its own solubility therein. Since oxygen is more soluble in water than nitrogen, the other main component of air, *dissolved* air contains more oxygen than does common air.

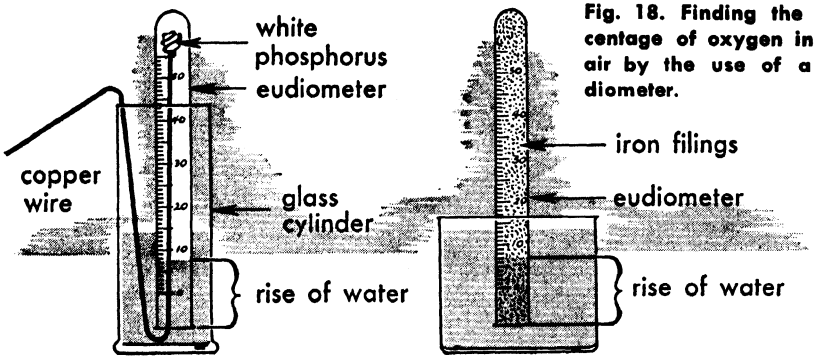


Fig. 18. Finding the percentage of oxygen in the air by the use of a eudiometer.

When scientists succeeded in changing air into a liquid by cooling it to a temperature of about −190°C., they found that liquid air does not have a definite boiling point. Instead of all the liquid air boiling at a definite temperature, as does water or any other pure compound, they found that nitrogen boiled off first. Other components of the air boiled off at higher temperatures. A pure compound has a definite boiling point, but liquid air does not. This is further proof that air is a mixture.

Finding the percentage of oxygen in air. The percentage of oxygen in air is found by using a chemical which will react with oxygen and remove it from the air. For example, we might place a small piece of white phosphorus on the coiled end of a copper wire and insert it in a *eudiometer,* or measuring tube, which is then inverted in a cylinder of water (see Fig. 18).

The phosphorus, which is easily oxidized, soon combines with the oxygen of the air in the eudiometer according to the equation:

$$4P + 3O_2 \rightarrow 2P_2O_3 *$$

This reaction continues until the last trace of oxygen has combined, forming phosphorus trioxide, white feathery crystals which readily dissolve in the water in the cylinder. Phosphorus pentoxide, P_2O_5, is formed also according to the equation:

$$4P + 5O_2 \rightarrow 2P_2O_5 *$$

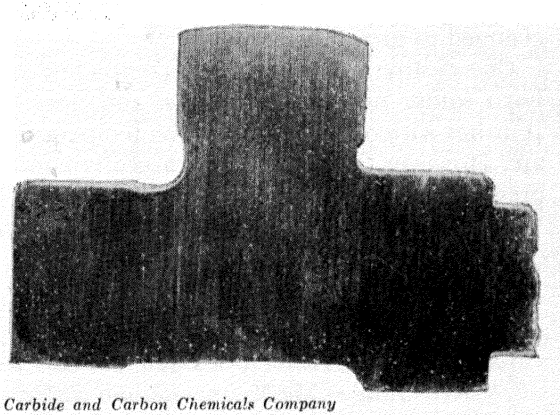
This is a white solid which readily combines with water and, hence, is used as a drying agent, especially for gases.

As the oxygen unites with the phosphorus, a partial vacuum is formed in the eudiometer, and the greater air pressure outside the

* Also written, respectively, P_4O_6 and P_4O_{10}.

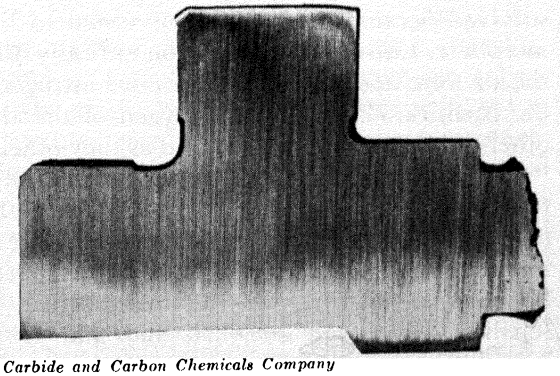
tube forces water up the tube. At the end of a few hours the chemical action ceases and the water stops rising. The volume of water that has risen in the eudiometer is equal to the volume of oxygen that was originally present in the air in the measuring tube. Because this rise in the height of the water is approximately one-fifth the height of the tube, this rise indicates that about 20 percent of air is pure oxygen. In performing this experiment, do *not* touch the phosphorus.

Instead of phosphorus, a less active element such as iron may be used. To perform this experiment, the inside of a eudiometer is moistened with water and enough iron filings are added to form a thin layer of iron on the inside walls of the tube, as shown in Fig. 18. The tube is then inverted in water, and left undisturbed overnight. Upon examination, it is found that most of the iron has changed to brown rust, an oxide of iron, and the water has risen about one-fifth the height of the eudiometer.



As some molten metals harden in the mold, tiny holes are formed due to the presence of dissolved gases. These holes make the casting unfit for use.

Carbide and Carbon Chemicals Company



To prevent formation of holes in the casting, nitrogen is bubbled through the molten metal in the mold. The nitrogen carries away the undesirable gases. This process is known as *nitrogen degassing*.

Carbide and Carbon Chemicals Company

Nitrogen is the most abundant element in the atmosphere. Nitrogen is the principal gas that remains after oxygen has been removed from air. It was first carefully studied in 1772, by Daniel Rutherford, uncle of Sir Walter Scott. Pure nitrogen may be prepared in the laboratory by *gently* heating ammonium nitrite, NH_4NO_2.

$$NH_4NO_2 \rightarrow N_2\uparrow + 2H_2O$$

The physical properties of nitrogen resemble those of its partner, oxygen, quite closely. It is colorless, odorless, and scarcely soluble in water (about two liters of nitrogen dissolve in 100 liters of water under standard conditions). It is even more difficult to liquefy than oxygen, requiring a temperature 13°C. lower. It is slightly lighter than oxygen. Dry air is about 78 percent nitrogen by volume.

Chemical properties of nitrogen. Since nitrogen under normal conditions is not chemically active, Lavoisier named this element *azote,* meaning *devoid of life.* However, because it is one of the elements found in niter (potassium nitrate), this name was later changed to nitrogen.

Chemically, nitrogen differs completely from oxygen. It does not burn under normal conditions, and does not support respiration. It unites with oxygen only at such temperatures as exist in the electric arc. However, at higher and carefully controlled temperatures and pressures, nitrogen combines with oxygen, hydrogen, and carbon. With calcium, magnesium, lithium, and wolfram, it forms a group of compounds called *nitrides.*

$N_2 + O_2 \rightarrow 2NO$ **(nitric oxide)**
$N_2 + 3H_2 \rightarrow 2NH_3$ **(ammonia)**
$N_2 + 2C \rightarrow C_2N_2$ **(cyanogen — a colorless, poisonous gas)**
$N_2 + 3Mg \rightarrow Mg_3N_2$ **(magnesium *nitride*)**

Life as we know it consists of plant and animal forms that have survived because they were well suited to living in the earth's atmosphere. Life on earth might be radically different if the oxygen of the air were not diluted with inactive nitrogen. Nitrogen tones down the chemical activity of the oxygen of the air. Hence burning and other oxidations are not as rapid as they otherwise would be.

How nitrogen is used. The vast storehouse of free nitrogen in air furnishes an almost limitless supply of this valuable element. Atmospheric nitrogen obtained from liquid air is used in making ammonia, ammonium compounds, and nitrates. These nitrogen compounds are essential in the manufacture of explosives and in fertilizers (see pages 268, 270, 468, and 470). Nitrogen thus plays a dual role, aiding both in supporting life and in destroying it.

Rayleigh is confronted with another riddle of the atmosphere. In 1894, Rayleigh (rā'lī), an English scientist, found that "pure" nitrogen obtained from air weighed a little more than an equal volume of nitrogen obtained from pure nitrogen compounds. This puzzled him. Dalton had declared that the weight of the atom never changed, regardless of its source.

The difference in weight that Rayleigh noticed was very small, and might have been ignored as caused by experimental errors. But after Rayleigh had spent months investigating this problem, he became convinced that the presence of some other element in the air was responsible for the difference in the weights of the samples of nitrogen. With the persistence of a true research scientist he finally tracked down the cause of this difference.

The discovery of argon, an inert gas of the atmosphere. Rayleigh, together with William Ramsay, studied the experiments of Cavendish and came across the following statement: "I made an experiment to determine whether the whole of the nitrogen of the atmosphere could be changed to nitric acid. Having condensed as much as I could, *only a small bubble of air* remained. So that if there is any part of the nitrogen of our atmosphere which differs from the rest, we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole."

Here was a clue to their problem. Small as this quantity was, Cavendish had not treated it as negligible or as an error in his work. Rayleigh and Ramsay therefore repeated his experiments and isolated a small volume of this gas from the nitrogen of the air. After subjecting it to every known test, they finally identified a new element, heavier than nitrogen, which, because of its chemical inertness, they named *argon*, meaning *lazy*.

Besides argon, minute quantities of five other inert gases are now known to be present in the atmosphere — *helium* (sun), *neon* (new), *krypton* (hidden), *xenon* (strange), and *radon* (from radium). The discovery and isolation of these gases from the air are other amazing examples of precise and painstaking research. When we consider that each of these gases is colorless, odorless, insoluble in water, and chemically inert, refusing to unite with even the most active elements, we begin to realize why they eluded chemists so long.

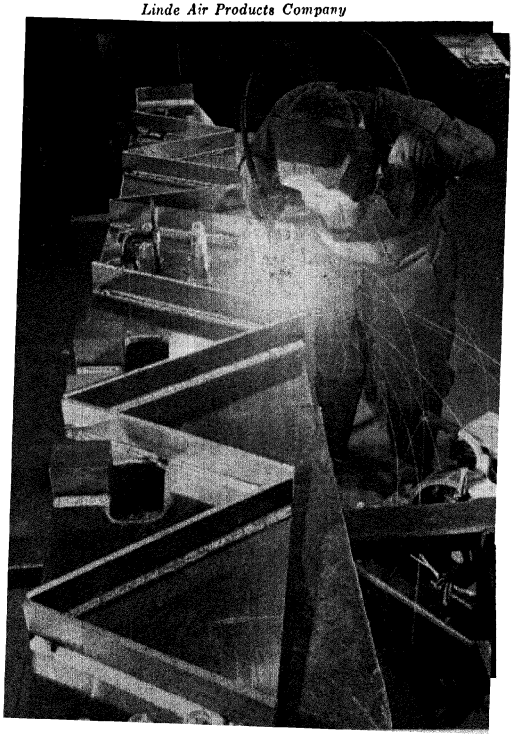
The inert gases go to work. For many years the inert gases remained chemical curiosities. Helium, first identified in the sun in 1868 and later found in considerable quantities in natural gas, was the first to be put to practical uses. It has taken the place of hydrogen in inflating the balloons and blimps of the Army and Navy and some

of the weather observation balloons of the Weather Bureau. When mixed with oxygen, it forms a *synthetic air* that is used under pressure in caissons and is supplied to deep-sea divers to prevent the *bends.*

The bends are a type of severe cramps caused by the sudden expansion and liberation of large quantities of nitrogen gas that have entered the blood under the great pressures to which deep-sea divers are subjected. When a diver rises to the surface where the air pressure is considerably lower, less helium is capable of remaining dissolved in his blood, and, therefore, some of this gas is liberated from the blood. Since helium is 40 percent less soluble in blood than is nitrogen, less helium gas will be forced out of solution by the decrease in pressure, and so the substitution of helium for the nitrogen of common air helps to prevent the bends.

Laziness preferred. With the demand for lightweight metal parts for airplanes, brought on by the tremendous need for aircraft in World War II, research on the problem of welding magnesium was stimulated and the helium-atmosphere process was perfected. In an atmosphere of helium, oxidation of the magnesium cannot take place, and the magnesium or magnesium alloys may be welded with ease. The development of this method of welding magnesium is an

Linde Air Products Company



This workman is welding structural aluminum by the sigma method. The term *sigma* is derived from the first letters of the words *shielded inert gas metal arc.*

example of the way in which the needs of society and the research of scientists are related.

Argon has replaced helium-arc welding for magnesium, and other metals. It is also used to fill electric-light bulbs. When an evacuated bulb is in use, metal evaporates from the filament, forming a deposit on the inside of the bulb. This deposit blackens the bulb, making it very inefficient. In an argon-filled bulb, this evaporation is retarded and the lamp may be operated at higher temperatures than if it had been evacuated only.

The ruby glow. The inert gases are also widely used in the glowing glass tubes so familiar in advertising signs. When an electric current is sent through a tube from which air has been removed and a minute amount of neon gas introduced, the gas glows with an orange-red light. The gas is at low pressure, about 12 mm. of mercury. The amount of current required is extremely low, about $\frac{1}{40}$ of an ampere, but the voltage varies between 6000 and 12,000 volts. Neon and krypton lights are also used to mark airplane routes and to signal to airplane pilots. Small neon glow lamps are used in testing high-frequency electric circuits such as those in radios.

When argon is used instead of neon, the light produced is blue. However, most of the blue tubes of this type are filled with mercury vapor rather than argon. Xenon gives a light blue light, and helium a cream-colored or pale orange light. Following page 382 is an illustration showing the colors produced by the inert gases in lighting.

The "idle" gases have thus been set to work. A leader in this field predicted that, in time, much of our lighting would be done by glowing gas in luminous tubes instead of by incandescent filaments. Certainly it is true that much outdoor lighting is now produced in this way, but the prediction would not apply to indoor lighting in which the field seems definitely being taken over by a newer development, *fluorescent* tubes (see page 448).

Radon gas, enclosed in sealed tubes, is used in the treatment of cancer. The exact function of the inert gases in the air is still not understood.

Our atmosphere also contains water vapor. Water vapor is always present in air in varying amounts. The waters of the earth are constantly evaporating. Plants give off immense quantities of water vapor during transpiration, and animals, too, exhale water vapor.

Rain, dew, snow, fog, and other similar phenomena are caused by the condensation of the invisible water vapor of the air. Frequently, a pitcher of ice water *sweats* on the outside. This sweat is the water that was formed when the water vapor of the air came in contact

with the cold outer surface of the pitcher and condensed. To determine accurately the amount of water vapor in the air, we can pass a known volume of air through a drying agent, such as calcium chloride, $CaCl_2$, or phosphorus pentoxide, P_2O_5. The increase in weight in the drying agent equals the weight of the water vapor in the sample.

$$CaCl_2 + 2H_2O \rightarrow CaCl_2 \cdot 2H_2O$$

Carbon dioxide, too, is present in the air. Millions of tons of carbon dioxide are poured into the air daily by the burning of organic substances, by the decay of dead plant and animal matter, and by the breathing of living things.

$$C + O_2 \rightarrow CO_2$$

Carbon dioxide is a colorless, odorless gas fairly soluble in water, and $1\frac{1}{2}$ times as heavy as air. Because carbon dioxide is already completely oxidized, it does not burn. When passed through lime-water (a water solution of calcium hydroxide), it forms a white precipitate, calcium carbonate, $CaCO_3$. This formation of a white precipitate is the common test for carbon dioxide.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$

To determine accurately the amount of carbon dioxide present in air, a known volume of air is passed through a concentrated solution of potassium hydroxide, KOH, and the amount of potassium carbonate, K_2CO_3, that forms is determined.

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

Carbon dioxide and its uses are discussed in Chapter 23.

Cause and effect of atmospheric pollution. An adult inhales about 37 pounds of air a day, which is five times the weight of the food and water that he consumes. We are very careful about getting pure water, and have laws to protect us against the sale of impure food. But we have not done as much about polluted air. In some cities legislation has been passed to cut down pollution of the air caused by smoke. Excessive smoke may impair health, damage crops, slowly destroy property, and reduce visibility. *Smog,* a combination of smoke and fog, is another serious problem (see pages 329, 616, and 617).

What is air conditioning? Not so many years ago, it was supposed that the air in a crowded room was unhealthful because it contained

a large percentage of carbon dioxide and a lowered percentage of oxygen. It has since been proved that even in a very crowded room the percentage of carbon dioxide never reaches a point where it becomes harmful. The amount of oxygen rarely gets below 20 percent, and it can be cut down even to 17 percent, at which point a candle is extinguished, without being injurious to health.

Research has shown that "bad air" is really caused by high temperature, lack of circulation, high percentage of water vapor, and various odors that have accumulated.

Warm air can hold more water vapor than an equal volume of cold air. A cubic meter of air at 20°C. (68°F.), for example, is capable of holding about 17 grams of water vapor, while the same volume of air at 11°C. (52°F.) can hold only about one-half as much. The *ratio* of the weight of water vapor present in air to the weight of water vapor it is capable of holding under the existing conditions of temperature and pressure is known as its *relative humidity*.

The temperature of the human body is controlled in part by the evaporation of perspiration. Evaporation absorbs heat. The amount of heat absorbed depends upon the amount of perspiration evaporated. The cooling sensation produced depends upon both the *amount* and the *rate* of evaporation.

Air with a high relative humidity, regardless of temperature, will evaporate little perspiration. Consequently, on hot, damp days we feel hotter than we do on hot days that are somewhat drier.

Tests have shown that in winter the air in many homes has a very low relative humidity. Such very dry air has a twofold bad effect. It tends to "dry us out." Evaporation of perspiration present proceeds rapidly with great cooling effect. Consequently, the temperature of dry air must be greater than the temperature of damper air for our sensations of warmth to be the same. It takes more fuel to maintain the higher temperature and, as a result, costs more. In addition, temperatures above 21°C. (70°F.) are likely to produce drowsiness and prevent us from doing our best work. Furthermore, such dry air tends to dry out the linings of the nose, mouth, and throat, thus causing great discomfort and reducing our resistance to common colds and other respiratory diseases.

Today, steady progress is being made in supplying properly conditioned air, not only to large auditoriums, factories, classrooms, banks, office buildings, and railroad trains, but even to subway cars and private homes. Air-conditioning equipment filters out dust and pollen from the air, exhausts stale air, keeps the relative humidity at the right point (about 50 percent), and maintains a comfortable

temperature (about 68°F.). It also destroys the dulling quality of "dead" air by keeping the air in motion. In addition to increasing mental and physical efficiency, air conditioning is essential in certain manufacturing processes, such as printing and the making of pills, chocolate, rayon, paper, tobacco products, and steel bearings.

Summary: The composition of the atmosphere. The chief constituents of samples of dry air taken near the surface of the earth are shown in the following table.

TABLE 3. PERCENTAGE COMPOSITION OF DRY AIR

CHIEF CONSTITUENTS OF DRY AIR	PERCENTAGE BY VOLUME	PERCENTAGE BY WEIGHT
Nitrogen	78.00	75.45
Oxygen	21.00	23.20
Argon	0.93	1.25
Carbon dioxide	0.04	0.05

Air contains *variable* quantities of water vapor and carbon dioxide; *small* amounts of the inert gases, argon, helium, krypton, neon, radon, and xenon; and also *minute* amounts of other gases, such as methane, carbon monoxide, hydrogen, nitrogen dioxide, and ozone, as well as very finely divided solids, such as dust, bacteria, spores, and pollen.

Liquid air. In *Gulliver's Travels,* a famous Academy was visited, and Jonathan Swift reports how some of its scientists were condensing air and letting the liquid flow like water. Probably Swift believed the liquefaction of air a dream never to be realized. Yet today liquid air is a common article of commerce and thousands of tons of it are used every year.

The principles underlying the manufacture of liquid air are: (1) when a liquid evaporates, it absorbs heat from its surroundings and thereby lowers their temperature; and (2) the sudden expansion of a gas produces this same effect. When air is compressed, cooled, and suddenly allowed to expand through a narrow opening, its temperature is lowered. If this process is repeated, a temperature is finally reached which is low enough to liquefy the gas. A more detailed treatment of the liquefaction of gases will be found on page 253.

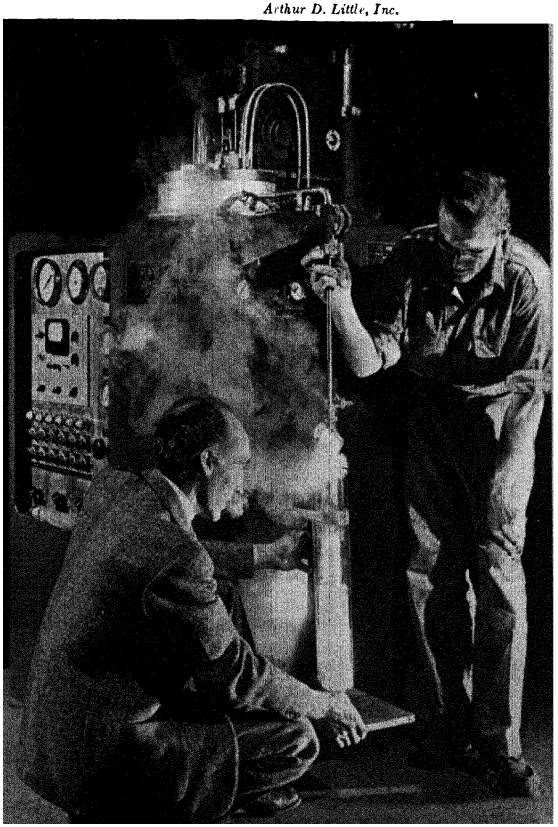
How the kinetic theory of matter explains the liquefaction of air. All matter is thought to be made up of small particles (atoms and molecules) that are in constant motion. In the case of gases, this motion is extremely rapid (air molecules under normal conditions

move at about 20 miles per minute). When any gas is cooled, its molecules move more slowly, until finally a temperature is reached at which the motion of the molecules of gas is so slow that they come close enough together to form larger groups or clusters of molecules, thus forming a liquid. When a gas expands, some heat is used in separating the molecules.

Compressing a gas has the effect of bringing the molecules closer together. By a simultaneous cooling and compressing, any gas may be liquefied. Some gases, such as chlorine, sulfur dioxide, and ammonia, are easily liquefied. Other gases, such as oxygen, nitrogen, hydrogen, and helium, require extremely low temperatures and high pressures to change them to liquids. It has been calculated that at −273°C. (*absolute zero*) all motion of the particles of matter ceases. The nearest approach to this temperature thus far attained was made in 1952 when scientists at our National Bureau of Standards reached a temperature within 0.0015° of absolute zero.*

* The measurement of absolute temperatures is discussed on p. 644.

Arthur D. Little, Inc.



Filling a flask with liquid helium in an experimental laboratory. Helium is liquefied by subjecting it to both cooling and pressure.

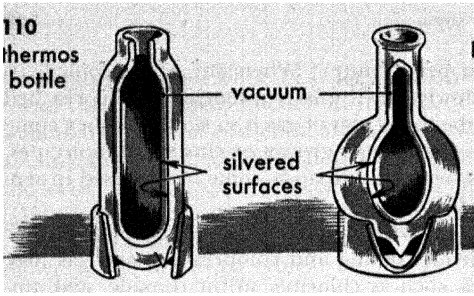


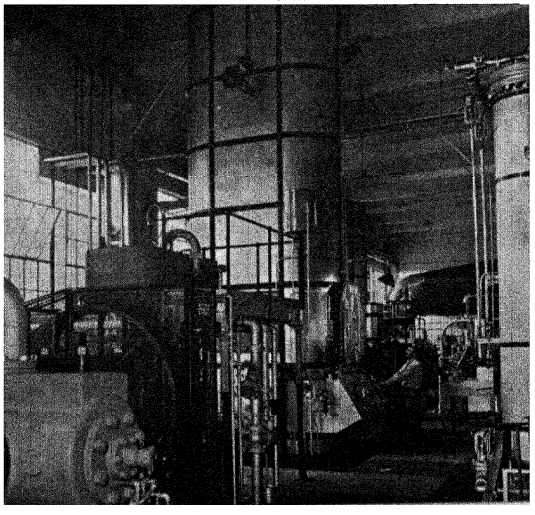
Fig. 19. A thermos bottle and a Dewar flask. Note similarities. What is the function of the silvered surfaces?

Properties and uses of liquid air. Liquid air is a pale blue liquid almost as heavy as water. It contains about 21 percent oxygen and boils at −190°C. When it evaporates, nitrogen boils off first and the mixture becomes richer and richer in oxygen, for the same reason that the boiling alcohol-water mixture in your car's radiator loses alcohol faster than water, because the boiling point of alcohol is lower than that of water.

Liquid air is used chiefly as a source of oxygen, nitrogen, and the inert gases, which boil off at different temperatures. The Nazis used liquid oxygen and alcohol to fuel the V-2 rocket bombs which they hurled against England in 1945.

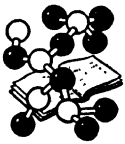
Because of the great tendency of liquid air to evaporate, small volumes of it are kept in special containers called *Dewar flasks,* which are similar in construction to the familiar *thermos bottle.* These flasks cannot be tightly stoppered, for any attempt to confine liquid air too closely results in explosion. Because of the danger of injury both from such explosions and from contact with a substance at such an extremely low temperature, persons handling liquid air must use great care.

Air Reduction Company, Inc.



Interior of an oxygen-nitrogen plant. The workman is standing in front of a column in which the two gases are obtained from liquid air.

The properties of substances change when immersed in liquid air. Liquid mercury becomes solid enough to be used as a hammer head. Rubber turns hard and brittle. The resistance of copper to an electric current is decreased 50 times.



YOU WILL ENJOY READING

Cady, H. P. "Liquid Air." *Journal of Chemical Education,* June, 1931, pp. 1027–1043. A fascinating account of experiments with liquid air.

Kaempffert, Waldemar. *Explorations in Science,* Chapter 7, pp. 102–108 is entitled, "This most excellent canopy, the air." The Viking Press, New York, 1953.

Ramsay, William. *The Gases of the Atmosphere,* pp. 148–181, 234–269. The Macmillan Co., London, 1915. Sir William tells of the discovery of argon and discusses other inert gases.



USEFUL IDEAS DEVELOPED

1. Air is a mixture of gases because (1) it has no definite composition, (2) when air dissolves in water, the dissolved air contains more oxygen than common air, and (3) liquid air does not have a definite boiling point.

2. Air conditioners cleanse the air, keep the relative humidity where it belongs (about 50 percent), maintain a comfortable temperature (68°F.), and keep the air in motion.

3. The kinetic theory of matter assumes that gases are made up of small particles (atoms and molecules) in active motion. Cooling the gas slows down this motion and brings the particles closer together until a liquid is formed. The molecules of liquids and solids are also in motion.



USING WHAT YOU HAVE LEARNED

Group A

1. Who first definitely proved that air has weight?

2. (a) What pressure does the atmosphere exert at sea level? (b) What causes this pressure?

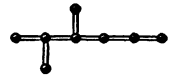
3. What are the differences between the troposphere, stratosphere, and Heaviside layer?

4. Does the composition of the atmosphere prove that air is a mixture? Explain.

5. Give two reasons other than composition for believing that air is not a compound.

6. State the composition of dry air by volume.

7. What substances are found in air in variable quantities?



8. Make a diagram illustrating a laboratory method for determining the percentage of O_2 in air.

9. (a) What is the gas that is left in the measuring tube used in determining the percentage of O_2 in air? (b) What are the impurities in this gas?

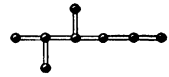
10. State four physical properties of N_2.

11. What is the chief chemical property of N_2?

12. Why is it wrong to call N_2 an inert gas?

13. Write a chemical equation illustrating the action of hot Mg on N_2.

14. Under what conditions does N_2 combine chemically with O_2 and H_2?



15. (a) State two functions of the N_2 of air. (b) State two commercial uses of N_2.

16. (a) Why is Mg difficult to weld? (b) Under what condition is it easily welded? (c) Development of this process is an example of what?

17. Name the six inert gases of the atmosphere.

18. What five properties are common to all six of the inert gases of the atmosphere?

19. Match each element listed in the first column with the correct item in the second column.

1) Ne	a) hidden
2) A	b) balloons
3) Kr	c) strange
4) He	d) luminous tubes
5) Xe	e) electric-light bulbs
	f) airplanes

20. Explain the "sweating" of a pitcher filled with ice water.

21. How would you determine the amount of water vapor present in air?

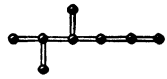
22. How would you determine the amount of CO_2 present in air?

23. State (a) four physical and (b) two chemical properties of CO_2.

24. What is air conditioning?

25. Name (a) two causes and (b) three effects of atmospheric pollution.

26. What two conditions in the air of a poorly ventilated room make it both uncomfortable and unhealthful?



27. What is relative humidity?

28. Upon what principle does the liquefaction of a gas depend?

29. Discuss the meaning of the kinetic theory of matter.

30. What is the chief use of liquid air?

31. State three properties of liquid air.

32. Compare the effectiveness of determining the percentage of O_2 in air by the phosphorus and the iron filings methods.

Group B

33. Why does the composition of air by weight differ from its composition by volume?

34. A piece of burning charcoal is plunged into liquid air. It keeps on burning with even greater splendor. Why does not the extreme cold of liquid air extinguish the burning charcoal?

35. Explain the presence of vast amounts of free N_2 in air, and only relatively small amounts of nitrogen compounds in the earth's crust.

36. In different samples of air the following substances are placed: $CaCl_2$, P, hot Mg, and $Ca(OH)_2$. Explain what happens in each case.

37. Why does a kettle of liquid air boil when placed on ice?

38. "Coal burned in our furnace returns to us in our bread." Explain.

39. What weight of dry air would be theoretically needed to extract ten grams of pure oxygen?



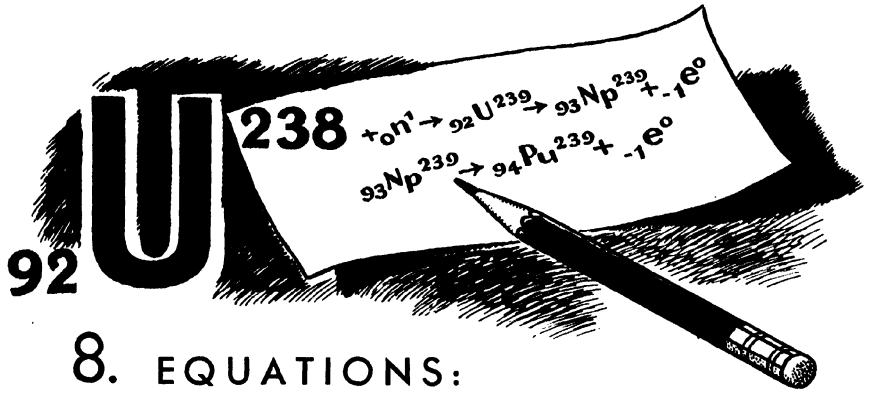
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Visit a neon-sign factory or an air-conditioned building or factory and make a full report on your visit to the class.

2. Prepare simple demonstrations to show that (1) air contains water vapor, and (2) your breath contains CO_2. Perform these experiments before your class the following day.

3. With the aid of a *wet and dry bulb thermometer,* determine the relative humidity of your classroom.

4. Prepare a report on the probable origin of the earth's atmosphere. Use a good book on physiography or one of the references listed.



8. EQUATIONS: SHORTHAND OF CHEMISTRY

> . . . *Here evidently we are at the birthplace of the chemical equation, yet we cannot find in the writings of Lavoisier this instrument as we know it; for our chemical equation depends as much on the atomic theory as on the doctrine of the conservation of mass.* Caven and Cranston, 1928

Chemical equations, the shorthand of chemistry. Chemists use symbols and formulas that are understood to represent elements and compounds by scientists in all parts of the world. But chemists make further use of these symbols and formulas. They use them to tell the story of chemical change — the reacting substances, the type of chemical change, the products of the reaction, and various other facts. All of these facts are expressed in the form of a *chemical equation,* which, in certain respects, is similar to the equations you have used in arithmetic and algebra.

Considering the chemical reaction that takes place when iron and sulfur are heated together, chemists and students of chemistry write as follows:

$$\mathbf{Fe + S \rightarrow FeS}$$

As you see, the two sides of the equation are separated by an arrow, →. This arrow means *yields,* or *forms,* and should be read using these or similar words. On the left side of the arrow, chemists write the symbols or formulas of the substances that react. On the right side of the arrow, they write the symbols and formulas of the products of the reaction. A *word-equation* that will express the same reaction as the chemical equation that we have just been discussing follows:

Iron *reacts with* sulfur *to yield* iron sulfide.

Equations represent reality. To write a chemical equation, we must know the formulas of the substances involved. To write a chemical equation correctly, we must know exactly what substances are reacting and what substances are the products of the reaction. The facts are determined before an equation is written.

We can write equations for only those chemical reactions known to be capable of actually taking place. *Chemical equations must represent actual conditions.* For example, it is incorrect to write He + S → HeS, because helium and sulfur do not react together, and helium sulfide, HeS, has never been prepared.

Balancing an equation. Lavoisier once wrote: "One may take it for granted that in every reaction there is an equal quantity of matter before and after the operation." Atoms do not disappear in the process of chemical reaction. Therefore, the number of atoms in the reacting substances must equal the number of atoms in the products of the reaction. *The number of atoms of each element must be the same on each side of the arrow.* Every correct equation conforms, in this way, to the law of the conservation of matter.

Points to remember in balancing equations.

1) Elements can occur in a free state, not combined with other elements. For reasons which you will learn later (pages 279–280), a number of these elements, including oxygen, hydrogen, nitrogen, chlorine, bromine, and iodine occur as molecules containing 2 atoms. They are written O_2, H_2, N_2, Cl_2, Br_2, and I_2, thus:

$$H_2 + Cl_2 \rightarrow 2HCl \text{ (hydrogen chloride)}$$
$$N_2 + O_2 \rightarrow 2NO \text{ (nitric oxide)}$$
$$Cu + Br_2 \rightarrow CuBr_2 \text{ (copper bromide)}$$
$$2H_2O \rightarrow 2H_2 + O_2$$

Standard Oil Company (N.J.)



Delicate measurements must be made to determine the actual conditions that are described by chemical equations.

2) In general, *a radical remains unaltered during a chemical change* and its symbols are carried over to the right side of the equation unchanged:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
$$2Na + 2HOH \rightarrow 2NaOH + H_2$$
$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

Balancing an equation consists of changing coefficients until the same total number of atoms of each element is shown on each side of the arrow.

Do not alter the subscript of a radical nor any other subscript in order to make an equation balance. Such alteration would mean a *change* in the actual composition of the compound. This in turn would mean an entirely different substance which does not actually appear in the chemical change. We may, however, alter coefficients of any element or compound without changing the meaning of the chemical symbols. The coefficient describes the number of molecules of a substance. By changing the number of molecules present in a chemical change, we do not alter the composition of the substances which are involved.

Your best preparation for writing equations correctly is a thorough knowledge of valence and of formulas. In addition, you should attack the problem in a systematic and thoughtful way. The following procedure should be helpful.

HOW TO BALANCE EQUATIONS

1) Write the equation without giving coefficients to any of the formulas.

2) Write any free element occurring in the equation without a subscript. Retain all other subscripts.

3) Select the compound with the greatest number of atoms. For one of its elements, compare the number of atoms appearing on each side of the equation. If the numbers differ, decide upon a coefficient or coefficients which will equalize the number of atoms on each side.

4) Repeat this procedure for the other elements until the equation is balanced, that is, until the same number of atoms of each element appears on each side of the equation.

5) Add the subscript to any free element in the equation which may require it. At this stage, free elements may have been given coefficients. If the coefficient of the free element is

an even number divide the coefficient by two when the subscript is added. The total number of atoms of the free element will then remain the same (for example, 6H contains the same number of atoms as $3H_2$).

6) If, however, the coefficient of the free element is an odd number, it cannot be divided by two. In this case, when the subscript is added to the free element, all other formulas on both sides of the equation must be multiplied by two.

EXAMPLE A: Write the equation for the reaction which takes place when potassium chlorate is heated to form potassium chloride and oxygen.

1) Write the equation without coefficients. Note that the free oxygen which is usually written O_2 is written at this stage without a subscript.

$$KClO_3 \rightarrow KCl + O$$

2) $KClO_3$ is the compound with the largest number of atoms. By inspection, we see that oxygen is the only element in the compound which does not appear with an equal number of atoms on the other side of the arrow. To make the O on the right balance the O_3 on the left, we multiply O by the coefficient *3:*

$$KClO_3 \rightarrow KCl + 3O$$

3) As we have just learned, free oxygen must be written as O_2. Add the subscript to the free oxygen on the right of the arrow. The coefficient *3* is not divisible by two, so when we add the subscript, we find there are six atoms of free oxygen on the right side of the arrow, but only three atoms of oxygen on the left side:

$$KClO_3 \rightarrow KCl + 3O_2$$

4) We may make the equation balance again by multiplying all other formulas by two:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

EXAMPLE B: Write the equation for the burning of benzene (C_6H_6) to form CO_2 and H_2O.

1) Write the unbalanced equation. Do not write the subscript for the free oxygen.

$$C_6H_6 + O \rightarrow CO_2 + H_2O$$

2) C_6H_6 is the compound with the largest number of atoms. It contains 6 atoms of carbon, but there is only one atom of carbon to the right of the arrow. Therefore, we place the coefficient *6* in front of CO_2.

$$C_6H_6 + O \rightarrow 6CO_2 + H_2O$$

3) C_6H_6 also contains 6 atoms of hydrogen, but there are only 2 atoms of hydrogen on the right side of the arrow. Therefore, we place the coefficient *3* in front of H_2O.

$$C_6H_6 + O \rightarrow 6CO_2 + 3H_2O$$

4) We now see that there are 15 atoms ($6 \times 2 + 3 \times 1$) of oxygen on the right, but only one atom of oxygen on the left. Therefore, we place the coefficient *15* in front of O.

$$C_6H_6 + 15O \rightarrow 6CO_2 + 3H_2O$$

5) Since free oxygen is written O_2, we add the subscript.

6) Since 15 is not divisible by two, we may bring the equation into balance once again by multiplying all other formulas by the coefficient *2*.

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$

If the coefficient of the oxygen had been an even number, we could have divided it by two when adding the subscript. It would then be unnecessary to multiply the other formulas by the coefficient *2*.

HOW TO CHECK EQUATIONS. To check an equation, proceed as follows:

1) Examine the first symbol on the left. Compare the number of atoms against the number of atoms of the same element on the other side of the equation. If the numbers are equal, put a small check over the symbols for the element.

2) Proceed to each symbol in turn until you have put a check over every symbol in the equation.

Thus, in checking the final equation in Example A above, $2KClO_3 \rightarrow 2KCl + 3O_2$, examine the first symbol, K. There are two atoms of potassium on each side. Put a check over the K on each side. Examine the next symbol, Cl. Again we have two atoms on each side. Check them. Finally, we have six atoms of oxygen on each side, which we check. All the symbols are then checked and accounted for:

$$\overset{\checkmark}{2}\overset{\checkmark}{K}\overset{\checkmark}{Cl}\overset{\checkmark}{O_3} \rightarrow \overset{\checkmark}{2}\overset{\checkmark}{K}\overset{\checkmark}{Cl} + \overset{\checkmark}{3}\overset{\checkmark}{O_2}$$

The equation is now balanced accurately. It is correct both mathematically and chemically. Following the same procedure, check the final equation in Example B.

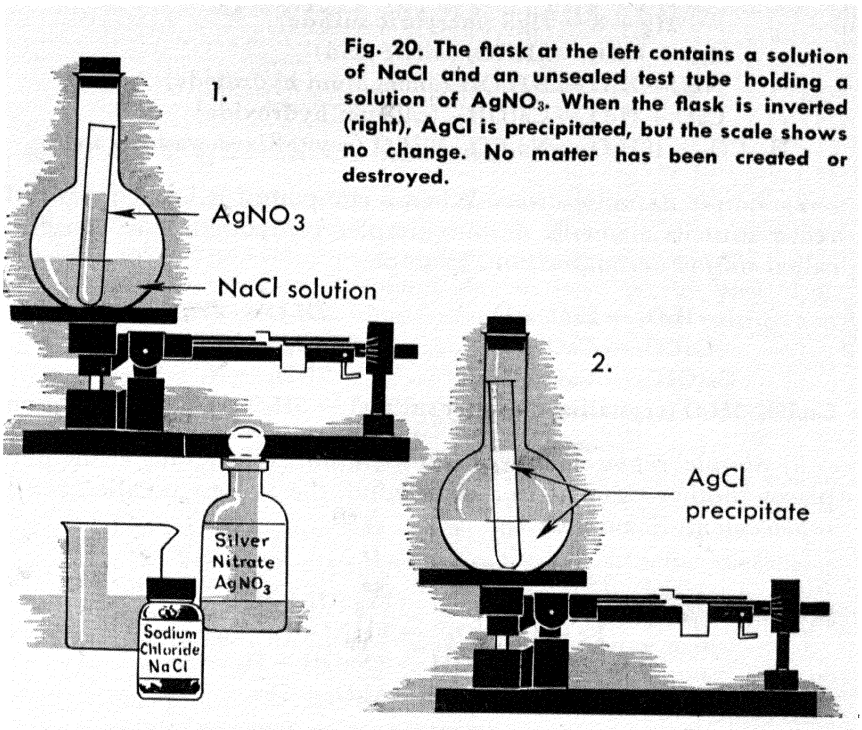


Fig. 20. The flask at the left contains a solution of NaCl and an unsealed test tube holding a solution of $AgNO_3$. When the flask is inverted (right), AgCl is precipitated, but the scale shows no change. No matter has been created or destroyed.

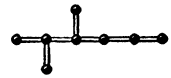
PRACTICE WORK ON BALANCING EQUATIONS

To be sure that you understand the suggestions just given for balancing equations, balance the following:

a) $NaClO_3 \rightarrow NaCl + O$
b) $Hg + O \rightarrow HgO$
c) $P_2O_5 + H_2O \rightarrow HPO_3$
d) $Mg + O \rightarrow MgO$
e) $Na + Cl \rightarrow NaCl$
f) $C + O \rightarrow CO$
g) $Cu + O \rightarrow CuO$
h) $Fe + O \rightarrow Fe_2O_3$
i) $O + P \rightarrow P_2O_3$
j) $P + O \rightarrow P_2O_5$
k) $SiO_2 + C \rightarrow SiC + CO$

What are the four types of chemical reactions? There are four general types of chemical reactions.

1) *Direct combination, or synthesis.* When two or more elements or compounds combine directly, forming a chemically more complex



6. Why must subscripts never be changed in balancing equations?

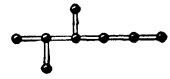
7. What is wrong with the following:

$$2Ne \text{ (neon)} + O_2 \rightarrow 2NeO?$$

8. Why may coefficients be changed in balancing an equation?

9. Why is a knowledge of valence so essential in writing equations?

10. Name five elements which, when free, must be written with the subscript *2*.



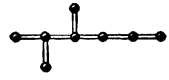
11. Correct this: $Mg + Br \rightarrow MgBr_2$.

12. Generally, what happens to a radical during a chemical change?

13. Balance the following equation, giving your reason for each step:

Acetylene (C_2H_2) + oxygen (O_2)
→ carbon dioxide (CO_2) + water (H_2O)

14. What are the four general types of reactions?



15. Give an example of an equation illustrating direct combination.

16. Give an example of an equation representing simple decomposition.

17. How do you recognize an equation representing simple replacement?

18. Give an example of an equation representing double replacement.

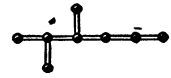
19. What is the general rule followed in balancing a double-replacement equation?

20. Complete and balance the following equation. Show how to check it to see if it is correctly balanced.

$$Na + HOH \rightarrow NaOH + H$$

21. Show in detail how to balance the equation representing the decomposition of sodium chlorate, $NaClO_3$.

22. When $CaCl_2 \cdot 2H_2O$ is heated, water is liberated. Write the equation.



23. Balance the following equations. Check each one. Do not write in this book.

a) $Cu + S \rightarrow Cu_2S$
b) $P + Cl_2 \rightarrow PCl_3$
c) $C + CO_2 \rightarrow CO$
d) $H_2S + Pb(NO_3)_2 \rightarrow HNO_3 + PbS$
e) $CaO + C \rightarrow CaC_2 + CO$
f) $SiO_2 + C \rightarrow SiC + CO$

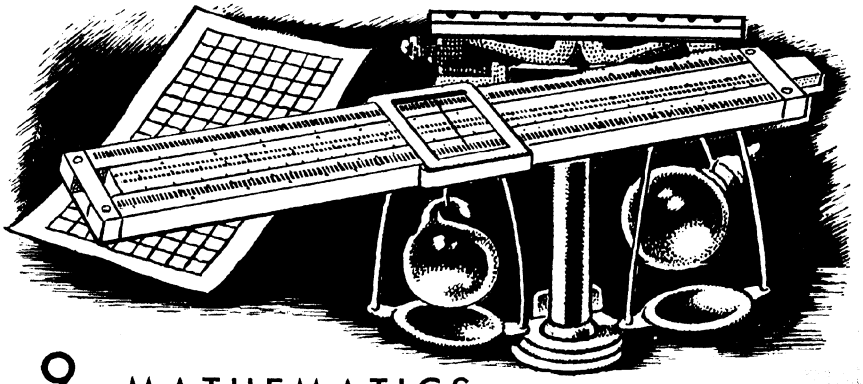
24. Complete and balance the following equations. Check each one. Do not write in this book.

a) $H_2O_2 \rightarrow$
b) $HgO \rightarrow$
c) $Fe + HCl \rightarrow$
d) $CuO + H_2 \rightarrow$
e) $BaO_2 + H_2SO_4 \rightarrow$
f) $AgNO_3 + KCl \rightarrow$
g) $Mg + H_2SO_4 \rightarrow$
h) $Ca(OH)_2 + CO_2 \rightarrow$

25. Write balanced equations for the following. Name each element and compound that appears in the equation. Check each equation.

a) The electrolysis of H_2O.
b) The laboratory preparation of O_2.
c) The equation representing Priestley's discovery of O_2.
d) The laboratory preparation of H_2.
e) The heating of Cu in air.
f) The preparation of H_2O_2.
g) The reduction of CuO by H_2.
h) The heating of crystallized washing soda.
i) The chemical reaction of the oxyhydrogen torch.
j) The action of Na on H_2O.
k) The passing of N_2 over hot Mg.
l) The reaction between H_2O and CO_2.

26. Is there anything in a balanced equation which did not have to be determined by experimentation?



9. MATHEMATICS OF CHEMISTRY

. . . As the usefulness and accuracy of chemistry depend entirely upon the determination of the weights of the ingredients and products, too much precision cannot be employed in this part of the subject, and for this purpose we must be provided with good instruments.

Lavoisier, 1743–1794

Measurement in chemistry. Chemists are chiefly concerned in analyzing substances or in making new substances. One question they always ask is *how much* of each element is present in a substance. Their measurements of quantity must be very exact. Sometimes their answer is in terms of the volume occupied by an element. More often the answer they want is in terms of weight.

Here in America, in everyday affairs, we measure the weight of substances in ounces and pounds. Chemists use a different kind of measurement. They weigh substances in grams, kilograms, and micrograms. They also measure the weight of atoms in terms of *atomic weight.*

All measures of weight are comparisons. When you say, "My friend, Charlie Ross, weighs 132 pounds," you are making a definite statement that anyone can understand. But what is a pound? You know what a pound of butter looks like, but a *pound* by itself doesn't look like anything.

Down in the Bureau of Standards in Washington is a carefully protected metal cylinder called the *prototype,* or *standard, kilogram.* Every measurement of weight made in our nation is a comparison with that particular kilogram. For example, the pound which we

use in everyday measurements of weight may be defined as 0.4536 of the standard kilogram.

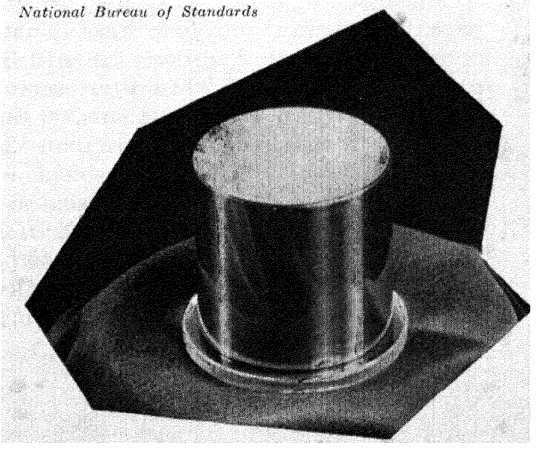
Just as the pound is divided into ounces, the kilogram may be divided into smaller units known as grams. One thousand grams equal one kilogram. The gram is a customary unit of weight in chemistry. When chemists speak of ten grams of iron, they are actually referring to an amount weighing $\frac{1}{100}$ of the standard kilogram in Washington.

Chemists also use a Table of Atomic Weights in which one atom of each element has a particular weight. The weight assigned to each element, like all measures of weight, is a comparison. How was this Table of Atomic Weights made?

Dalton determines atomic weights. As you know, Dalton believed that the atoms of different elements have different weights. Dalton knew that if he could find the weights of the atoms, the progress of chemistry would be speeded. He realized that he could not actually weigh an atom of an element. In fact, it took more than 100 years from the time of Dalton's experiments until accurate methods and precise instruments made it possible to determine the actual weights of atoms.

However, Dalton knew that elements combine according to fixed ratios by weight. For example, 22.997 grams of sodium combine with 79.916 grams of bromine to form sodium bromide — a ratio of approximately 1 : 3.5. The two elements never vary in the ratio of their weights in forming this compound. In a similar manner, all elements combine according to certain specific ratios by weight. Dalton believed that the ratios of these combining weights depended upon the weights of the atoms of each element. He believed further that, by studying the ratios of the weights in which elements combine, he would be able to determine the relative weights of the atoms of the elements.

National Bureau of Standards



The prototype kilogram No. 20 is a platinum-iridium cylinder 39 mm. in diameter and 39 mm. high. It is kept at Washington, D.C., in the laboratories of the Bureau of Standards.

He selected the atom of hydrogen for his standard and assigned to it the atomic weight *1*. By choosing the lightest element for a standard, he made sure that the atomic weight of each of the other elements would be greater than one. Then in a series of experiments, he found how the weight of the atoms of 13 other elements compared with his standard. He found that an atom of oxygen weighed seven times as much as an atom of hydrogen and assigned to oxygen the atomic weight of *7;* he found that an atom of phosphorus weighed nine times as much as an atom of hydrogen and assigned to phosphorus the atomic weight of *9*. These weights have since been found in error, but that in no way detracts from the value of Dalton's accomplishment.

Dalton prepares an historic table. From his experimental data, Dalton prepared a list of the 14 elements arranged according to the increasing relative weight of their atoms. This was the first *table of atomic weights.* It was first made public on October 21, 1803 "before a select group of nine members and friends in the rooms of the Literary and Philosophical Society of Manchester." Although inaccurate, the table compiled by this Quaker schoolteacher remains a monument to his foresight and intellectual accomplishment. His achievement was a crucial advance in chemistry and formed the keystone of his theory.

What is the atomic weight of an element? Later investigators followed Dalton's method, but used oxygen as a standard rather than hydrogen. They found oxygen a better choice because it combines with far more elements than hydrogen. The atomic weight of oxygen was given the whole number 16. Many of the other elements have atomic weights that are whole numbers. The weight of hydrogen remains approximately one — actually 1.0078 in comparison to oxygen.

The modern Table of Atomic Weights appears on the opposite page. For practical purposes, since the atomic weight of hydrogen is approximately one, hydrogen can still be used as the basis of comparison. The number 200.6 after *mercury* means that one atom of mercury weighs a little less than 200 times as much as an atom of hydrogen. It weighs a little more than $12\frac{1}{2}$ times as much as an atom of oxygen.

The atomic weight of an element is a number that shows the comparison of the weight of one of its atoms to the weight of one atom of oxygen, which is considered to be 16.

Always remember that atomic weights are not measured weights like an ounce or a gram. They are merely relative weights. The

TABLE 4. APPROXIMATE ATOMIC WEIGHTS

ELEMENT	SYMBOL	APPROX. AT. WT.	ELEMENT	SYMBOL	APPROX. AT. WT.
Aluminum	Al	27	Lead	Pb	207
Antimony	Sb	121.8	Lithium	Li	7
Arsenic	As	75	Magnesium	Mg	24.3
Barium	Ba	137.4	Manganese	Mn	55
Bismuth	Bi	209	Mercury	Hg	200.6
Boron	B	11	Nickel	Ni	58.7
Bromine	Br	80	Nitrogen	N	14
Cadmium	Cd	112.4	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Platinum	Pt	195
Chlorine	Cl	35.5	Potassium	K	39
Chromium	Cr	52	Radium	Ra	226
Cobalt	Co	59	Silicon	Si	28
Copper	Cu	63.5	Silver	Ag	108
Fluorine	F	19	Sodium	Na	23
Gold	Au	197	Strontium	Sr	87.6
Hydrogen	H	1	Sulfur	S	32
Iodine	I	127	Tin	Sn	118.7
Iron	Fe	56	Zinc	Zn	65.4

actual measured weight of each of the atoms is an extremely small quantity, inconvenient to use in most calculations. For example, the actual weight of an atom of oxygen is about 0.000,000,000,000,000,000,000,026 gram.

The Table of Atomic Weights is the foundation of chemical mathematics. Realizing the importance of accurate atomic weights, many chemists performed a tremendous number of experiments to make the Table of Atomic Weights as free from error as possible. Chemists of all countries cooperated in this huge undertaking. In our own country, Theodore W. Richards and his students at Harvard spent almost half a century in this epoch-making work. National boundaries were forgotten and men from all over the world pooled the results of their experiments to give us our present Table of Atomic Weights. Research chemists, industrial chemists, and student chemists all depend upon the Table of Atomic Weights in making their chemical calculations.

Solving type problems in chemistry. Most of the problems met in elementary chemistry can be grouped conveniently into five types. The first two, and one variety of the third are described below. Two additional varieties of the third type are discussed in Chapter 19 and two more types, more complex and less frequently met, are discussed on pages 636–641.

With a thorough understanding of the *type* problems discussed in this book, you should have no trouble in solving practically all the common chemical problems. Frequent reflective practice is, of course, necessary for mastery. Hence problems of various types are included in the questions at the end of each of the remaining chapters.

The meaning of symbols. A knowledge of the meaning of chemical symbols is essential in solving the various types of chemical problems. The symbol for an element, like *K*, does three different jobs. First, it may be used to name the element. Second, it may be used to mean one atom of that element. Third, it may stand for one atomic weight of the element. Thus *K* is the symbol for potassium, for one atom of potassium, and for 39 units of potassium in any system of measuring weight (as 39 grams, 39 ounces, 39 pounds).

The chemical symbols for a formula like *KCl* also do three jobs. First, they represent the name of the compound, potassium chloride. Second, they represent one molecule of potassium chloride. Third, they represent one *molecular weight* of the compound. All of the type problems involve the use of both *atomic weight* and *molecular weight.*

TYPES OF PROBLEMS

TYPE 1: TO FIND THE MOLECULAR WEIGHT * OF A COMPOUND FROM ITS FORMULA

Molecular weight is the ratio of the weight of one molecule of a compound to the atomic weight of oxygen (16). Like atomic weight, it is only a relative weight. *The molecular weight of a compound is obtained by adding together the atomic weights of each of the atoms in one molecule of the compound.*

Procedure.

1. Find the atomic weights of the elements in the chart on page 127. Place these numbers under the symbols and add them.

* Some compounds do not exist as molecules and therefore cannot have a molecular weight. However, the formulas of these compounds are written in the conventional manner. The steps given in this discussion for finding *molecular weight* may also be used for finding the *formula weight* of the non-molecular compounds. For the purposes of this book, formula weight may be considered the same as molecular weight.

EXAMPLE: Find the molecular weight of potassium chloride, KCl.

K Cl
39 + 35.5 = 74.5, the mol. wt. of KCl

2. When an element is followed by a subscript, be sure to multiply the atomic weight of the element by the subscript.

EXAMPLE: Find the molecular weight of magnesium sulfate, $MgSO_4$.

Mg S O_4
$24 + 32 + (16 \times 4) = 24 + 32 + 64$
$= 120$, the mol. wt. of $MgSO_4$

3. When a formula is preceded by a numerical coefficient, multiply the total molecular weight by the coefficient to find the relative weight (rel. wt.).

EXAMPLE: Find the relative weight of two molecules of magnesium carbonate, $2MgCO_3$.

2 (Mg C O_3)
2 [24 + 12 + (16 × 3)]
2 (24 + 12 + 48)
2 (84) = 168, the rel. wt. of 2 molecules of $MgCO_3$

4. When a radical is enclosed in parentheses followed by a subscript, multiply the sum of the atomic weights of all the elements of the radical by the subscript.

EXAMPLE: Find the molecular weight of calcium bicarbonate, $Ca(HCO_3)_2$.

Ca (H C O_3)$_2$
40 + [1 + 12 + (16 × 3)]2
40 + (1 + 12 + 48)2
40 + (61)2
40 + 122 = 162, the mol. wt. of $Ca(HCO_3)_2$

5. Water of crystallization (see page 68) is chemically part of certain compounds and is separated from the rest of the formula by a dot. The dot stands for *plus* and is not to be considered a multiplication sign.

EXAMPLE: Find the molecular weight of crystallized copper sulfate, $CuSO_4 \cdot 5H_2O$.

$$\begin{aligned} &\mathbf{Cu \quad S \quad O_4 \cdot 5H_2 \quad O} \\ &\mathbf{64 + 32 + (16 \times 4) + 5(1 \times 2 + 16)} \\ &\mathbf{64 + 32 + 64 \quad + 5(18)} \\ &\mathbf{64 + 32 + 64 + 90 = 250,\ the\ mol.\ wt.\ of\ crystallized\ copper\ sulfate.} \end{aligned}$$

The gram-molecular weight or mole. A very convenient unit in many calculations is the *gram-molecular weight* or *mole,* which is used in chemical equations (see pages 282–283) and in preparing standard solutions (see pages 207–208). A mole is the molecular weight of a substance expressed in grams. For example, a mole of potassium chloride (see Procedure 1) is 74.5 grams.

PRACTICE WORK ON PROBLEMS OF TYPE 1

1. Calculate the molecular weight of (a) KBr and (b) NaI.

2. Find the molecular weights of (a) LiCl and (b) ZnO.

3. What is the weight of a mole of K_3PO_4?

4. Find the molecular weights of (a) H_2SO_4, (b) $CaCO_3$, and (c) $BaSO_3$.

5. Calculate the molecular weights of (a) $Cu(HCO_3)_2$, (b) $Ba(NO_3)_2$, and (c) $Al_2(SO_4)_3$.

6. Calculate the molecular weight of $Na_2S_2O_3 \cdot 5H_2O$ (commonly called *hypo*).

7. What is the weight of a mole of gypsum, $CaSO_4 \cdot 2H_2O$?

8. Find the molecular weight of plaster of Paris, $(CaSO_4)_2 \cdot H_2O$.

9. The formula of glauber salt is $Na_2SO_4 \cdot 10H_2O$. Find the relative weight of three molecules of this substance.

10. Calculate the relative weight of $4Na_2B_4O_7 \cdot 10H_2O$.

TYPE 2: TO FIND THE PERCENTAGE COMPOSITION OF A COMPOUND FROM ITS FORMULA

The percentage composition of a compound is found by computing the percentage by weight of each different element in the compound. This is a simple percentage problem.

Procedure. Divide the atomic weight of each element by the molecular weight of the compound and multiply the fraction thus obtained by 100.

EXAMPLE A: Find the percentage composition of nitric acid, HNO_3.

$$\begin{array}{l} \text{H} \quad \text{N} \quad \text{O}_3 \\ 1 + 14 + (16 \times 3) \\ 1 + 14 + 48 = 63, \text{ the mol. wt. of } HNO_3 \end{array}$$

% of hydrogen

$$= \frac{\text{at. wt. of H}}{\text{mol. wt. of } HNO_3} \times 100 = \frac{1 \times 100}{63} = 1.6\%$$

% of nitrogen

$$= \frac{\text{at. wt. of N}}{\text{mol. wt. of } HNO_3} \times 100 = \frac{14 \times 100}{63} = 22.2\%$$

% of oxygen

$$= \frac{\text{rel. wt. of 3O}}{\text{mol. wt. of } HNO_3} \times 100 = \frac{48 \times 100}{63} = 76.2\%$$

$$\text{Total} = \overline{100.0\%}$$

EXAMPLE B: Find the percentage of water of crystallization in $BaCl_2 \cdot 2H_2O$.

$$\begin{array}{l} \text{Ba} \quad \text{Cl}_2 \cdot 2\text{H}_2 \quad \text{O} \\ 137 + (35.5 \times 2) + 2(1 \times 2 + 16) \\ 137 + 71 \quad + 2(18) \\ 137 + 71 + 36 = 244, \text{ the mol. wt. of } BaCl_2 \cdot 2H_2O. \end{array}$$

$$\text{Percentage of water} = \frac{\text{rel. wt. of } 2H_2O}{\text{mol. wt. of crystal}} \times 100$$

$$= \frac{2(2 + 16)}{244} \times 100 = \frac{3600}{244} = 14.7\%$$

EXAMPLE C: Find the percentage composition of $Na_2SO_4 \cdot 10H_2O$.

$$\begin{array}{l} \text{Na}_2 \quad \text{S} \quad \text{O}_4 \cdot 10\text{H}_2 \quad \text{O} \\ (23 \times 2) + 32 + (16 \times 4) + 10(1 \times 2 + 16) \\ 46 + 32 + 64 + 180 = 322, \text{ the mol. wt. of the compound.} \end{array}$$

Now find the total atomic weight of each element in the compound, thus:

$$\begin{array}{lll} \text{Sodium} = 2 \text{ atoms} = 23 \times 2 = & 46, & \text{the total at. wt. of Na} \\ \text{Sulfur} = 1 \text{ atom} = & 32, & \text{the total at. wt. of S} \\ \text{Oxygen} = 14 \text{ atoms} = 16 \times 14 = & 224, & \text{the total at. wt. of O} \\ \underline{\text{Hydrogen} = 20 \text{ atoms} = 20 \times 1 =} & \underline{20,} & \underline{\text{the total at. wt. of H}} \\ \text{Sum of the at. wt.} = & 322, & \text{the mol. wt. of the compound.} \end{array}$$

% of sodium	$= \frac{46}{322} \times 100 =$	14.3%
% of sulfur	$= \frac{32}{322} \times 100 =$	10.0%
% of oxygen	$= \frac{224}{322} \times 100 =$	69.5%
% of hydrogen	$= \frac{20}{322} \times 100 =$	6.2%
	Total =	100.0%

EXAMPLE D: Find the weight of iron in 80 lb. of an ore containing 90 percent ferric oxide, Fe_2O_3.

The weight of ferric oxide in the ore is 90 percent of 80 lb., or 72 lb.

Fe_2 O_3

$(56 \times 2) + (16 \times 3) = 160$ = mol. wt. of Fe_2O_3

Percentage of iron in $Fe_2O_3 = \frac{112}{160} \times 100 = 70\%$

Therefore 70% of 72 lb., or 50.4 lb., is the weight of the iron in the ore.

PRACTICE WORK ON PROBLEMS OF TYPE 2

1. Calculate the percentage composition of (a) water, (b) hydrogen peroxide, and (c) mercuric oxide.

2. Calculate the percentage composition of (a) H_2CO_3, (b) N_2O_4, and (c) $CaSO_4 \cdot 2H_2O$.

3. Find the percentage composition of chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$.

4. Calculate the percentage composition of crystallized potassium ferrocyanide, whose formula is $K_4Fe(CN)_6 \cdot 3H_2O$.

5. Find the percentage of oxygen in a compound whose formula is $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

6. How much aluminum can be obtained from 100 lb. of its cryolite ore which, upon analysis, shows the presence of 80 percent Na_3AlF_6?

TYPE 3: PROBLEMS BASED ON CHEMICAL EQUATIONS

Because the symbol of an element and the formula of a compound may represent definite weights, an equation also may be considered to represent definite weights of the substances taking part in the reaction. Thus, $2Ag + S \rightarrow Ag_2S$ may be read, *216 grams of silver, plus 32 grams of sulfur yield 248 grams of silver sulfide.* Note that the actual weights are based on the atomic weights.

Problems based on chemical equations may be broadly divided into three groups: A. Straight-weight problems; B. Weight-volume problems; and C. Straight-volume problems.

Group A is discussed below. Groups B and C are discussed later in the book.

TYPE 3A: STRAIGHT–WEIGHT PROBLEMS

Straight-weight problems involve finding one weight in an equation when another is given.

EXAMPLE: How many grams of calcium carbonate will be formed by the complete reaction between 222 g. of calcium hydroxide and carbon dioxide?

Procedure.

1. Write the balanced equation.

$$Ca(OH)_2 + CO_2 \rightarrow H_2O + CaCO_3$$

2. Write the given weight *over* its formula. Write x over the formula of the substance whose weight is to be found. Cross out all other formulas in the equation.

$$\overset{222\text{ g.}}{Ca(OH)_2} + \cancel{CO_2} \rightarrow \cancel{H_2O} + \overset{x\text{ g.}}{CaCO_3}$$

3. Since the same relationship exists between the actual weights as exists between the molecular weights represented in the equation, write the molecular weights of the substances involved *under* their respective formulas. Do not ignore any coefficient.

$$\begin{array}{ccc} \overset{222\text{ g.}}{Ca\ (O\ H)_2} & \rightarrow & \overset{x\text{ g.}}{Ca\ C\ O_3} \\ 40 + (16 + 1)2 & & 40 + 12 + (16 \times 3) \\ 40 + (17 \times 2) & & 40 + 12 + 48 \\ 74 & & 100 \end{array}$$

4. Write the mathematical equation represented by the known and unknown weights. Solve for x.

$$\frac{222}{74} = \frac{x}{100}$$

$$74x = 22{,}200$$

$$x = 300, \text{ the number of grams of } CaCO_3 \text{ produced}$$

Alternate method. We can avoid the use of an equation involving x by solving the problem as follows:

$$\frac{\text{wt. of substance used}}{\text{mol. wt. of substance used}} \times \text{mol. wt. of substance formed} = \text{Answer}$$

$\frac{222}{74} \times 100 = 300$, the number of grams of $CaCO_3$ produced.

PRACTICE WORK ON PROBLEMS OF TYPE 3A

1. How much magnesium is required to react with sufficient hydrochloric acid to produce 10 g. of hydrogen?

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

2. 434 g. of mercuric oxide, HgO, were decomposed by heat. How much mercury was formed?

3. How much potassium chlorate would be needed to prepare 384 g. of oxygen?

4. How much hydrogen would be needed to reduce completely 160 g. of cupric oxide, CuO?

5. 11.5 g. of sodium react completely with water. What weight of sodium hydroxide is formed?

6. By the electrolysis of water 12 lb. of hydrogen were liberated. What weight of oxygen was formed at the same time?

7. (a) What weight of magnesium will be needed to react with sulfuric acid to produce 30 g. of $MgSO_4$? (b) What weight of hydrogen will be evolved?

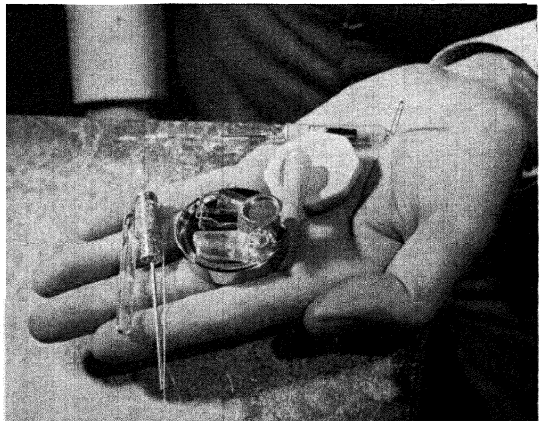
8. After heating, 10 g. of crystallized copper sulfate gave 6.4 g. of the anhydrous salt, $CuSO_4$. Calculate the number of molecules of water of crystallization in the original compound.

Let x represent the number of molecules of water of crystallization.

$$\underset{10\text{ g.}}{CuSO_4 \cdot xH_2O} \rightarrow \underset{6.4\text{ g.}}{CuSO_4} + \underset{3.6\text{ g. (that is, } 10 - 6.4)}{xH_2O}$$

Now complete the problem.

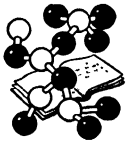
Standard Oil Company (N.J.)



Delicate instruments such as these are used in microchemistry, the branch of chemistry which involves handling extremely small quantities of matter.

9. After being heated, 10 g. of crystallized washing soda gave 3.71 g. of Na_2CO_3. Calculate the number of molecules of water of crystallization.

10. If 4 g. of crystallized barium chloride lost 0.59 g. upon being heated to constant weight, find the formula of the crystalline salt.



YOU WILL ENJOY READING

Jaffe, Bernard. *Chemical Calculations.* World Book Co., Yonkers, 1947. A systematic presentation of the solution of type problems, with 1000 problems arranged progressively according to lesson assignments.

Kendall, James. *At Home among the Atoms.* D. Appleton-Century Co., New York, 1932. "A Few Figures" explains atomic weights in a novel way. Tells how atomic weights are found.



USEFUL IDEAS DEVELOPED

1. The atomic weight of an element is a number that represents the ratio of the weight of 1 of its atoms to the weight of 1 atom of oxygen. Atomic weights are all relative weights.

2. The molecular weight of a compound is the ratio of the weight of 1 molecule of the compound to the atomic weight of oxygen (16).

3. A chemical symbol, in addition to representing an element, represents one atomic weight of that element.

4. A mole of a substance is its molecular weight expressed in grams.



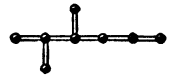
USING WHAT YOU HAVE LEARNED

Group A

1. (a) Who issued the first table of atomic weights? (b) Why was it later decided to use the weight of the oxygen atom as a standard instead of the weight of the hydrogen atom?

2. Exactly what is meant by saying that oxygen has an at. wt. of 16?

3. Find the mol. wt. of the compounds that have the following formulas: (a) cupric acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$; (b) chloroplatinic acid, H_2PtCl_2; (c) microcosmic salt, $HNaNH_4PO_4 \cdot 4H_2O$. Refer to Table 4 on page 127.

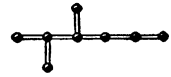


4. Find the percentage composition of each of the following compounds: (a) $BaCO_3$, (b) $KMnO_4$, (c) $K_4Fe(CN)_6$. Check each result.

5. Determine the percentage composition of each of the following compounds: (a) $BaSO_4$; (b) KCN; (c) $(NH_4)_2CO_3$.

6. Calculate the percentage of H_2 in alum,

$$KAl(SO_4)_2 \cdot 12H_2O.$$



7. Find the percentage of water of crystallization in

$$Sr(NO_3)_2 \cdot 5H_2O.$$

8. A ton of limestone, $CaCO_3$, was heated in a lime kiln until all of it was changed to quicklime, CaO. The equation for this reaction is: $CaCO_3 \rightarrow CaO + CO_2\uparrow$. How much quicklime was formed? To answer this question, first decide what type of problem this is: What four steps have you learned to take in solving such a problem? Solve the problem.

9. Find the weights of (a) H_2 and (b) $ZnSO_4$ formed by the complete reaction of 130 g. of Zn and sufficient H_2SO_4.

Group B

10. 320 g. of Fe_2O_3, on being reduced, form 224 g. of Fe. What is the at. wt. of oxygen?

11. 11.95 g. of lead sulfide, PbS, will produce 10.35 g. of lead. From this fact, and knowing that the at. wt. of S is 32, calculate the at. wt. of Pb.

12. Of what use to the manufacturing chemist is knowledge of the percentage composition of a compound? Select from the chapter on Cu an ore of that metal and illustrate.

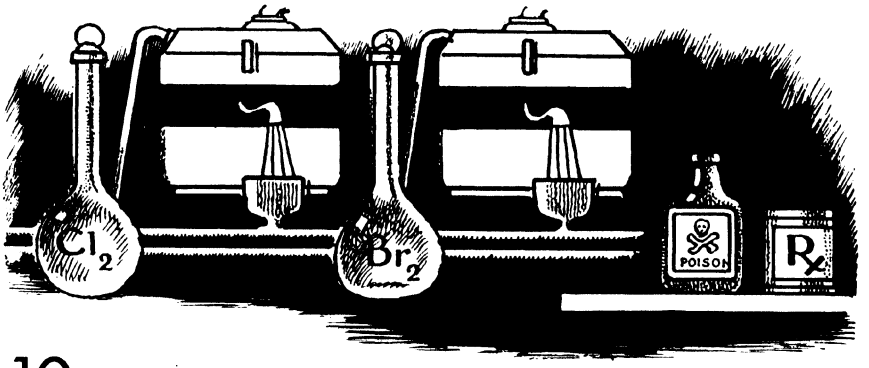
13. Suppose a chemist were going to manufacture HCl from NaCl and H_2SO_4. What helpful information could he gain from the following equation representing the reaction that would occur? $2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Consult a manufacturing chemist or an analytical chemist and discuss with him how he uses chemical mathematics in his business or profession. Report your findings to your class.

2. Construct a large graph to represent the percentage of each element in crystallized washing soda, $Na_2CO_3 \cdot 10H_2O$. Use different colors for each element. Show also the percentage of H_2O in this compound.



10. CHLORINE
AND THE HALOGEN FAMILY

. . . Search for the truth is in one way hard and another easy, for it is evident that no one can master it fully nor miss it wholly. But each adds a little to our knowledge of Nature and from all the facts assembled there arises a certain grandeur.
Aristotle

A Swedish druggist discovers chlorine. One of the scientists who lived and worked at about the same time as Priestley, Cavendish, and Lavoisier was a Swedish pharmacist who is well known to the world of chemistry. He not only prepared oxygen earlier than Priestley, but also, in 1774, discovered chlorine. Scheele is the only great chemist whose whole lifework was accomplished behind the counter or in the prescription laboratory of one drugstore or another!

When he had discovered the greenish-yellow chlorine gas that made his nose and throat sting and almost blinded him, he wrote to a friend: "Oh how happy I am; I seldom think of eating, or drinking, or where I live; I scarcely pay attention to my pharmaceutical business. But to watch new phenomena, this is my consuming interest." At 43, as a result of prolonged exposure to unhealthful conditions in his crude laboratory, Scheele died — a martyr to the rapidly developing and expanding science of experimental chemistry.

How chlorine is prepared in the laboratory. The method used by Scheele to prepare chlorine is still the common laboratory method used today. Two compounds are used — manganese dioxide and hydrochloric acid. When this mixure is heated, chlorine is liberated from the hydrochloric acid.

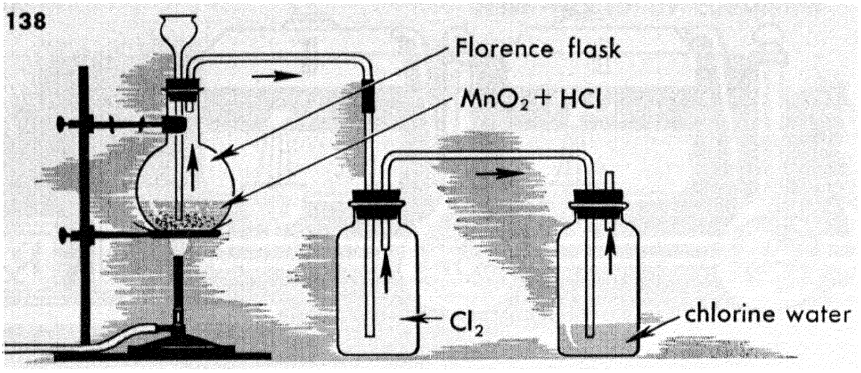


Fig. 21. Laboratory preparation of chlorine. What property of chlorine makes it wise to pass the excess gas into water?

Although chlorine gas is fairly soluble in water, it may be collected by water displacement. Since it is heavier than air, it is usually collected by displacing air (see Fig. 21).

The concentrated hydrochloric acid used in this reaction supplies the chlorine. In this reaction the manganese dioxide acts as an oxidizing agent, combining with the hydrogen of the acid and liberating free chlorine. The equation for this reaction is:

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

This equation may be considered to represent two reactions. The first is of the double-replacement type:

$$MnO_2 + 4HCl \rightarrow MnCl_4 + 2H_2O$$

and the second, a simple decomposition:

$$MnCl_4 \rightarrow MnCl_2 + Cl_2$$

Other oxidizing agents such as potassium chlorate or lead dioxide, PbO_2, may be used instead of manganese dioxide.

The physical properties of chlorine. Chlorine is a greenish-yellow gas, two and one-half times as heavy as air. It is fairly soluble in water, forming yellowish *chlorine water* (one volume of water dissolves about two volumes of chlorine gas under normal laboratory conditions). It has a penetrating odor and attacks the membranes of the nose, throat, and lungs. Inhaling ammonia or alcohol vapor counteracts this irritating action to some extent. Chlorine was the first gas to be liquefied. It liquefies at about $-34°C.$ at normal pressure. Faraday, who was the first to liquefy it, wrote to a friend in 1823, "I hope to be able to reduce many other gases to the liquid form." He did.

Chemical properties of chlorine. Chlorine is a typical nonmetal. It has a valence of one, that is, it combines with monovalent hydrogen, atom for atom. Chlorine is very active chemically. It unites with nearly all other elements, forming compounds called *chlorides*, just as oxygen forms *oxides*. Thus, a bit of sodium reacts brilliantly when heated with moist chlorine.

Here is a thrilling example of the marvels of chemistry. Sodium, a silvery, poisonous solid, unites with chlorine, a greenish-yellow, poisonous gas, producing a white solid, common salt, which is essential in the diet of both man and all animals.

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

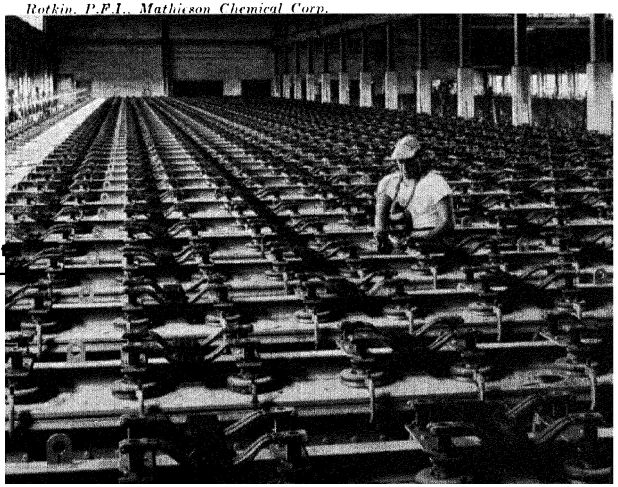
Chlorine has a strong attraction for hydrogen. When hydrogen and chlorine are mixed and exposed to strong light or ignited by a spark, they combine with explosive violence, forming hydrogen chloride gas. The equation for this reaction is:

$$H_2 + Cl_2 \rightarrow 2HCl$$

If a jet of hydrogen burning in air is thrust into a jar of chlorine, it will continue to burn, giving off hydrogen chloride as the product of combustion.

So powerful is the attraction of chlorine for hydrogen that it will tear hydrogen away from some of its compounds. Thus, when turpentine, a compound of carbon and hydrogen, is poured over a piece of filter paper which is then thrust into a bottle of chlorine, a flash of light occurs and a black powder is formed. The black powder is the free carbon which remains after the hydrogen from the turpentine has combined with the chlorine, forming hydrogen chloride. Chlorine will combine with water, liberating oxygen.

Rotkin, P.P.I., Mathieson Chemical Corp.



In this industrial plant chlorine is being manufactured in mercury cells.

How chlorine is prepared for industrial use. The electrolysis of *brine,* a water solution of sodium chloride, is the source of most of the chlorine used today. The electric current liberates free chlorine at the carbon anode. At the cathode the sodium liberated reacts immediately with the water, forming free hydrogen and sodium hydroxide.

$$2NaCl \rightarrow Cl_2 + 2Na$$
$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

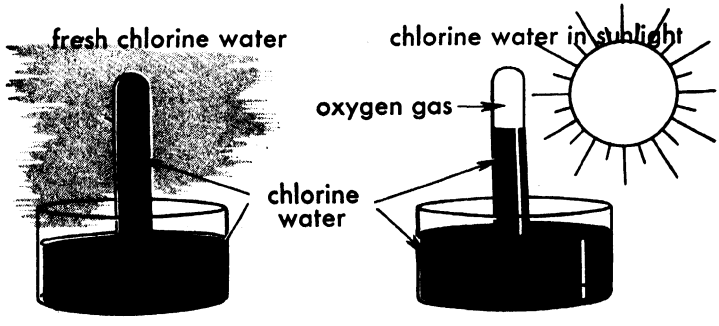
The combined equation, then, is:

$$2NaCl + 2H_2O \rightarrow Cl_2\uparrow + H_2\uparrow + 2NaOH$$

The chlorine gas is dried by passing it through concentrated sulfuric acid, and then liquefied. The yellow, liquid chlorine is stored in steel cylinders, each holding from one to 300 pounds of chlorine free from water vapor. This process, by which three valuable products — chlorine, hydrogen, and sodium hydroxide — are formed from two low-cost, plentiful compounds by means of an economical outlay of electric energy, is described in greater detail on page 212 under the industrial preparation of sodium hydroxide. Some chlorine is also obtained by the electrolysis of molten NaCl (see page 378).

The scientist serves humanity. Soon after the discovery of chlorine, Berthollet hit upon the idea of using the *bleaching* action of chlorine (which Scheele had noticed) industrially. He declined to patent his process or make any profit from it, but instead turned it over to the French government. This action of Berthollet is characteristic of many scientists, who believe that because they were freely helped toward making their discoveries by the work of those who preceded them, so they should freely pass on the results of their own labors.

Fig. 22. Chlorine bleaches indirectly. In the presence of sunlight chlorine reacts with water, liberating nascent oxygen.



Patents on chemical processes are sometimes turned over by their discoverers to *foundations,* which license them to manufacturers. These foundations receive fees or royalties for the use of the process. These funds may be used by the foundations in making further research possible.

Chlorine bleaches paper and textiles. "Dephlogisticated marine acid air," as chlorine was called before Davy showed it to be an element, was a chemical curiosity in 1774. Today, it is an industrial necessity, and more than two million tons of it are produced in this country annually.

The chief use of chlorine is in the bleaching, or decolorizing, of textiles, chiefly cotton and linen, and of wood pulp. It cannot be used for bleaching silk or wool because it destroys their fibers. Chlorine bleaches indirectly, by oxidation. Oxygen, liberated by the action of chlorine on water, combines chemically with certain coloring matters and dyes, which, upon oxidation, become colorless. This reaction is:

$$Cl_2 + H_2O \rightarrow 2HCl + O\uparrow$$

Chlorine is used as a bleaching agent either in the free condition, in chlorine water, or in some unstable chlorine compounds, such as *bleaching powder,* $CaOCl_2$, and calcium hypochlorite, $Ca(ClO)_2$. *Laundry bleach,* used extensively today, is made by adding liquid chlorine to a very cold solution of sodium hydroxide. This product is known as *Javelle water* and contains sodium hypochlorite, NaClO, a salt of hypochlorous acid, HClO.

$$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$$

Sodium hypochlorite decomposes easily, liberating atomic oxygen.

Dilute solutions of sodium hypochlorite, in strengths ranging from four to six percent, are marketed as "Clorox," "Rose-X," and a number of other trademarks. Such household bleaches are used very widely in home laundering and in removing stains. In bleaching with chlorine, care must be taken not to expose the materials to the action of the chlorine for too long a time, since continued action will make the fibers very weak. After the bleaching agent has been used, the fabrics should be thoroughly rinsed in fresh water to remove all traces of the bleach. In industrial bleaching, after removal from the bleaching tank, an *antichlor,* such as sodium thiosulfate ($Na_2S_2O_3$), commonly called *hypo,* is added to remove the excess chlorine, and then the material is thoroughly rinsed in running water.

Chlorine saves lives. Although it consumes only about ten percent of normal production, a second very important use of chlorine is in the purification of water. When chlorine is added to water, atomic oxygen, liberated from the water by chlorine, reacts with the bacteria present and kills them by oxidation. Only three pounds of chlorine are used for each million gallons of water. In the United States more than 75 percent of all drinking water is treated with chlorine. As a result, the death rate from typhoid fever, a disease caused by typhoid bacilli which may be present in drinking water, has been cut down considerably. This treatment also kills algae and other low plant and animal life. For field use, in areas where pure water is not available, explorers, scouts, and others carry tablets of a chlorine-producing substance such as "halazone" which contains $Ca(ClO)_2$.

Chlorine is also used as an antiseptic and disinfectant. A substance that checks the growth of bacteria is called an *antiseptic,* while a *germicide* kills the bacteria outright. A substance that either kills or checks the growth of bacteria is called a *disinfectant.* Since much illness is caused by poisons, or *toxins,* formed by bacteria, it is imperative that these bacteria be killed or at least prevented from multiplying.

"Zonite," a trade preparation containing NaClO, is used as a general household disinfectant. Because chlorine disinfectants if used improperly may destroy body tissue, such preparations should be used with great care. Several widely used insecticides are chlorine compounds (see page 540).

And chlorine destroys human life, too. Chlorine played a double role during World War I. While chlorine disinfectants and water chlorination were saving thousands of lives, free chlorine in the form of clouds of poisonous gas was choking out many other lives. Chlorine, and later phosgene, $COCl_2$, and mustard gas, $(ClCH_2CH_2)_2S$, caused terrible suffering in World War I, even though the use of poisonous gases had been "outlawed" by a conference at The Hague in 1907.

How to test for the presence of a chloride. Free chlorine may be recognized by its characteristic color and odor, but compounds of chlorine cannot be identified so easily. Because chlorides are present in so many common substances, a simple test for a chloride is desirable.

All chlorides are soluble in water, with the exception of the chlorides of silver, mercury, and lead. Because silver chloride is insoluble in water, chlorides are recognized by their reaction with a solution of silver nitrate. When a solution of silver nitrate is added

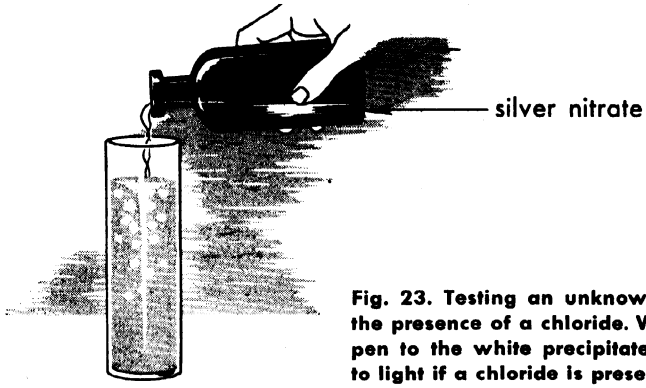


Fig. 23. Testing an unknown solution for the presence of a chloride. What will happen to the white precipitate on exposure to light if a chloride is present?

to a solution of a chloride, a white insoluble substance, a precipitate, forms. On exposure to light, the color of this precipitate changes gradually to purple and then to black.

$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl \downarrow$$

This color change, when silver nitrate is added to an unknown solution, suggests that probably a chloride is present. But some substances that are not chlorides form similar compounds. Therefore, the formation of such a precipitate on the addition of silver nitrate to a solution is not an entirely reliable test for a chloride.

A chemical test for a substance has one important requirement — it must be *specific,* that is, no other substance will react to the test in the same way as the substance for which the test was designed. Fortunately, silver chloride is insoluble in dilute nitric acid; other substances that might at first be mistaken for it are soluble in dilute nitric acid and disappear at once when this acid is added. The addition of nitric acid, therefore, is the final step in this test, distinguishing the chloride from other compounds.

An element is known by the company it keeps. The halogens (salt formers) are a group of elements that resemble one another chemically, and whose physical properties differ from one another in regular gradation, as shown in Table 5. Such a group of elements is called a *chemical family.* The members of the halogen family are fluorine, chlorine, bromine, iodine, and astatine, a radioactive element. Table 5 shows the relationship among the members of the halogen family.

Making bromine in the laboratory. Like chlorine, bromine is prepared by the oxidation of its hydrogen compound by manganese dioxide. A mixture of potassium bromide, sulfuric acid, and manganese dioxide is heated in a test tube (see Fig. 24). The H_2SO_4 reacts with the KBr, forming HBr, which is then oxidized by the MnO_2. Although at room temperature bromine is a liquid, it is liberated as

ELEMENT	ATOMIC WEIGHT (APPROX.)	PHYSICAL PROPERTIES				
		STATE	COLOR	ODOR	SOLUBILITY IN WATER	BOILING POINT
FLUORINE, F_2	19	Gas	Pale yellow	Penetrating	Decomposes water	$-187°C$
CHLORINE, Cl_2	35.5	Gas	Greenish-yellow	Irritating	Fairly soluble	About $-34°C$
BROMINE, Br_2	80	Liquid	Red	Suffocating	Fairly soluble	About 61°C
IODINE, I_2	127	Solid	Purplish-black	Resembles chlorine	Least soluble of halogens	Above 200°C

a brownish vapor at the temperature of the experiment. As this brownish vapor passes into the water, some of the bromine dissolves; the rest collects as a layer of bromine under the water. This method of collecting pure bromine by distillation is relatively safe.

$$2KBr + 2H_2SO_4 + MnO_2 \rightarrow K_2SO_4 + MnSO_4 + 2H_2O + Br_2$$

Great care should be taken in working with bromine, because it is poisonous and attacks the skin, causing severe burns. Particular care should be taken to protect the eyes from bromine vapor.

Taking bromine from the sea. Most bromine is extracted from the minute percentage (0.0065%) of bromides present in sea water. Free chlorine replaces the bromine of the bromides. Some of our bromine is also obtained from the bromides found in salt wells and salt lakes. The principal chemical reaction is:

$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$

Bromine helps engine efficiency. Much of the bromine produced in the United States is used in the manufacture of "Ethyl fluid," an anti-knock mixture composed of ethylene dibromide and tetraethyl lead (TEL). Large quantities of bromine are also used in making silver bromide, the light-sensitive chemical that forms the most important part of the coating of photographic films. Bromine and bromine compounds are used also in making tear-gas bombs. Bromine is used in appreciable quantities as an oxidizing agent in the manufacture of certain dyes and drugs.

Potassium bromide or sodium bromide acts as a *depressant* on the central nervous system. Their action is followed by drowsiness and even sleep. Such chemicals are called *sedatives.* They are used in the

	CHEMICAL PROPERTIES						
	VALENCE	ACTION WITH HYDROGEN	ACTION WITH METALS	ACTION WITH WATER	ORDER OF ACTIVITY	DISCOVERY	CHIEF ORE
	One	Forms HF	Forms fluorides	$H_2O + F_2 \rightarrow 2HF + O$	Most active	Moissan (mwä-säN'), 1886	CaF_2
	One	Forms HCl	Forms chlorides	$H_2O + Cl_2 \rightarrow 2HCl + O$	Next active	Scheele, 1774	NaCl
	One	Forms HBr	Forms bromides	$Br_2 + H_2O \rightarrow 2HBr + O$	Less than chlorine	Balard (bà-lär'), 1826	$MgBr_2$
	One	Forms HI	Forms iodides	$I_2 + H_2O \rightarrow 2HI + O$	Least active	Courtois (koor-twä'), 1812	$NaIO_3$ MgI_2

TABLE 5
THE HALOGEN FAMILY

treatment of insomnia and asthma and are frequently found in headache and sleeping powders. Heavy, continuous doses of bromides may have harmful effects on the body. Bromides should be used only on the advice of a physician.

Methyl bromide, CH_3Br, is used widely in commercial and industrial fumigation to kill insects and other low forms of plant and animal life. It is used for this purpose in boxcars, warehouses, and food processing and packaging plants.

How iodine is prepared in the laboratory. Like chlorine and bromine, iodine is prepared by the oxidation of its hydrogen compound by manganese dioxide. A mixture of potassium iodide, sulfuric acid, and manganese dioxide is heated in a test tube as shown in Fig. 25.

$$2KI + 2H_2SO_4 + MnO_2 \rightarrow K_2SO_4 + MnSO_4 + 2H_2O + I_2$$

The violet vapor of iodine, which is produced at the temperature of the reaction, condenses, forming purplish-black crystals on the inside of the test tube. This process of collecting iodine is called *sub-*

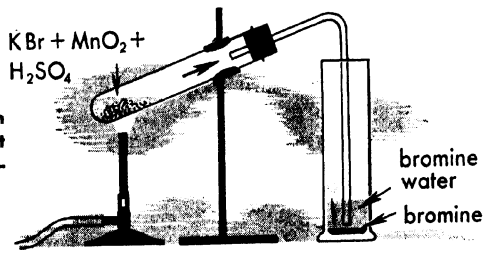


Fig. 24. Preparation of bromine in the laboratory. Why is bromine not collected in the same way as chlorine?

ELEMENT	ATOMIC WEIGHT (APPROX.)	PHYSICAL PROPERTIES					CHEMICAL PROPERTIES						
		STATE	COLOR	ODOR	SOLUBILITY IN WATER	BOILING POINT	VALENCE	ACTION WITH HYDROGEN	ACTION WITH METALS	ACTION WITH WATER	ORDER OF ACTIVITY	DISCOVERY	CHIEF ORE
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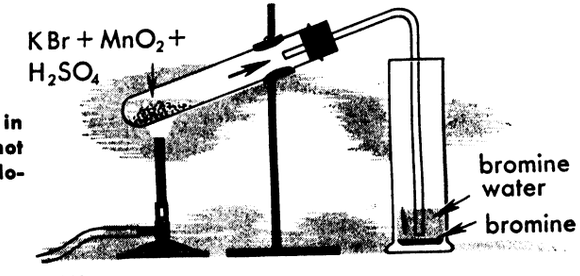


Fig. 24. Preparation of bromine in the laboratory. Why is bromine not collected in the same way as chlorine?



Dow Chemical Company

Methyl bromide used as a fumigant destroys all grain insects.

limation. A substance is said to *sublime* when it passes directly from the solid state to the gaseous state and then condenses back to the solid state without passing through the liquid state. Camphor is another substance that sublimes.

The industrial preparation of iodine. About 90% of our iodine is obtained from brine that comes up with the oil in California oil fields. This brine contains NaI and MgI_2. Chlorine is passed through the brine and replaces the iodine. The iodine is recovered by adsorption on activated carbon. (*Adsorption* is the clinging of molecules of one substance to the surface of another — see page 327.) The principal reaction is:

$$MgI_2 + Cl_2 \rightarrow MgCl_2 + I_2$$

The rest of our iodine comes from $NaIO_3$, found as an impurity in Chile saltpeter, $NaNO_3$.

Iodine, too, saves lives. The chief use of iodine is in the preparation of *tincture of iodine,* a two percent solution of iodine and potassium iodide in ethyl alcohol, which is an excellent antiseptic. As silver iodide, iodine is used to some extent in photography together with silver bromide. It is used also in the manufacture of *iodoform,* CHI_3, a yellow powder used as an antiseptic, and in the manufacture of "Aristol," an improvement over iodoform. Iodine is also used in the production of certain dyes and methyl iodide, CH_3I.

Is iodine necessary to health? Iodine is an important constituent of the human body. There is a definite relation between the presence of iodine in the thyroid gland and the prevalence of certain disorders. The thyroid gland, located in the neck, secretes a compound called *thyroxin,* containing about 65 percent iodine, which helps to regulate the rate of oxidation in the body.

When the thyroid gland receives too little iodine, *goiter,* an enlargement of the thyroid, results, caused apparently by the attempt of the gland to increase its size in order to produce more thyroxin. To offset this deficiency, iodides may be added to drinking water or about 0.02 percent of sodium iodide added to so-called *iodized salt.*

Extreme underactivity of the thyroid gland in newborn babies and young children may result in *cretinism* (krē'tĭn-ĭzm) — misshapen dwarfishness, low mentality, sluggishness, dullness, slow heart action. Synthetic thyroxin is used in the treatment of this thyroid disorder. Overactivity of the thyroid gland often produces the opposite effect — the thin, nervous, highly energetic person, whose movements are quick, and whose heart action is rapid. See page 34 for a discussion of basal metabolism tests in diagnosis of thyroid disturbances.

Iodine is also necessary to other forms of animal life. Large quantities of iodides are added to commercial feeds for chickens, cattle, dogs, cats, and other animals, and to fertilizers for forage crops.

Replacement power of the halogens. If free chlorine is added to a solution of a bromide or an iodide, free bromine or free iodine is liberated. Free chlorine replaces the two less active halogens.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$
$$2NaI + Cl_2 \rightarrow 2NaCl + I_2$$

The addition of free bromine to a solution of an iodide releases free iodine.

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

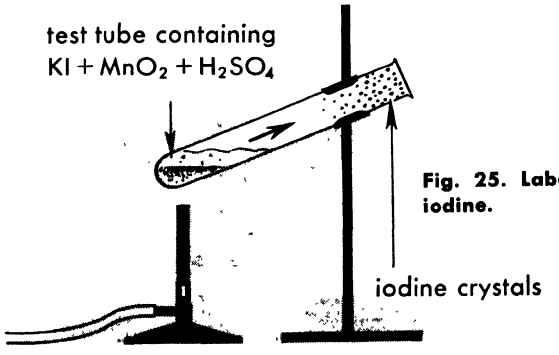


Fig. 25. Laboratory preparation of iodine.

However, the addition of iodine to a solution of either a bromide or a chloride has no effect, for the less active halogen will not replace the more active halogen from its compound. As mentioned earlier, the commercial preparation of bromine depends on the replacement power of chlorine.

How we test for the presence of bromides and iodides. Many uses are made of the replacement power of the halogens. The tests for bromides and iodides are based on it. Chlorine water is added to a solution of the unknown salt, and a few drops of carbon disulfide, CS_2, which is not soluble in water, are also added. If, after shaking the mixture, the carbon disulfide settles out as a distinct layer with a brownish-red coloration, then the original salt was a bromide, the free bromine liberated coloring the carbon disulfide. If the carbon disulfide acquires a purple coloration, the original salt was an iodide.

Carbon disulfide is used because free bromine and iodine are much more soluble in this liquid than in water. Hence, most of the liberated bromine and iodine dissolve in the carbon disulfide, thus coloring it much more than they would color water. Carbon disulfide, because it is a better solvent, will extract any bromine or iodine from the water solution. This process of separation, frequently used in industry, is called *extraction by partition.*

Fluorine, the most active of all the elements. Fluorine was not isolated until 1886. Because of its extreme chemical activity, which causes it to unite violently with metals, glass, porcelain, and water, its separation as a pure element was a very difficult undertaking. Finally, Henri Moissan succeeded by liquefying pure hydrogen fluoride, adding some potassium fluoride, and at a temperature of −23°C. passing an electric current through the mixture. Fluorine was liberated at the anode.

The anode used industrially today is made of graphite, which is not attacked by this pale yellow gas. Fluorine is employed in making uranium hexafluoride used in atomic energy plants where many of the lubricants are chemically inert fluorocarbon compounds. The plastic, "Teflon," is another fluorine compound. The new rat and ground squirrel poison, 1080, is a fluorine compound, and sodium fluoride is used in some insecticides.

Fluorine prevents tooth decay. The amount of tooth decay, or *dental caries,* has been found to vary directly with the quantities of fluorides present in the local water supply. Too much fluoride produces very hard but mottled teeth, a condition in which the enamel becomes discolored badly. When too little fluoride is present, there is much tooth decay. Water fluoridation (about one part NaF per

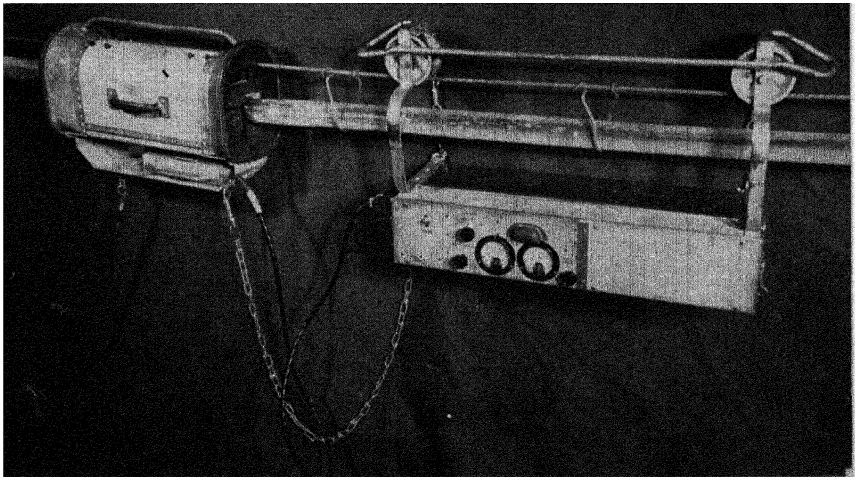
million parts water) is now widely practiced to protect children up to about the age of 12 while tooth enamel is being formed.

Fluorine refrigerants. A *refrigerant* is a substance used to absorb heat by changing from a liquid to a gas. In refrigeration, the material from which heat is absorbed is cooled. Almost as long as mechanical refrigerators have existed, their manufacturers have searched for better refrigerants. Something was wrong with nearly all the original refrigerants. They were either toxic, flammable, corrosive, or possessed disagreeable odors. And then a family of compounds was developed, and introduced in 1931 under the trademark "Freon." These compounds, produced by the halogenation of simple compounds of carbon and hydrogen, are far superior to sulfur dioxide, ammonia, ethyl chloride, and methyl chloride as refrigerants. All are practically odorless, nontoxic, nonflammable, and noncorrosive.

The first of the "Freons" to be produced was *dichlorodifluoromethane,* CCl_2F_2, and a later one was *dichlorotetrafluoroethane,* $C_2Cl_2F_4$. There are several others, each with slightly different properties that make it particularly well adapted to a special use. Because of their extreme volatility and the speed with which they penetrate every nook and cranny of a confined space, the "Freons" are used as propellants in dispersing insecticides. Aerosol bombs used for killing household pests usually contain an insecticide and a liquefied "Freon" gas under pressure. When the pressure is released, the expanding gas quickly distributes the insecticide throughout a room or closet.

This electronic device, called a "sniffer," is used to detect breaks in telephone cables through which moisture might enter. The cable to be tested is filled with a "Freon" gas. Then the sniffer is pulled along the cable from the ground. Escaping gas activates a "Freon"-sensitive detector, ringing a bell.

Bell Telephone Laboratories



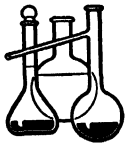


YOU WILL ENJOY READING

Consumer Reports (*Consumers Union Reports*), April, May, June, 1939. Consumers Union of U.S., New York. Excellent reports on various antiseptics.

Harrow, Benjamin. *Eminent Chemists of Our Time* (2nd ed.). D. Van Nostrand Co., New York, 1927. Read the life of Moissan and his isolation of fluorine.

Sanders, Gardiner, and Wood. "Chlorine and Caustic Manufacture." *Industrial and Engineering Chemistry,* September, 1953, pp. 1824–1835. Includes history, production figures, photos, and diagrams showing how diaphragm and mercury cells work.



USEFUL IDEAS DEVELOPED

1. The halogens are a group of elements that resemble one another chemically, and whose physical properties differ in regular gradation. The halogen group is one of several such groups of elements.

2. A substance that passes directly from the solid to the gaseous state and directly from the gaseous to the solid state is said to sublime.

3. The ability of one element to replace another in that element's compounds is widely used in chemical reactions. The halogens may be listed according to their replacement power.

4. The separation of a substance from a solution containing that substance by means of a better solvent is known as *extraction by partition.*

5. Like Berthollet, many scientists believe they should freely pass on to others the results of their own labors, and so help all humanity.



USING WHAT YOU HAVE LEARNED

Group A

1. Who discovered Cl_2, and in what year was it isolated?

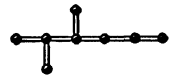
2. Make a labeled diagram showing the laboratory preparation of Cl_2.

3. What is the function of MnO_2 in the laboratory preparation of Cl_2?

4. What other substance might be used instead of MnO_2 in the preparation of Cl_2?

5. (a) Give two reasons for collecting Cl_2 by the displacement of air. (b) Why should any excess of Cl_2 be passed into water?

6. Write a balanced equation representing the laboratory preparation of Cl_2.



7. State four physical properties of Cl_2.

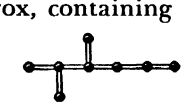
8. Faraday liquefied Cl_2 in 1823. It was the first gas to be liquefied. Suggest a reason.

9. If a brightly burning paraffin taper is inserted in a bottle of Cl_2, a heavy black smoke is given off. Explain.

10. By what process does Cl_2 bleach? Explain.

11. (a) Why is it necessary to rinse materials that have been bleached with Cl_2? (b) Why cannot Cl_2 be used to bleach silk and wool?

12. Because of what chemical property are bleaching powder, $CaOCl_2$, and Clorox, containing NaOCl, able to bleach?



13. Find the percentage of Cl_2 in bleaching powder.

14. (a) Distinguish between the terms *antiseptic* and *germicide*. (b) What term embraces both?

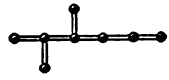
15. Make a list of all the uses of Cl_2 that you know.

16. Chloride of lime, or bleaching powder, has the formula $CaOCl_2$. It is made from $Ca(OH)_2$ and Cl_2. Write the equation for its preparation.

17. Give a brief account of the preparation of some laundry bleach.

18. Chlorine played a double role in wartime. Explain.

19. How much Cl_2 can be prepared by the action of 348 g. of MnO_2 on sufficient concentrated HCl?



20. (a) Describe fully the test for a chloride. (b) Write the equation for the reaction that takes place.

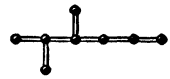
21. Illustrate the statement, "An element is known by the company it keeps."

22. (a) Compare the physical properties of the members of the halogen family. (b) Compare their chemical properties.

23. In what ways do the halogens (a) resemble one another, and (b) differ from one another?

24. List the halogens in the order of their chemical activity.

25. Illustrate what is meant by the replacement power of the halogens.



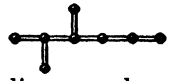
26. Does the following equation represent an actual chemical reaction? Explain. $2KCl + Br_2 \longrightarrow 2KBr + Cl_2$

27. Describe two uses of the replacement power of the halogens.

28. Make a labeled diagram of the laboratory preparation of Br_2.

29. (a) What is a sedative? (b) State three other uses of Br_2.

30. Describe the commercial preparation of Br_2.



31. Using a labeled diagram, describe the laboratory preparation of I_2.

32. (a) What is sublimation? (b) What is tincture of iodine?

33. How is iodine obtained for industrial use?

34. How is the most active of all the chemical elements prepared?

35. (a) What is one cause of mottled teeth? (b) What is fluoridation?

36. What is the relationship of F_2 to dental caries?

37. (a) What compounds of F_2 are superior refrigerants? (b) Why?

Group B

38. Compare Cl_2 and O_2 with respect to: (a) chemical activity, (b) behavior with H_2, (c) valence. Explain each answer fully.

39. (a) What is the relationship between lack of iodine and goiter? (b) Why is goiter not so prevalent in New York City as it is in some other parts of the United States?

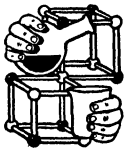
40. A bottle of tincture of iodine was found, after long use, to contain only a dark solid. (a) Would it be safe to use it after adding pure ethyl alcohol? (b) Explain your answer.

41. If you had some NaI, how would you prepare a solution of tincture of iodine from it?

42. I_2 is produced from California oil-well brines and from other brines in Michigan. Can you suggest a way in which this I_2 is extracted?

43. How much fluorine would be needed to make one ton of dichlorotetrafluorethane, $C_2Cl_2F_4$?

44. (a) What factors must a manufacturer consider when he chooses raw materials for use in manufacturing a substance on a large scale? (b) Show how these factors apply in the manufacture of Cl_2.



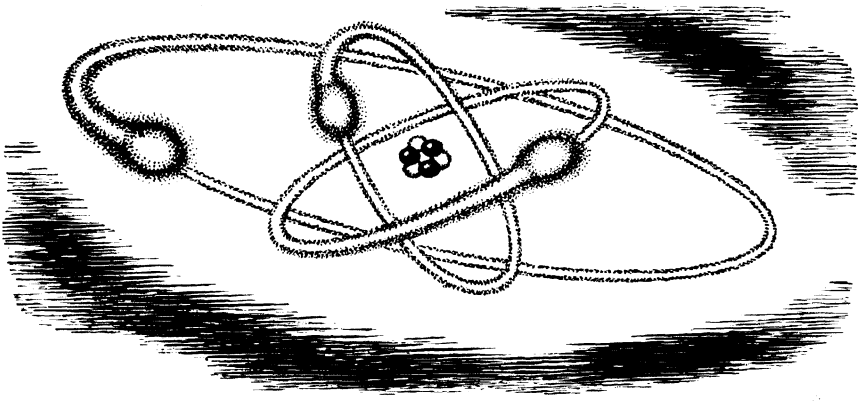
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make a study of advertisements of antiseptics and disinfectants in magazines and newspapers. What appeals are made in these advertisements to induce you to buy a particular brand? Are the appeals chiefly scientific, pseudo-scientific, fear-provoking, or do they appeal chiefly to your pride, sense of superiority, your desire for social approval, and so forth? Illustrate your report with actual advertising copy.

2. Ink eradicators frequently contain two solutions. No. 1 contains a solution of a very weak acid and No. 2 contains a solution of sodium hypochlorite. Prepare such an ink eradicator using vinegar or citric acid for No. 1 and Javelle water or Clorox for No. 2. Demonstrate its use before your class.

3. Victor Meyer, an eminent German chemist, prepared a compound in 1886 which is now known as *mustard gas.* Meyer was the first chemist to prepare this chemical during his theoretical investigations. Thirty years later chemists, cooperating with the Germany military machine, made this compound available for use as a poison gas. Should society take a hand in suppressing such discoveries which might be used against mankind? Write a brief paper either in favor of this point of view or against it, or arrange in class for a discussion or debate on this topic.

4. Study the quotation at the beginning of this chapter. Prepare a brief report to the class on the meaning of this quotation. Illustrate your report with an example from the history of science.



11. ELECTRONS AND OTHER PARTICLES

. . . Our experiences and observations alone never lead to finalities. Theory, however, creates reliable roads over which we may pursue our journeys through the world of observation. Anton Reiser, 1930

The electron theory gives us a clearer picture of matter and its changes. Formulating accurate theories takes remarkably clear insight, courage, and creative imagination. The theories and principles of science are among the most truly creative products of the mind of man. The atomic theory of Dalton is one of the great theories upon which modern chemistry is built. It shows us that atoms do not combine in a haphazard, irregular manner but form molecules in accordance with unvarying natural laws. However, it gives us no idea *why* this is so.

A more recently developed theory, which is called the *electron theory,* supplements the atomic theory and gives this explanation. It provides answers also to such questions as why the extreme chemical activity of fluorine, the comparative inactivity of nitrogen, and the inertness of argon; why elements and radicals possess the valences that they have, and many other questions. The electron theory is the fruit of many scientists who worked in many countries. It made possible the atomic age.

Static electricity. About 2600 years ago, the Greeks discovered that when amber is rubbed with cloth, it becomes capable of attracting tiny bits of straw or dry leaves. Through the centuries, men have

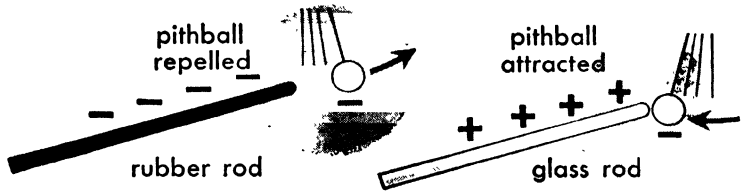


Fig. 26. Demonstration of static electricity.

discovered that other materials may be given this property. Glass, when rubbed with silk, or hard rubber, when rubbed with fur, will also attract light objects. The force which causes this attraction was named *electricity* from the Greek word for amber. Today, we refer to the electricity caused by friction or rubbing as *static* electricity.

Benjamin Franklin attempts to explain negative and positive electricity. Suspend a pith ball by a silk thread. Touch it with a hard-rubber rod which has been rubbed with fur. As soon as contact is made, the pith ball will be driven away, or repelled, from the rod. Then bring near the pith ball a glass rod which has been rubbed with silk. The ball will be attracted toward the glass rod.

This simple experiment demonstrates that the glass and the hard-rubber rods were charged with opposite kinds of electricity. When the neutral pith ball was touched by the hard-rubber rod, it became charged with the same kind of electricity as the rod. It was then pushed away from the rod, proving that objects with the same electric charges repel one another. However, the ball was drawn toward the glass rod, proving that objects with opposite electric charges attract one another.

In 1747, Benjamin Franklin, one of the most versatile men America has ever produced, received a static electricity machine from a friend in England. Franklin, son of a soap-maker who had fled from England because of religious persecution, was then 41 years old. Because of a very successful business career, he was rich enough to retire from business and devote himself to scientific experimentation. He had already organized the first scientific society in the New World, an organization which later became the American Philosophical Society.

Franklin performed many experiments with his static electricity machine, and that same year he announced his own views on the nature of electricity. He wrote: "The electric fire (electricity) is not created by friction, but collected, being really an *element diffused among matter.* The electrical matter consists of particles extremely subtile. . . . Hence have arisen some new terms among us: we say B is electrised *positively;* A, *negatively.* Or rather B is electrised *plus;*

A, *minus.*" Franklin was the first person to use these present-day terms in referring to electricity. He later induced his good friend Priestley to write a history of electricity, and thus, in part, directed Priestley's scientific career.

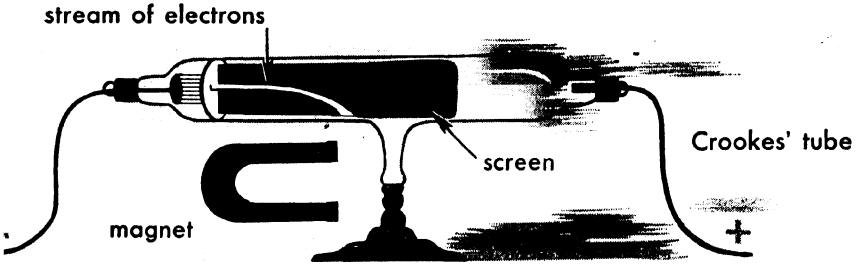
Franklin's electric theory was not altogether correct, for he believed that if a body has too much electricity it is charged positively (+); if it has not enough, it is charged negatively (−); and if it has just enough, it is neutral. Even though his ideas were not altogether correct, his reasoning and his terminology for electricity were more modern than those of any other eighteenth-century scientist. So great was the creative imagination of Franklin that he came very close to arriving at the modern concept of the electric nature of matter, a point of view reached only after some 150 years of further experimentation.

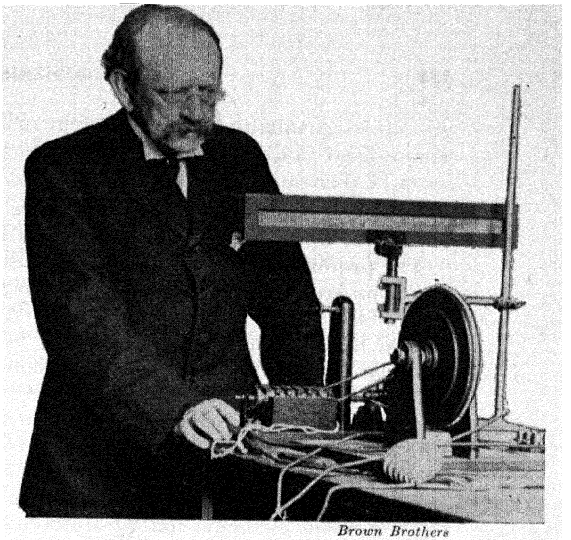
Today we refer to the charge which was produced on the hard-rubber rod mentioned above as negative (−), and that produced on the glass rod as *positive* (+).

The electron is discovered. Almost a century and a half after Franklin, William Crookes, an Englishman, studied the effect of passing a current of high-voltage electricity through a glass tube from which nearly all the air had been pumped. He noticed that a beam of light issued from the negative plate, or *cathode,* of the tube. When a magnet was brought near the tube, the beam would bend. Since ordinary light is not affected by a magnet, the beam showed a property of matter rather than of light.

Another Englishman, J. J. Thomson, undertook to explain the strange behavior of these *cathode rays.* In 1897, after 20 years of brilliant research, he announced his results. He said that cathode rays are composed of particles of negative electricity, torn away from the atoms of the air in the tube. To these particles, Thomson gave the name *electrons.* The cathode ray was bent because the negative electrons would be attracted by the positive pole and repelled by the negative pole of a magnet.

Fig. 27. Crookes' tube. Notice how the positive pole of the magnet deflects the cathode ray.





Brown Brothers

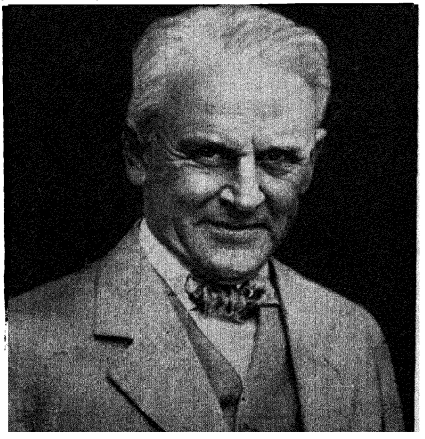
Joseph John Thomson was born at Manchester in 1856. He followed Rayleigh as head of the Cavendish Laboratory of Experimental Physics at Cambridge University.

The discovery of the electron also explained the phenomenon of static electricity. When one object is rubbed with another, electrons are transferred. Thus, when glass is rubbed with silk, the glass loses electrons to the silk and is left with a positive charge; amber, when rubbed with fur, takes electrons from the fur and becomes negatively charged.

Thomson's discovery of the electron completely upset the theory that the atom is the smallest unit of matter, since electrons were found in all atoms. It also proved that the idea of an indivisible atom was inaccurate.

Subsequently, Robert A. Millikan, an eminent American scientist, succeeded in computing the mass of a single electron. He found it to be about $\frac{1}{1837}$ of the mass of one hydrogen atom. (*Mass* is the amount of matter that a substance contains. It does not vary, as does

Brown Brothers



Robert Andrews Millikan (1868–1953) won the Nobel physics prize in 1923 for his work in isolating and weighing the electron.

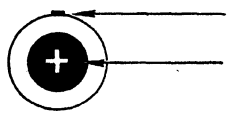


Fig. 28. The hydrogen atom

weight, with the gravitational pull of the earth. However, weight is dependent upon the amount of matter a substance contains.)

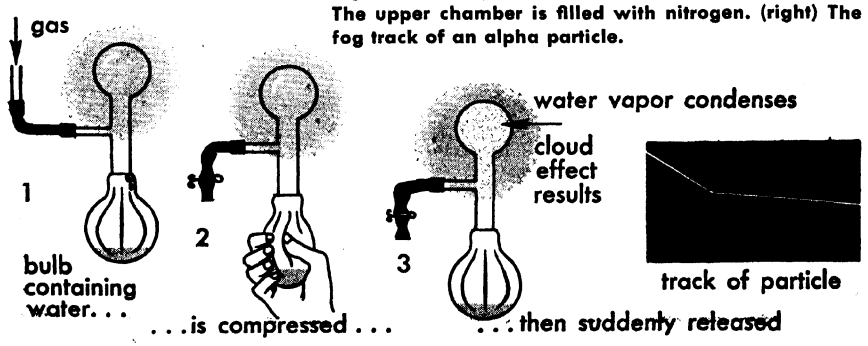
The proton is discovered. After Thomson discovered the electron, one of his students, Ernest Rutherford, began to ponder over the nature of the rest of the atom. An atom itself is electrically neutral. Surely, he thought, in the *electrically neutral* atom there must be some *positive* electricity to counterbalance the *negative* electron.

After much research, which began in 1911, Rutherford determined that all atoms contain one or more particles of positive electricity which he named the *proton*. The proton, which is a positively charged atom of hydrogen, is 1837 times as heavy as the electron.

The structure of the atom according to the electron theory. Atoms of the various elements contain different numbers of electrons and protons. In general, however, the arrangement of these particles follows a similar pattern in all elements. Rutherford gave us the first picture of the structure of the atom. It resembles our own solar system with its sun and revolving planets. The "sun" of the atom is called the *nucleus*. It is composed partly of protons around which, at a relatively great distance, revolve *planetary electrons*. A diagram of the simplest of the atoms, that of hydrogen, is shown above.

It was Rutherford who found that electrons and protons were not evenly distributed in the atom but that the heavy protons were all located in the center. He shot helium atoms (alpha particles) through a cluster of nitrogen atoms and photographed the results by means of a cloud chamber and special camera devised by C. T. R. Wilson, another English scientist. He found that only in an extremely few cases the path or *fog track* of the helium bullet was not straight, but was thrown sharply off its course. On the basis of the volume of the nitrogen atom and the ratio of straight fog tracks to bent ones, he calculated that the protons must all be con-

Fig. 29. (left) Apparatus for producing the cloud effect. The upper chamber is filled with nitrogen. (right) The fog track of an alpha particle.



centrated in the tiny nucleus of the atom. The diameter of the nucleus is about $\frac{1}{100,000}$ that of the whole atom. Helium bullets passing through the rest of the atom met no solid, positively charged protons.

Size of the atom. Most of us are baffled in attempting to imagine the size of the particles within the atom and the distances between them. The diameter of a hydrogen atom is about $\frac{1}{40,000,000}$ inch. If an atom were magnified about 30 trillion times, its diameter would be about 10 miles. At the center would be the nucleus, about the size of a tennis ball. The electrons, each about the size of a hazelnut, would revolve about the nucleus in orbits in somewhat the same way as the planets of our solar system revolve about the sun.

This description is actually an oversimplification of the structure of the atom. However, it tells us an important fact. Atoms, which compose every element and compound, are largely empty space!

The neutron: A notable scientific prediction. All of the protons of an atom are located in the nucleus. However, not all of the electrons of an atom are planetary; some electrons, too, are found within the nucleus. But how can negatively charged electrons and positively charged protons exist side by side in the nucleus? To explain this, Dr. W. D. Harkins predicted the existence of a new particle. An electron within the nucleus, he said, does not exist as a separate particle, but is combined with a proton forming an electrically neutral particle which he named the *neutron*. Since the weight of the electron is extremely slight, it may be disregarded in figuring the weight of the neutron. The neutron has been found to have about the same mass as the proton.

In 1920, the existence of the neutron was theoretically established by W. D. Harkins of the University of Chicago. Twelve years later, it was actually discovered by James Chadwick, working in Rutherford's laboratory. The ultimate verification of Harkins' work by Chadwick demonstrates the value of pure theory and creative imagination in science. For his part in the discovery, Chadwick was knighted in 1944.

The electron and proton are so close together in the neutron that the volume of the neutron is millions of times smaller than that of any atom. It has, therefore, an extremely high density. This fact has been used to explain the extremely high densities of certain stars. Since the neutron is electrically neutral, electric forces do not repel it. Therefore, the neutron has great penetrating powers.

We may say that, in general, *all matter is composed of three kinds of fundamental electric particles: electrons, protons, and neutrons.*

Scientists have discovered other electric particles within the atom, as shown in Table 8, but the three mentioned here are considered the most important.

How the structure of an atom may be represented graphically. The atom of each element contains a particular number of electrons, protons, and neutrons different from the number in the atom of every other element. Two American scientists, Lewis and Langmuir, developed a theory of the arrangement of planetary electrons which explains why each element has different chemical properties.

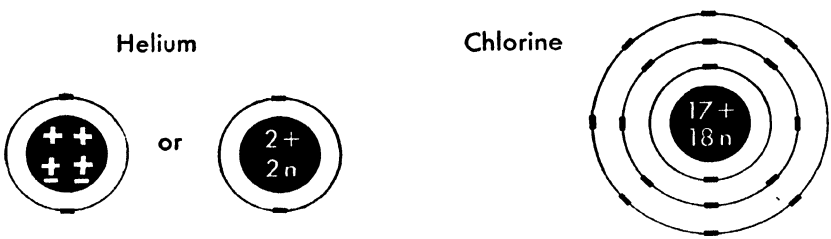
According to this theory, the electrons outside the nucleus (planetary electrons) arrange themselves in successive rings, or shells. The first ring is complete when it contains 2 electrons; the second ring is complete when it contains 8 electrons; the third ring is complete when it contains 18 electrons; the fourth, when it contains either 18 or 32 electrons. *However, the outermost ring never contains more than eight electrons.* According to Lewis and Langmuir, an atom with 30 planetary electrons will have its first ring complete with 2 electrons, second ring complete with 8 electrons, third ring complete with 18 electrons, and fourth ring incomplete with 2 electrons. What is the electron structure of an atom with 48 planetary electrons?

The number of protons in the nucleus of the atom is equal to the number of planetary electrons. This equality keeps the atom electrically neutral. Thus, an atom with 30 planetary electrons will have 30 protons in its nucleus.

Of all the elements, hydrogen has the simplest atom. Its nucleus consists of one proton. Revolving about this nucleus is one planetary electron. The nucleus of the helium atom contains two protons (2+) and two neutrons (2n); two planetary electrons (2—) revolve about it. Fig. 30 shows how we may graphically represent the helium atom and also the chlorine atom (atomic number 17).

The periodic table of Mendeleyeff. In 1869, Mendeleyeff (men'-de-lā'ef), a Russian chemist, published a table of the elements arranged in order according to their increasing atomic weights. He noticed, that when arranged in this manner, the elements fell into

Fig. 30. Diagrams of the helium and chlorine atoms.



GROUP ▶ / SERIES ▼	ZERO	I	II	III	IV	V	VI	VII
2	He	Li	Be	B	C	N	O	F
3	Ne	Na	Mg	Al	Si	P	S	Cl
4	A	K	Ca	Sc	Ti	V	Se	Br

eight distinct groups. Within each group, the elements have similar physical and chemical properties.

Let us examine part of this table carefully. Note that hydrogen is omitted, and that the table begins with helium, the element with the next heaviest atomic weight. Lithium (Li), with an atomic weight of 6.940 follows, and so on through fluorine (19.0). These eight dissimilar elements comprise one series or *period.*

The element following fluorine in order of atomic weight is neon (Ne). It has chemical properties similar to those of helium (He) and falls directly below it in the table. Directly below helium is argon (A) with similar properties. Thus helium, neon, argon, and certain succeeding elements comprise Group Zero. This group of elements is known as the family of *inert gases* (see Chapter 7). The elements in Group VII are known as the *halogen family* (see Chapter 10). The other groups are also made up of closely related elements.

Moseley discovers the law of atomic numbers. Prior to 1912, the numerical position of an element in a table of atomic weight was called the *atomic number* of the element. It occurred to Rutherford that this number might also represent the number of *protons* in the nucleus of the atom. One of his students, Henry G. J. Moseley, undertook to find out whether Rutherford's idea was valid.

Moseley's experiments bore out Rutherford's theory. The atom of each element was found to contain a number of protons in its nucleus corresponding to the element's numerical position in the periodic table of atomic weights. The hydrogen atom, which appears first in the periodic table, has only one proton in the nucleus of its atom; uranium, which appears in the ninety-second position in the periodic table, has 92 protons in the nucleus of each atom. Moseley showed that *the atomic number of any element is equal to the number of free protons in the nucleus of its atom.* This is known as the law of atomic numbers. Since the number of free protons in the nucleus is equal to the number of electrons around the nucleus, the atomic number of an element is also equal to the number of planetary electrons.

For the first 17 elements in the table of atomic numbers, it is helpful to remember that the atomic number is equal to half the atomic

weight (disregarding fractions). Thus the atomic number of chlorine (atomic weight 35.457) is 17.

The periodic table of atomic numbers. Mendeleyeff's periodic table based upon atomic weights served science for 50 years. In 1912, however, it was displaced by the new periodic table developed by Moseley from his law of atomic numbers.

Moseley's table is more fundamental than Mendeleyeff's and easily accounts for some of the discrepancies in the latter. For example, the element argon has an atomic weight of 39.944 and the element potassium an atomic weight of 39.10. Argon should, therefore, follow potassium in the table based on atomic weights. But the properties of argon put it in the group of inert elements, preceding potassium. Moseley's researches, which showed that the atomic number of argon is 18 and that of potassium is 19, eliminated this problem. When Moseley developed his table, all of the elements had not been discovered. Therefore the atomic numbers did not run entirely consecutively from one to 92. Since then the missing elements have been discovered, as you may see from the modern periodic table below.

A new definition of atomic weight. As we have learned, the electron, for most purposes, may be considered weightless, and the proton and neutron may be considered equal in mass. Thus, the most abundant hydrogen atom, which contains a single proton and no neutrons, may be considered equal to one proton in weight; the helium atom, which contains two protons and two neutrons, weighs four times as much as the hydrogen atom. We may say that the *atomic weight* of hydrogen is one and the *atomic weight* of helium is four. Thus, according to the electron theory, *the atomic weight for each element may be defined as the sum of the protons and neutrons in the nucleus of an atom* of that element. Look at the diagrams of various atoms in Fig. 32. What is the atomic number of each? the atomic weight?

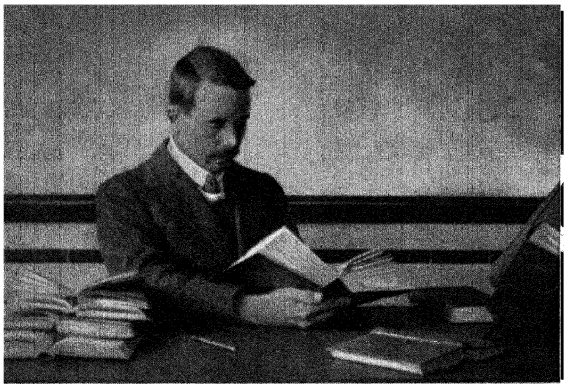
How the electron theory explains isotopes. In 1815, William Prout, a London physician, announced the theory that all the chemical elements are made up of groups of hydrogen atoms only. Prout's theory was not taken seriously for 100 years until Moseley's work on atomic numbers made Prout's conclusion more plausible.

Since the nucleus of an atom of any element is composed of only

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	
SERIES	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII	
1 ▶		1 Hydrogen 1.0080								
2 ▶	2 Helium 4.003	3 Lithium 6.940	4 Beryllium 9.013	5 Boron 10.82	6 Carbon 12.01	7 Nitrogen 14.008	8 Oxygen 16.00	9 Fluorine 19.000		
3 ▶	10 Neon 20.183	11 Sodium 22.997	12 Magnesium 24.32	13 Aluminum 26.98	14 Silicon 28.09	15 Phosphorus 30.975	16 Sulfur 32.066	17 Chlorine 35.457		
4 ▶	18 Argon 39.944	19 Potassium 39.1	20 Calcium 40.08	21 Scandium 44.96	22 Titanium 47.90	23 Vanadium 50.95	24 Chromium 52.01	25 Manganese 54.93	26 Iron 55.85	27 Cobalt 58.94	28 Nickel 58.69
		29 Copper 63.54	30 Zinc 65.38	31 Gallium 69.72	32 Germanium 72.60	33 Arsenic 74.91	34 Selenium 78.96	35 Bromine 79.916			
5 ▶	36 Krypton 83.8	37 Rubidium 85.48	38 Strontium 87.63	39 Yttrium 88.92	40 Zirconium 91.22	41 Niobium 92.91	42 Molybdenum 95.95	43 Technetium 99	44 Ruthenium 101.7	45 Rhodium 102.91	46 Palladium 106.7
		47 Silver 107.880	48 Cadmium 112.41	49 Indium 114.76	50 Tin 118.70	51 Antimony 121.76	52 Tellurium 127.61	53 Iodine 126.91			
6 ▶	54 Xenon 131.3	55 Cesium 132.91	56 Barium 137.36	57 Lanthanum* 138.92	72 Hafnium 178.6	73 Tantalum 180.88	74 Wolfram 183.92	75 Rhenium 186.31	76 Osmium 190.2	77 Iridium 193.1	78 Platinum 195.23
		79 Gold 197.2	80 Mercury 200.61	81 Thallium 204.39	82 Lead 207.21	83 Bismuth 209.00	84 Polonium 210	85 Astatine 211			
7 ▶	86 Radon 222	87 Francium 223	88 Radium 226.05	89 Actinium 227?	90 Thorium 232.12	91 Protoactinium 231	92 Uranium** 238.07				

*Following lanthanum are 14 elements known as the rare earth elements (at. no. 58-71).
**Following uranium are eight newly created elements of the actinide series (at. no. 93-100).

TABLE 6. **PERIODIC TABLE OF THE ELEMENTS**



Henry G. J. Moseley (1887–1915), a pupil of Ernest Rutherford, discovered the law of atomic numbers in 1912. His brilliant career was ended by his death at 27 during World War I.

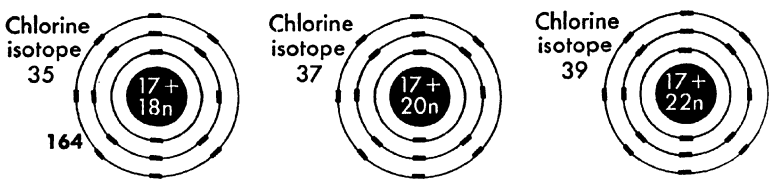
neutrons and protons, and since the weight of each of these units is really the weight of the hydrogen atom, it may have occurred to you that the atomic weights of all the elements ought to be whole numbers. But the fact that many atomic weights, for example, chlorine (35.457), are not whole numbers could not be brought into harmony with this idea.

In 1913, Theodore W. Richards found two different kinds of lead with atomic weights of 206 and 207, respectively, and, in the same year, two kinds of neon with different atomic weights were reported also. The name *isotopes* was given to *atoms of the same element having the same chemical properties but different atomic weights.* Discoveries of isotopes of many other elements soon followed, one of which (tin) is now known to have as many as 10 stable isotopes and, hence, 10 different atomic weights.

The discovery of isotopes removed the obstacles to the acceptance of Prout's idea. For elements, as we know them, are really mixtures of isotopes having different atomic weights, each of which is a whole number. Thus ordinary chlorine gas is really made up of some atoms with an atomic weight of 35, other atoms of atomic weight 37, and still others of atomic weight 39. Its accepted atomic weight, 35.457, is the average of the atomic weights of the three different weights of chlorine atoms in any sample of the gas. Here was another startling discovery which helped to destroy Dalton's idea of an atom whose atomic weight never changed.

The electron theory explains isotopes as caused by a different number of neutrons in each kind of atom. Thus, isotopes of chlorine with atomic weights of 35, 37, and 39 behave alike chemically because they have the same arrangement of planetary electrons. They differ

Fig. 31. Diagrams of the isotopes of chlorine.



in weight because of a difference in the number of neutrons in their nuclei. We must, then, redefine the term *element. A substance of which all atoms have the same atomic number is an element.*

How the electron theory explains valence. From the diagram of the chlorine atom (Fig. 31), you can see that its outermost ring contains 7 electrons. One more electron is needed to make the 8 electrons needed to complete this ring.

An atom whose outermost ring is nearly complete has a tendency to *borrow* enough electrons to complete this ring. An atom whose outermost ring has few electrons tends to *lose* electrons. *The number of electrons gained or lost by an atom of an element is the valence of that element.* Since the chlorine atom needs to borrow only 1 electron to complete its outer ring, its valence is 1. In borrowing this electron it becomes negatively charged and, as a result, the valence of chlorine is *negative.* Hence, the valence of chlorine is -1.

An atom that lends electrons becomes positively charged. Hence, elements whose atoms lend electrons have *positive* valences. Thus, the sodium atom with an atomic number of 11 (roughly half of 22.997) may be pictured as shown in Fig. 32. As you see, the outermost ring contains 1 electron which the atom may lend. Hence the valence of sodium is $+1$.

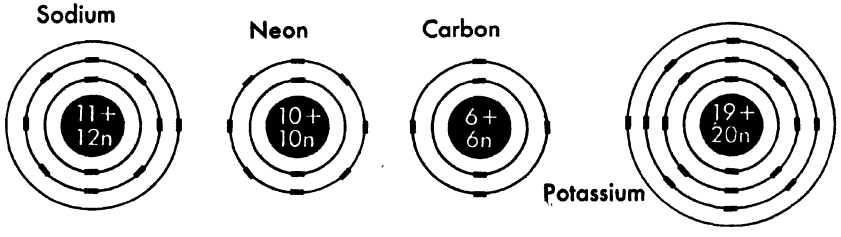
An atom whose outer ring is complete will neither lend nor borrow electrons. Elements whose atoms are of this type have a valence of 0. The atom of neon is shown in Fig. 32.

Electrons in the outermost ring of an atom, which may be either borrowed or lent, are called *valence electrons.*

How the electron theory explains metals and nonmetals. *A metal is a lender of electrons.* That is, the outermost ring of an atom of a metal has less than four, or half the number (eight) required to complete it. When such an atom lends electrons, it necessarily becomes positively charged. The valence of metals, therefore, is considered positive.

The atom of a *nonmetal is a borrower of electrons.* That is, its outermost ring has more than four, or half the number of electrons (eight) required to complete it. By borrowing electrons, such an atom becomes negatively charged. The valence of nonmetals is, therefore, negative.

Fig. 32. Diagrams of various atoms.



If the outermost ring of an atom of an element has just half the number of electrons required to complete it, it may either borrow or lend electrons. Such an element is said to be *amphoteric.* A common example of an amphoteric element is carbon (atomic weight 12), whose diagram appears in Fig. 32.

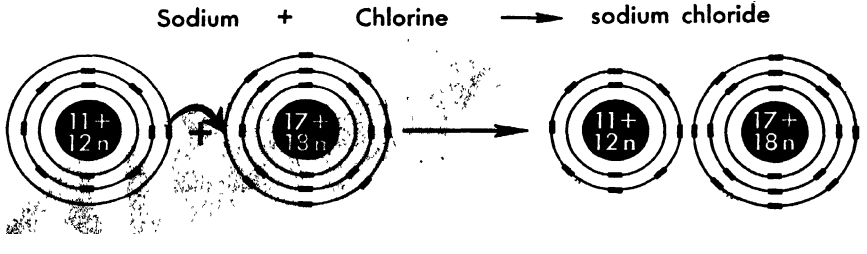
How the electron theory explains electric currents. According to modern theory, *an electric current is a flow of electrons.* Atoms of metals, such as copper, silver, and gold, are good conductors of electricity, because some of their electrons are held loosely, and can move freely through the solid. In general, nonmetals are poor conductors, because their electrons are not held as loosely as those of metals.

How the electron theory explains chemical activity. An atom tends to complete its outer ring of electrons. If an element such as neon or argon already has its outer ring complete, that element is inert. That is, its atom will not lend or borrow electrons, and hence the element is completely inactive chemically. *In general, the smaller the number of electrons an atom must either borrow or lend to complete its outer ring of electrons, the greater is the chemical activity of that atom.*

An atom, then, with either 1 or 7 electrons in its outermost ring is extremely active. Such an atom is fluorine, whose atomic weight is 19, and atomic number is 9. It has 7 electrons in its second ring and will borrow 1 more electron. Potassium, whose atomic weight is 39, has only 1 electron in its fourth ring, and hence can lend only 1 electron. Atoms such as those of oxygen and magnesium have 2 electrons to borrow or lend and are quite active. Atoms of nitrogen and aluminum have 3 electrons to borrow or lend and are not very active. *Generally, the farther away the outer ring of an atom is from the nucleus, the less is the attraction of the nucleus for its electrons.*

This helps explain the chemical behavior of metals. For example, potassium is more active than sodium since the electron in its *fourth* ring can be lost more easily than the electron in the *third* ring of sodium. *Conversely, the closer the outer ring of an atom is to the nucleus, the stronger is the attraction of the nucleus for its electrons.* This fact helps explain the chemical behavior of nonmetals. Fluorine is more active than iodine since its *second* ring has

Fig. 33. Chemical union of sodium and chlorine according to the electron theory.



a greater attraction for the electrons of other atoms than does the *fifth* ring of iodine. Both of these rules should be considered rough guides. Many exceptions occur since the whole problem of chemical activity is quite complex.

PRACTICE WORK ON THE ELECTRON STRUCTURE OF ATOMS

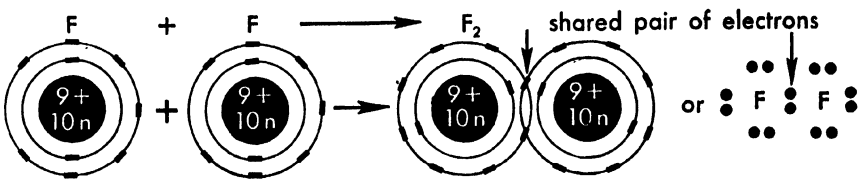
1. The at. wt. of sulfur is 32. Make a picture of its atom according to the electron theory, and explain its valence and chemical activity.
2. With the aid of a diagram, show why helium, at. wt. 4, is inert.
3. With the aid of diagrams, show why lithium, sodium, and potassium belong to the same family of elements.
4. What are the valence and chemical activity of an element whose outer ring contains 4 electrons?
5. With a diagram, explain the valence of the (OH) radical.

How the electron theory explains chemical union and electrovalence. Chemical activity is the tendency of atoms to complete their outer rings and form stable compounds. *Chemical union is, therefore, the shifting or sharing of electrons in the outer electron rings until a stable condition is reached.*

A metallic atom with a valence of +1 exhibits a strong attraction for a nonmetallic atom whose outer ring needs 1 electron to complete it. For example, the union of sodium, a very active metal with a valence of +1, with chlorine, a very active nonmetal with a valence of −1, may be represented thus:

The extra electron on the outer ring of the sodium atom shifts over to the vacant space in the almost complete outer ring of the chlorine atom. Now the two outer rings are both complete and the resulting compound, sodium chloride, is very stable. Its water solution conducts electricity. *Compounds formed by the shifting of single electrons are polar or ionic compounds.* Their valence is called *electrovalence.*

Fig. 34. Formation of a molecule of fluorine according to the electron theory.



How the electron theory explains covalent compounds. In many chemical reactions, there is no actual *shifting* of single electrons but rather an *equal sharing* of a pair or pairs of electrons. The compounds formed are *nonpolar compounds* and the valence is called *covalence.* This kind of combination is generally very strong and the molecules so formed hold together well. Nonpolar compounds are stable and generally do not conduct electricity. Many organic compounds, such as alcohol, glycerin, and sugar, are nonpolar.

The fluorine molecule (see Fig. 34) illustrates the sharing of a pair of electrons. There is neither a gain nor a loss of electrons — simply a sharing. Molecules of other gases that consist of 2 atoms, such as oxygen and chlorine, exhibit this same sharing of electrons. Polar and nonpolar compounds are discussed more fully on page 238.

How the electron theory explains oxidation and reduction. In the equation $CuO + H_2 \rightarrow Cu + H_2O$, copper oxide is reduced to copper and hydrogen is oxidized to water. The valence of Cu has changed from plus two (in CuO) to zero in free copper, and the copper has gained 2 electrons ($Cu^{++} + 2\epsilon \rightarrow Cu^0$). The hydrogen has lost an electron and changed to H^+ in $H_2{}^+O^{--}$ ($H^0 - \epsilon \rightarrow H^+$).

Oxidation has been defined thus far as the union of a substance with oxygen. Reduction, similarly, has been defined as the removal of oxygen from a compound. From the viewpoint of the electron theory these terms take on much broader meanings. *A loss of electrons resulting in an increase in the valence of an element is called oxidation. A gain of electrons resulting in a decrease in the valence of an element is called reduction.*

Oxidation and reduction in this broader sense need not involve either oxygen or hydrogen. Thus, in the replacement of the iodine in potassium iodide by chlorine, as explained in the preceding chapter, we have an oxidation-reduction reaction. According to the electron theory, this reaction is:

$$K^+I^- + Cl^0 \rightarrow K^+Cl^- + I^0$$

The iodine in KI has lost an electron and changed to free iodine, I^0. It has been oxidized by chlorine which has gained an electron and changed from free chlorine to the negative chloride *ion,* Cl^- (see page 232).

How the electron theory aids in balancing equations. We may see from this oxidation-reduction equation how each atom of iodine lost an electron and was oxidized and how each free chlorine atom gained an electron, forming a chloride ion with a negative charge. This was a relatively simple reaction. But how is a more complex oxidation-

reduction equation balanced and how does our understanding of the electron theory help us to find correct coefficients to use in balancing the equation? Let us consider some examples:

EXAMPLE A: It is desired to reduce ferric chloride, $FeCl_3$, to ferrous chloride, $FeCl_2$, by the use of the evil-smelling gas, H_2S – a common reducing agent. In the reaction, free sulfur and hydrochloric acid are formed also.

1) Write the unbalanced equation for the reaction.

$$FeCl_3 + H_2S \rightarrow FeCl_2 + S + HCl$$

2) Select the atoms which, according to the electron theory, are either reduced or oxidized, that is, either gain or lose electrons. Place the valences involved at the upper right of the symbol of each atom.

$$Fe^{+++}Cl_3 + H_2S^{--} \rightarrow Fe^{++}Cl_2 + S^0 + HCl$$

3) By inspection, we see that each atom of iron gains one electron and is reduced; each atom of sulfur loses two electrons and is oxidized. The number of electrons involved in the oxidation of H_2S is twice as great as the number of electrons involved in the reduction of one molecule of $FeCl_3$. Therefore, twice as many molecules of $FeCl_3$ must have been reduced. Indicate this by writing the coefficient *2* before $FeCl_3$ in the equation. Then balance the equation by the methods you have already learned.

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + S + 2HCl$$

In actual practice, chemists usually consider only the changes in valence of the atoms involved rather than the shifting or sharing of electrons. The sum of the changes in valence on both sides of the arrow must be equal. Consequently, this method of balancing equations is known as the *valence-change method.*

EXAMPLE B: Using the valence-change method, write the equation for the reaction between the oxidizing agent, potassium permanganate, and hydrochloric acid. The products are potassium chloride, manganese chloride, water, and free chlorine.

1) Write the unbalanced equation, omitting the subscript from the free chlorine. It is not necessary to indicate the valence of those atoms which retain the same valence throughout the reaction.

$$KMn^{+++++++}O_4 + HCl^- \rightarrow KCl + Mn^{++}Cl_2 + H_2O + Cl^0$$

2) Note that the following changes occur:

a) Each atom of manganese in $KMnO_4$ gains five electrons in combining with chlorine to form $MnCl_2$; therefore the valence loss of the manganese is five.

(b) Each atom of chlorine loses one electron in becoming free chlorine; therefore the valence gain of each atom of liberated chlorine is one.

3) The five valences lost by the manganese must be balanced by the valence gained by the chlorine since no other element changes valence in the reaction. To do this, we must show that for each molecule of $KMnO_4$ used, five atoms of Cl are liberated. Therefore, write the coefficient *5* before the free Cl:

$$KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + 5Cl$$

4) As we know, free chlorine exists as a molecule composed of two atoms, therefore we add the subscript, *2*, to Cl. In order to keep the valence changes in balance, we consider that two molecules of $KMnO_4$ are used in liberating five molecules of Cl_2. Therefore, write the coefficient *2* before $KMnO_4$.

$$2KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + 5Cl_2 \uparrow$$

5) Complete the balancing of the equation in the usual manner. Check your work carefully.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \uparrow$$

From this discussion, we can formulate the following method of balancing oxidation-reduction equations:

1) Write the unbalanced equation.

2) Write the changes in valence at the upper right of the symbols of the atoms that are oxidized and those that are reduced.

3) Find the valence gains and losses and decide on the coefficients that will make them equal. Remember that molecules composed of two atoms may be involved and adjust the coefficients accordingly.

4) Complete the balancing of the equation by the usual method.

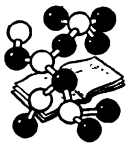
Changing theories and the spirit of modern science. In 1924, the electron theory, backed by a mass of experimental evidence, was quite generally accepted. In that year, Prince de Broglie (dẽ brô'y') suggested that the electron is not merely a particle of electricity, as the electron theory explained, but like light, is composed of, possesses, or perhaps is attended by, a group of waves.

By 1927, two Americans, Davisson and Germer, proved de Broglie's theory experimentally, showing that both electrons and protons possess a property of light (a wave phenomenon). In 1929, de Broglie was honored with the Nobel prize in physics for his theory.

The theory that matter possesses *wave properties* created an upheaval in the existing theories. However, we still find it convenient to regard the electron, proton, and neutron as tiny individual particles. If new facts show we are wrong, we shall scrap this concept.

In every phase of science, this practice is followed. Old ideas are retained as long as they are useful. They may be altered somewhat to fit newly-discovered facts. However, if enough new data are accumulated to prove them incorrect, the old theories are abandoned. It is the belief of scientists that tradition should never be allowed to stand in the way of greater enlightenment.

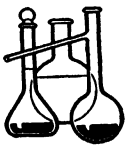
Albert Einstein, one of the most eminent of living scientists, when he was suddenly confronted with new facts which could not fit his own theories, expressed the spirit of science thus: "The new facts have smashed my old ideas like a hammer blow!" And he went on to change some of his most cherished theories.



YOU WILL ENJOY READING

Jaffe, Bernard. *Crucibles: The Story of Chemistry,* pp. 289–311. Simon and Schuster, New York, 1948. A sketch of Henry Moseley, whose lifework was done in 4 short years. Before the world knew this genius, he died.

Moulton, Forest R., and Schifferes, Justus J., Ed. *The Autobiography of Science,* pp. 502–509. Doubleday Doran & Co., New York, 1945. Contains the original papers dealing with the origin of the electron theory.



USEFUL IDEAS DEVELOPED

1. Electric charges caused by rubbing or friction are called static electricity.

2. Electrons are tiny particles of negative electricity. A cathode ray is a stream of electrons. Our knowledge of electrons is the result of the work of William Crookes, J. J. Thomson, Robert A. Millikan, and others.

3. Protons are particles of positive electricity. A proton is 1837 times heavier than an electron. It was discovered and named by Ernest Rutherford.

4. A neutron is an electrically neutral particle composed of one electron and one proton. Its mass is about the same as that of a proton, or of the atom of the lightest hydrogen isotope.

5. All atoms are composed of electrons, protons, and neutrons with the exception of the atom of the lightest hydrogen isotope which is composed of one electron and one proton. Protons and neutrons are located in the nucleus of the atom. Electrons revolve about the nucleus in orbits. The relative distance between the nucleus and the planetary electrons is so great that we may say the atoms of all elements are largely empty space.

6. A fixed number of electrons is required to complete each electronic orbit of the atom. The first ring is complete when it contains 2 electrons; the second, when it contains 8; the third, when it contains 18; the fourth, when it contains 32. The outermost ring never contains more than 8 electrons.

7. The atomic number of any element is the number of free protons in the nucleus of its atom. According to the law of atomic numbers, the elements can be arranged in a periodic table in the order of their increasing atomic numbers.

8. The atomic weight of any element is the sum of the protons and neutrons in the nucleus of one of its atoms.

9. Isotopes are different forms of the same element. They possess the same chemical properties, but have slightly different physical properties. Isotopes of an element all have the same atomic number, but different atomic weights.

10. The valence of an element is the number of electrons that its atom must borrow or lend to complete its outermost ring. Electrons in the outermost ring of an atom which may be borrowed or lent are valence electrons.

11. An element is metallic if the outer ring of its atom contains less than half the number of electrons necessary to complete the ring. In other words, metals are lenders of electrons.

12. An element is nonmetallic if the outer ring of its atom contains more than half the number of electrons necessary to complete the ring. In other words, nonmetals are borrowers of electrons.

13. An element is amphoteric if the outer ring of its atom contains exactly half the number of electrons necessary to complete this outer ring.

14. An electric current is a flow of electrons.

15. Chemical activity depends upon the number of electrons in the outermost ring of the atom of an element. When the outermost ring is complete, the element is inert; if the outermost ring lends or borrows one electron, the element is

very active; if the outermost ring lends or borrows three electrons, the element is not very active.

16. Chemical union is the shifting or sharing of the electrons in the outer rings until a stable condition is reached.

17. Electrovalent compounds are those formed by the shifting of single electrons; covalent compounds are those formed by the sharing of a pair or pairs of electrons.

18. Oxidation, a loss of electrons, increases the valence of an element. Reduction, a gain of electrons, decreases the valence of an element.

19. New theories are constantly being advanced about the nature of matter. Recently it has been suggested that both the proton and electron possess wave properties. It is necessary for scientists to be ready to give up theories when facts show that newer theories are more nearly accurate.



USING WHAT YOU HAVE LEARNED

Group A

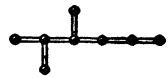
1. (a) How may static electricity be produced? (b) How did the discovery of electrons explain this phenomenon?

2. (a) Who discovered the electron? (b) How did his discovery explain the behavior of cathode rays? (c) Who determined the mass of the electron? (d) What were his findings?

3. (a) Who discovered the proton? (b) What principle of electricity led him to his discovery? (c) Do the protons of different elements differ?

4. (a) What is the neutron? (b) What scientists took part in its discovery? (c) Why is the neutron considered approximately equal in mass to the proton?

5. (a) Describe the general arrangement of protons, electrons, and neutrons in an electrically neutral atom. (b) Describe the atom in terms of the solar system.



6. Explain how elements differ according to the electron theory.

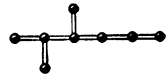
7. (a) Who developed the first periodic table of atomic weights? (b) What was learned from arranging the elements in such a table?

8. (a) What relationship between atomic number and protons was demonstrated by Moseley? (b) Why is Moseley's periodic table more fundamental than Mendeleyeff's?

9. (a) For the first 17 elements, what is the general relationship between atomic number and atomic weight? (b) Illustrate your answer.

10. (a) Define atomic weight in terms of the electron theory. (b) Why do most elements have atomic weights which are not whole numbers?

11. (a) What is an isotope? (b) Explain why all isotopes of an element have the same chemical properties.



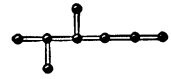
12. (a) How does the electron theory explain valence? (b) How does it explain the behavior of metals? (c) of nonmetals? (d) of amphoteric elements?

13. Explain the relationship between the number of electrons in the outer ring of an atom and the chemical activity of that element.

14. (a) Make a diagram of the structure of the element whose atomic number is 20. (b) Describe some of the element's chemical properties.

15. Phosphorus (P) has an atomic weight of 30.98. (a) Diagram the structure of its atom. (b) Describe its chemical nature.

16. An atom has a nucleus containing 17 protons and 18 neutrons. (a) Make a structural diagram of the atom. (b) Describe its chemical properties.

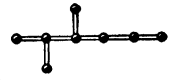


17. The atomic weight of beryllium (Be) is 9.02. (a) What are the atomic number, valence, and chemical properties of beryllium? (b) Is it a metal or nonmetal?

18. The atomic weight of curium, one of the newly-discovered elements, is 242; its atomic number is 96. How many neutrons are in the nucleus of one of its atoms?

19. Make a diagram of (a) the oxygen atom and (b) the sulfur atom. (c) Explain, in terms of the electron theory, why they resemble one another chemically.

20. (a) Draw a diagram of the structure of a molecule of potassium bromide, KBr. (b) Using your knowledge of the electron theory, explain why the two atoms unite.



21. What is the difference between electrovalence and covalence?

22. How does the electron theory explain why two atoms of hydrogen unite with one atom of oxygen to form one molecule of water?

23. How does the electron theory explain the fact that certain elements are more active chemically than others?

24. In terms of the electron theory, explain why some compounds are stable and others unstable.

25. Explain oxidation and reduction in terms of the electron theory. Use the equation for the reducing action of H_2 on CuO to make your answer clearer.

Group B

26. Study the theories Benjamin Franklin held regarding the nature of electricity. Compare his views with the modern theory.

27. (a) What is a cloud chamber? (b) For what purpose is it used? (c) What are alpha particles? (d) fog tracks?

28. What evidence is there that protons are always found inside the nucleus of an atom?

29. Using the valence-change method, balance the following equations:

a) $HCl + MnO_2 \rightarrow MnCl_2 + H_2O + Cl_2 \uparrow$
b) $Cl_2 + H_2O \rightarrow 2HCl + O \uparrow$
c) $KClO_3 \rightarrow KCl + O_2 \uparrow$
d) $S + HNO_3 \rightarrow H_2SO_4 + NO \uparrow$

30. Why does carbon have the 2 valences, $+2$ and $+4$?

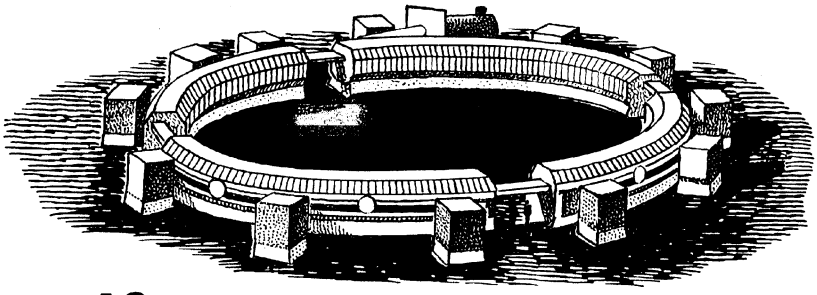
31. Explain why the valence of a free element must be zero.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Harkins predicted the discovery of the neutron, and Mendeleyeff predicted the discovery of several elements. Both predictions were verified. Such incidents in the history of science are not as rare as in other fields such as economics and politics. Give reasons for this.

2. Construct a model of the sodium atom based on the electron theory. You may use wire for the orbits, a small ball for the nucleus, and copper rods for the electrons.



12. NUCLEAR ENERGY AT LAST!

The United States knows that peaceful power from atomic energy is no dream of the future. That capability, already proved, is here now — today. I propose an atomic energy agency under the United Nations to apply atomic energy to the needs of agriculture, medicine, and other peaceful activities . . . to provide abundant electrical energy in the power-starved areas of the world. Dwight D. Eisenhower, December 8, 1953

The dream of harnessing the energy of the atom. The atomic bomb dropped on Japan on August 6, 1945, was one of those incredible pinnacles toward which fate drives unsuspecting man. Thousands of scientists who had studied the atom and discovered the electron, proton, and neutron had little idea of the genii they were uncorking. Chiefly, they were men and women trying to learn more about the nature of matter, each concerned with his own particular problem.

A few scientists, it is true, saw the possibility of someday learning enough about the atom to enable man to release the tremendous forces locked within it. If it could be done, the energy locked within a single lump of coal would be enough to drive a huge ocean liner around the world. As scientists, they hoped for an achievement which they believed to be even greater than the discovery of electricity. They dreamed of opening a door to an age of limitless power and thus lifting the standards of living of all the peoples of the world.

When the news of triumph finally came, it surprised even the most optimistic of scientists. The great marvel, said President Truman, ". . . is not the size of the enterprise, its secrecy or its cost, but the

achievement of scientific brains in putting together infinitely complex pieces of knowledge held by many men in different fields of science into a workable plan." The story of some of these men and the bits of knowledge they accumulated has been told in earlier chapters. More of the story can now be told.

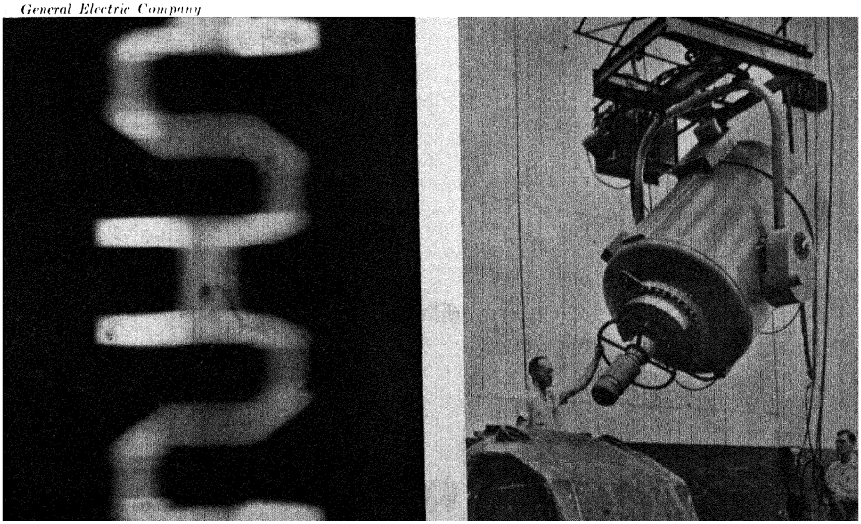
An amazing scientific discovery startles the world. Late in 1895, William Roentgen (rŭnt'gĕn) was working in a dark room with a Crookes tube covered with black paper. He noticed that while an electric discharge was passing through the tube, a small screen covered with a chemical, *barium platinocyanide,* lying on a table several feet away, gave off a strange glow.

This was curious and unusual behavior. He thought it must be caused by rays, powerful enough to penetrate not only the glass of the Crookes tube but several feet of air as well. He tested the penetrating power of these strange rays by producing them in front of several objects of varying hardness, including a hand behind which he had placed a sensitized photographic plate. To his astonishment, the film when printed showed a hand with the bones much darker than the surrounding flesh. He had, so to speak, taken pictures through an opaque solid, a truly remarkable feat!

These rays in some ways acted like light, but differed from light in being of much shorter wave lengths which could pass through even solid objects. He named these rays *x-rays.* X-rays are produced by the bombardment of matter by a stream of rapidly moving electrons, or cathode rays. In the cathode tube, as the cathode rays strike the anode, they release a small part of the energy as x-rays.

X-ray machines (right) are used in industry to detect flaws inside metal castings like the crankshaft (left).

General Electric Company

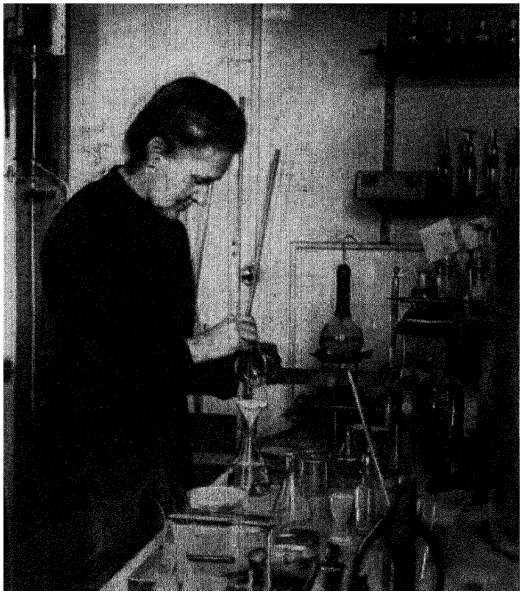


Another accident, and the curtain rises on the drama of radioactivity. Soon after the discovery of x-rays, another accident occurred in the laboratory of Henri Becquerel (běk-rěl′). He was testing the effect of sunlight on various ores, among which he had, fortunately, included an ore of uranium.

Quite by chance he placed a piece of the ore containing the element uranium upon a fresh photographic plate enclosed in a light-tight envelope lying on a table in his darkroom. When he examined this plate, he found that it had been changed under the very spot on which the ore had rested. This was not the sort of accident to reach the front page of the newspapers, as the discovery of x-rays had done. But its results were tremendously important.

A new world of radioactivity is discovered. Becquerel could not explain what had happened. He repeated the experiment with other ores containing uranium. *Pitchblende,* he found, emitted similar rays, which affected a photographic plate even more than the other uranium compounds. He suspected some unknown element to be the cause, and asked Madame Marie Curie (kü-rē′), a Polish girl working as a science teacher and research worker in Paris, to undertake the isolation of this unknown element.

Madame Curie and her husband, Pierre, set out to track down the cause of this peculiar behavior of pitchblende. They boiled and cooked a ton of this ore, sent to them from the pitchblende mines of Austria; they filtered and separated out impurity after impurity. Years of almost endless work passed, and, though they labored under extreme difficulties, Madame Curie wrote years later: "It was in that



Marie Curie in her laboratory. For her isolation of radium and polonium, Madame Curie was awarded the Nobel prize for chemistry in 1911.

miserable shed of a laboratory that we passed the best and happiest years of our lives." Finally in 1898 they succeeded in obtaining a few crystals of a salt of a new element, which they named *radium.*

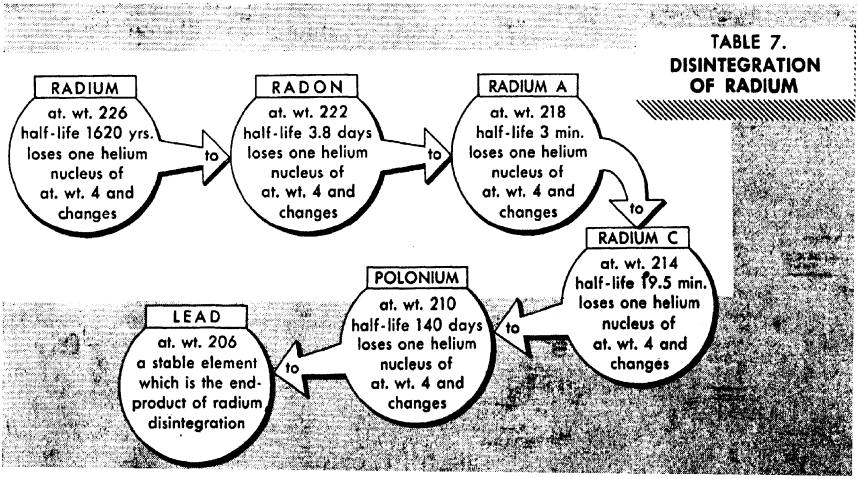
The new discovery was made public. A strange element had been discovered by a woman. Its salts shine in the dark like tiny electric-light bulbs and emit heat continuously. This element is a powerful poison — even acting from a distance. It causes severe burns, and has brought premature death to a number of scientists who have handled it for long periods. It makes the air around it a good conductor of electricity.

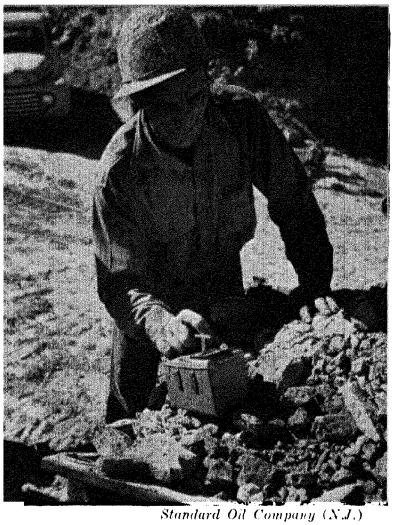
Because radium captured the imagination of the entire world, its discovery was a great stimulus to further research. This led to the discovery that a number of other elements resemble radium in their ability to break down and emit several kinds of rays. This property, called *radioactivity,* is possessed by thorium, uranium, polonium, radon, and several other elements.

In 1902, Rutherford and Soddy, another English scientist, explained the disintegration or breaking down of radium. Atoms of radioactive elements, they said, are not stable. They explode spontaneously, giving off three types of rays: alpha and beta particles and *gamma* rays. The gamma rays are similar to x-rays; the beta rays are electrons. Rutherford later showed that the alpha rays are electrified particles consisting of nuclei of helium atoms. The disintegration or decay of radium is indicated in Table 7.

What is the half-life of an element? The half-life of an element is the time required for the radioactivity of a given amount of an element to decay to half its original value. For example, starting with one gram of radium, it takes 1620 years for half of it to change to lead. At the end of the next 1620 years, half of the 0.5 gram which is left changes to lead, and this process continues at the same rate.

TABLE 7. DISINTEGRATION OF RADIUM





Standard Oil Company (N.J.)

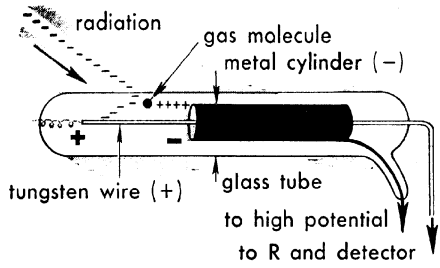


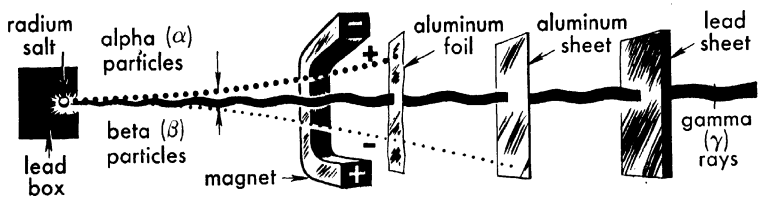
Fig. 35. Geiger counter. An entering electron produces a discharge, causing current to flow in the high resistance *R* until the fall of potential across *R* reduces the potential and discharge stops. The tube is then ready for the arrival of a second electron. (left) Use of the Geiger counter to test uranium ore for the amount of radiation.

The Geiger counter, detector of nuclear disintegration products. One type of Geiger counter consists of an argon-filled tube containing a metal cylinder and a thin wire. Between these two electrodes, a very high voltage is maintained and so adjusted that the tube is on the verge of discharge. When an electron enters the tube and collides with a gas molecule, the tube is discharged and a flow of current is produced. This current operates a headphone, or produces a loud click or flash of light. The greater the radiation, or the closer the tube is to the nuclear disintegration, the greater the effect.

Alpha particles are also detected by the Geiger counter. Neutrons, which have no charge, are detected indirectly with the use of a tube which contains a boron compound. The boron nucleus absorbs neutrons and produces particles which may be detected. Gamma rays are detected by the secondary electrons they produce.

Alpha particles, which travel at 10,000–20,000 mi./sec., have the least penetrating ability. About five centimeters of air, a sheet of paper, or a thin sheet (0.1 mm.) of aluminum will stop them. Beta particles (electrons), liberated at speeds more than six times that of alpha particles, require several meters of air and several millimeters of aluminum to absorb them. Gamma rays have still greater pene-

Fig. 36. Alpha, beta, and gamma rays have different penetrating powers and are affected differently by a magnetic field.



trating power — several centimeters of aluminum are required to stop them. Fast neutrons have the greatest penetrating power. All produce burns. Radiation absorption is measured in *roentgens* (r.).

Uses of radium. Radium, and radon gas sealed in tubes, are used in treating skin diseases and cancer.

Considerable quantities of radium are used in the detection of flaws in castings, forgings, and welds. Parts for aircraft and turbine casings are among the many kinds of equipment tested in this way.

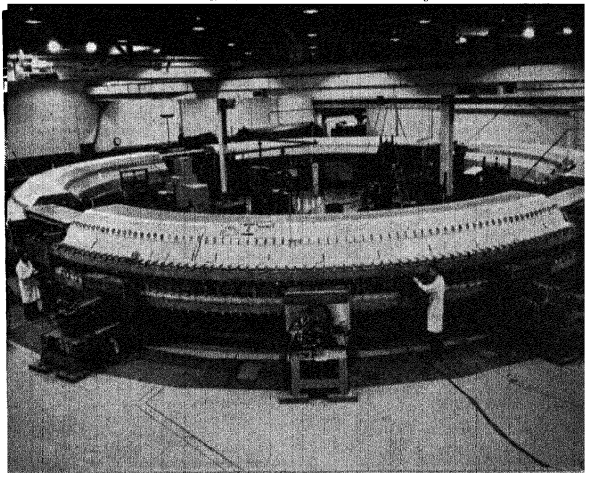
The method of testing is simple. From 25 to 1000 milligrams of radium sulfate are placed in the center of a circle of articles to be tested. X-ray films are placed on the backs of the specimens. The penetrating gamma rays from the radium salt produce a shadowgraph on the film, quite like the kind obtained with x-rays. Defects as small as 0.25 percent of the thickness of the article can be seen clearly.

The price of radium is about $20,000 a gram. *Carnotite*, an ore of both radium and uranium, is found in Utah and Colorado. The rich deposits of pitchblende discovered on the shore of remote Great Bear Lake in northern Canada in 1931 compete on a favorable basis with the huge deposits in the Belgian Congo which constitute our most important source of uranium.

The attack upon the nucleus of the atom. The disintegration of radioactive elements indicates that the building blocks of the atom's nucleus consist of neutrons and free protons, both of which can be emitted. Helium nuclei, which are liberated also by radioactive elements, are themselves composed of neutrons and free protons.

In the effort to learn more about the nucleus, scientists began bombarding atoms with various kinds of swiftly moving projectiles. One of the most important machines for acceleration of particles is the *cyclotron* developed in 1929 by Ernest O. Lawrence. Some other

Brookhaven National Laboratory



The magnet in this giant cosmotron at Brookhaven has an inside diameter of over 60 feet and weighs 2200 tons.

accelerators for *smashing atoms* are the *betatron,* which accelerates electrons, and the *synchroton, cosmotron,* and *bevatron,* all of which speed up protons to even greater speeds than the cyclotron.

During these researches, several discoveries were made — the *positron, artificial radioactivity,* and *mesons.* The positron is an extremely short-lived particle, having the same mass as the electron but opposite charge. It was discovered and named by Carl D. Anderson, of the California Institute of Technology, in 1932. When a positron reacts with an electron, both particles disappear and gamma radiation is formed.

In the nucleus of the atom a tremendous energy lies like a coiled spring caused, in part, by the many protons which repel each other because they are all of the same electric charge. Mesons may be the binding energies that hold the protons in the nucleus together. There are several types of mesons. The heavier meson (*pi*-meson) is produced when a nucleus is broken up during a collision. The lighter meson (*mu*-meson) is a decay product of the heavy meson. Mesons are very short-lived — less than a millionth of a second.

Summary: Units of matter thus far identified. Let us pause for a few minutes to list these units of matter, their mass, charge, and other related items of information.

TABLE 8. UNITS OF MATTER

NAME	MASS	CHARGE	WHERE FOUND	HOW OBTAINED OR FORMED	DISCOVERED BY AND WHEN
Electron (ϵ)	1/1837 that of the hydrogen atom	Negative	Outside nucleus	In Crookes tube, as cathode rays	Joseph John Thomson, 1897
Proton (+)	Approximately that of hydrogen	Positive	Inside nucleus	Stripping an electron from hydrogen	Ernest Rutherford, 1911
Neutron ($_0n^1$)	Approximately that of hydrogen	Neutral	Inside nucleus	Bombarding beryllium with helium	James Chadwick, 1932
Positron ($_{+1}\epsilon^0$)	Same as the electron	Positive	Inside nucleus	Radioactive nitrogen disintegration	Carl D. Anderson, 1932
Meson*	Heavy, or *pi,* meson is about 285 times that of electron. Light, or *mu,* meson is about 215 times that of electron.	Positive, negative, and neutral	Inside nucleus; as secondary cosmic rays in upper atmosphere	Bombarding atoms with primary cosmic rays (protons) or with helium nuclei of 300 million or more electron-volts in cyclotron	Carl D. Anderson and S. Neddermeyer discovered the *mu*-meson in 1937 and C. F. Powell the *pi*-meson in 1947.

*This particle was predicted by H. Yukawa, a Japanese, in 1934. It was named *meson,* meaning *intermediate particle.* It changes into something else in less than a millionth of a second, and it is supposed to travel at a speed nearly that of light.

Ancient and modern alchemy. As you know, modern chemistry sprang from *alchemy,* which was practiced for more than 20 centuries. The chief goals of the alchemists were to change the base metals, such as lead and iron, into gold and to find an elixir that would cure all disease. Although among the alchemists there were many honest enthusiasts, the annals of their queer practice are filled with accounts of liars and charlatans. In many museums of Europe we can still see shiny, yellow metals reputed to be gold, made by the deceptions of the "gold-cooks" of European courts.

Today the alchemists' dream of changing one element into another, called *transmutation,* has come true. Radium changes, of its own accord, into helium, lead, and other elements. Besides this natural transmutation, however, chemists have succeeded in artificially transmuting many nonradioactive elements. The first such transmutation was achieved in 1919 by Rutherford, who bombarded nitrogen with helium nuclei. The nucleus of the nitrogen atom was changed, and one proton was liberated, the remaining nucleus becoming the heavy isotope of oxygen with atomic weight 17.

How nuclear reactions are written. Transmutation or nuclear reactions are like chemical equations and must balance. The sum of the subscripts must be the same on both sides, and so must the sum of the superscripts.

Rutherford's transmutation may be expressed as follows.

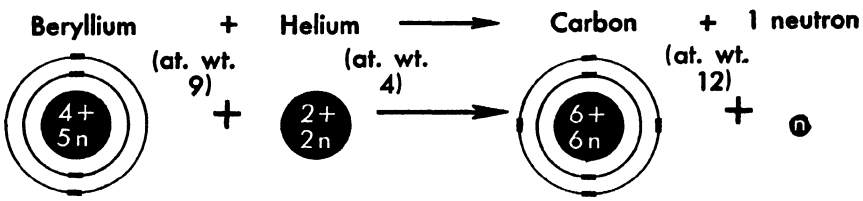
$$_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{8}O^{17} + {}_{1}H^{1}$$

The subscripts ($7 + 2 \rightarrow 8 + 1$) represent atomic numbers and the superscripts ($14 + 4 \rightarrow 17 + 1$) atomic weights.

Recent experiments indicate that other elements may be built up from lighter elements, for example, carbon from beryllium (a rare metal lighter than aluminum). This transmutation, (Fig. 37), may be used to produce high-speed neutrons by mixing powdered beryllium with a trace of a radium salt which emits helium particles.

Transmutation, as you see, involves changes in the nuclei of atoms rather than in the shifting or sharing of electrons which produces only *chemical* changes.

Fig. 37. Transmutation of beryllium into carbon.



The search for the key to nuclear energy. Albert Einstein, in 1905, advanced the idea that matter and energy were really different forms of the same thing, and that matter could be changed into energy — at least theoretically. He developed a mathematical equation to express the conversion of matter into energy:

$$E = mc^2$$

where E is energy expressed in ergs,* m is mass expressed in grams, and c is the speed of light, expressed in centimeters per second.

According to this matter-energy conversion equation, one pound of matter (for example, one pound of coal or of uranium) is equivalent to about 11 billion kilowatthours, if completely changed into energy. This is about two and one-half times the amount of electric energy produced in an entire year by the largest steam-electric generating plant in the country. In *burning* the same amount of coal, approximately four kilowatthours of energy are obtained. In terms of energy produced, oxidation is, therefore, an extremely inefficient process.

These ideas, of course, were all theory. However, a bit of confirmation came in 1932. In that year, Cockcroft and Walton, working in Rutherford's laboratory, bombarded lithium with high-speed protons produced by accelerating hydrogen nuclei by means of high voltages. They obtained *helium* (alpha particles) with energies almost 100 times as great as the energy that was used to break the lithium atom. This extra energy comes from the conversion of matter into energy, in accordance with the equation formulated by Einstein, thus:

Lithium	**+ hydrogen**	**→ 2 helium**	**+ energy**
$_3Li^7$	$+ {}_1H^1$	$\rightarrow 2\,{}_2He^4$	**+ 600,000 electron-volts**
Mass 7.0180	**+ mass 1.0076**	**→ mass 2(4.0029)†**	
	8.0256	**→ 8.0058**	
	Approximate loss of mass = 0.02		

* 1 erg = 1/980 gm.-cm. of work = approximately the energy required to lift a postage stamp to a height equal to its thickness. The speed of light is 186,000 mi./sec. or 30,000,000,000 cm./sec.

† Note that the atomic weight of the isotope of the lithium used differs from the atomic weight given in the table on page 162, which is an average of the atomic weights of all the isotopes of lithium. The hydrogen here refers to the proton, which is slightly lighter than the hydrogen atom, whose weight is given in the table on page 162. The weights given in the table on page 162 have been rounded off to three decimal places; hence, helium is shown there as 4.003 instead of 4.0029 as in this equation.

However, the method used by these experimenters was not efficient, and there was no great excitement over their news.

The key is found. In the meantime, other scientists were working in this same field. In 1934, a young Italian physicist, Enrico Fermi (fär'mī), who later left fascist Italy to become professor of physics at Columbia University, bombarded uranium with neutrons and thought he had created a new element No. 93. Then four years later Otto Hahn and F. Strassman repeated Fermi's experiment in Berlin. They bombarded uranium with slow neutrons and, instead of producing a new artificial element, they obtained two other natural elements and a great deal of energy. Unable to explain what had happened, Hahn and Strassman nevertheless published their findings.

Lise Meitner (mīt'nĕr), an eminent woman scientist working with Hahn, interpreted the results and passed the information on to Niels Bohr, Nobel prize winner in physics, in Copenhagen. Dr. Meitner was forced to flee Germany by the Nazis. Dr. Meitner believed that when uranium is bombarded by slow neutrons, the atom of uranium actually splits by a process called *nuclear fission,* forming barium and krypton. But what is even more important, great quantities of energy are released, perhaps as much as 11 million kilowatthours per pound of uranium. And, this is only a small part of the energy that would be produced if *all* the uranium were converted into energy.

The stage is set. Very soon after, a most important conference was held in Washington, D.C. Atomic physicists from American colleges and famous scientists from foreign nations were present. Niels Bohr was there, and so was Enrico Fermi. At this meeting, Bohr and Fermi discussed the ideas of Meitner. Bohr suggested that it was the U–235 in the uranium that actually split. Fermi suggested that, in the fission of uranium by neutrons, other neutrons might be emitted. These emitted neutrons could attack other uranium atoms. If this were true, the possibility of a *chain,* or self-propagating, *reaction* that would unlock the door to nuclear energy was near at last.

Brown Brothers



Enrico Fermi (1901–1954), winner of the 1938 Nobel prize for physics, played an important role in our government's nuclear research program both during and after World War II.

Before the meeting in Washington was over, experiments to confirm nuclear fission had begun, and confirmation of the emission of neutrons was soon obtained. By midsummer of 1940, the important facts regarding nuclear fission had been discovered and were known by many scientists. And although a chain reaction had not been obtained, its possibility was clear and several methods of producing it had been suggested. Then suddenly, World War II clamped tight the door of censorship on all research relating to the release of nuclear energy. For five years, the outside world was kept in the dark.

Nuclear energy unleashed! With the sudden dropping of the first atomic bomb on Hiroshima in August, 1945, the veil was partly lifted on research on nuclear fission and the production of chain reactions. Early in 1940, Franklin D. Roosevelt and Winston Churchill had pooled the efforts of British and American scientists on a research program, the like of which the world had never seen. Its goal was the release of nuclear energy for the production of a weapon with which to win the war against the Axis nations more quickly. Knowledge that research on such a weapon was being carried on in Nazi laboratories compelled quick, cooperative action. The race was on — the prize, the world. The United States government invested two billion dollars in ". . . the greatest scientific gamble in history — and won."

The term *atomic energy* has long been used to describe the tremendous power which is released when nuclear fission occurs. However, the term *nuclear energy* is now preferred since it is more truly descriptive of the processes involved.

A chain reaction from U–235. The first controlled chain reaction was achieved on December 2, 1942, at the University of Chicago. The fissionable material used was pure U–235 obtained from natural uranium ores containing a mixture of three isotopes: U–234, U–235, and U–238. Even though only about one part in 140 of this mixture is pure U–235, this isotope is used because it is most susceptible to nuclear fission by slow neutrons. What happens in the nuclear fission of U–235 may be represented as:

$$\text{U–235} + \text{neutron} \rightarrow \text{Ba} + \text{Kr} + \text{2 or 3 neutrons} + \text{energy}$$

At Oak Ridge, Tennessee, U–235 was laboriously separated from its other isotopes by an electromagnetic method. A compound of uranium, UF_6, was passed in the form of a gas between the poles of a magnet. The lighter isotope, U–235, was deflected more than its heavier partners and thus separated.

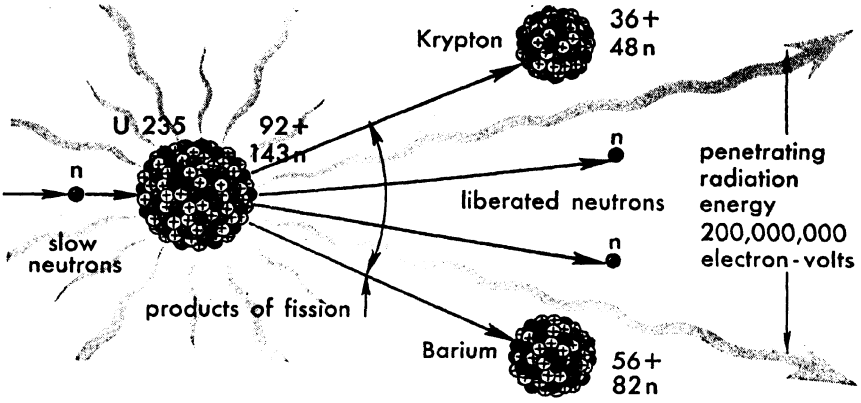
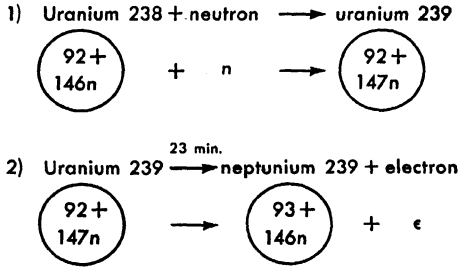


Fig. 38. A possible chain reaction.

A newly created element, plutonium, for the A-bomb. Few details about the A-bombs exploded over Hiroshima and Nagasaki have been released. It is definitely known, however, that two fissionable elements were produced for use in bombs; namely, U–235 and plutonium. Plutonium, which has fission properties similar to U–235, is a newly created element of atomic number 94. It was named for the planet Pluto, which lies beyond Uranus in the solar system. Together with another new element, neptunium of atomic number 93, plutonium was first prepared in 1940 with the aid of Lawrence's cyclotron by E. M. McMillan and P. H. Abelson.* These were momentous discoveries.

The formation of neptunium and plutonium may be represented by the following three equations:



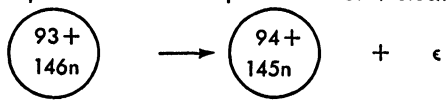
* Traces of these two elements were later found in some uranium ores.

In 1945, elements 95, americium (Am), and 96, curium (Cm), were obtained by bombarding plutonium and uranium with swiftly moving helium nuclei.

Then came elements 97, berkelium (Bk), and 98, californium (Cf), in 1949 and 1950. These elements were named after Berkeley and California, the city and state in which they were first produced. Elements 99 and 100 were created in 1954.

This change occurs by the breaking down of one neutron in the nucleus of U–239 into one proton and one electron, which escapes.

3) Neptunium 239 $\xrightarrow{2.3\ \text{days}}$ plutonium 239 + electron



This change occurs by the breaking down of one neutron in the neptunium 239 nucleus into one proton and one electron, which escapes.

Plutonium, in turn, becomes U–235 by natural radioactive disintegration, or more rapidly by the action of slow neutrons to which it is extremely sensitive. The change is indicated by the following nuclear equation:

$$_{94}\text{Pu}^{239} \longrightarrow {}_{92}\text{U}^{235} + {}_{2}\text{He}^{4}$$

Plutonium → U–235 + helium

What is meant by "critical size"? An A-bomb is set off by suddenly bringing together two separate blocks of fissionable material, each of which is smaller than the *critical size,* but which together form a mass just above this critical size. For a bomb explosion to occur, the number of neutrons captured with fission must be greater than the number of neutrons which escape. The number of neutrons which escape depends on the surface area, whereas the number captured depends upon the volume. As the quantity of fissionable material increases, the volume increases faster than the surface area. Critical size means the size at which the neutrons captured exceed the number which escape and fission occurs.

Plutonium is produced in nuclear reactors or "piles." The nuclear reactor built at Oak Ridge, Tennessee, is essentially a large cube of graphite bricks containing a number of horizontal channels into which is placed pure uranium in the form of solid cylinders or slugs enclosed in aluminum casings. Graphite is used to slow down neutrons and is called a *moderator.* Heavy water is another good moderator. Slow neutrons are more effective in producing fission than are neutrons that travel at normal speeds. The bricks are built up in layers, and since the structure was built by piling one layer of bricks upon another, it is called an *atomic pile.*

A chain reaction is started with neutrons liberated from a bit of beryllium mixed with radium in the center of the pile. The concentration of neutrons is controlled by cadmium or boron-steel rods, which absorb neutrons easily. Several nuclear reactions take place as

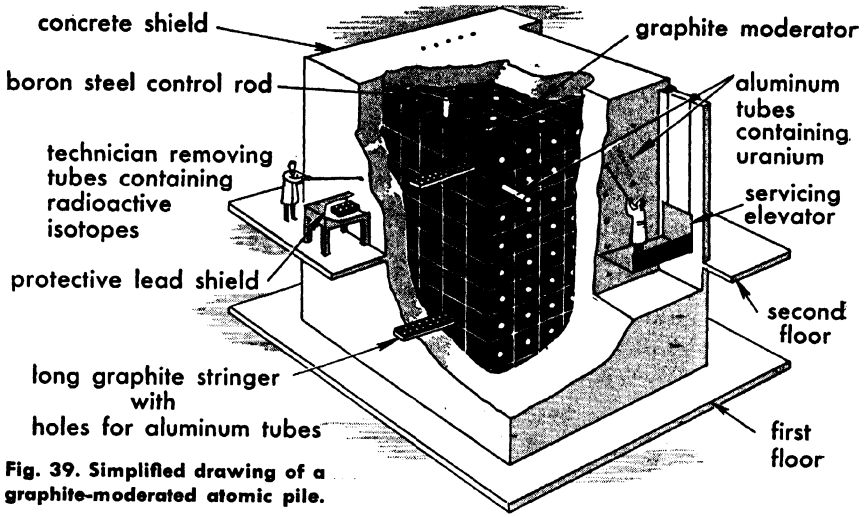


Fig. 39. Simplified drawing of a graphite-moderated atomic pile.

Adapted from a drawing of the Atomic Energy Commission

shown on page 187. When the uranium slugs are ready for processing, they are pushed out at the back of the reactor and new ones are fed in at the front. The slugs fall into tanks of water where the U–239 gradually changes into Np–239 and finally into plutonium. The slugs are then dissolved in acid, and the plutonium is separated chemically from the rest of the elements present. This chemical process of separation is much easier than physical separation of U–235 from U–238.

Since dangerous radiations and radioactive material are produced during these changes, all operations are performed by remote control. The whole pile is surrounded with several feet of concrete to shield and protect the operating personnel. Several reactors are in operation in this country. The one at Oak Ridge is air-cooled, while the pile at Hanford, Washington, is water-cooled. Intensive research on other coolants is now being carried on. Metals, such as sodium, in a liquid state have been found useful for this purpose.

The atomic pile liberates tremendous amounts of heat. Efforts to build industrial nuclear reactors which will utilize this huge source

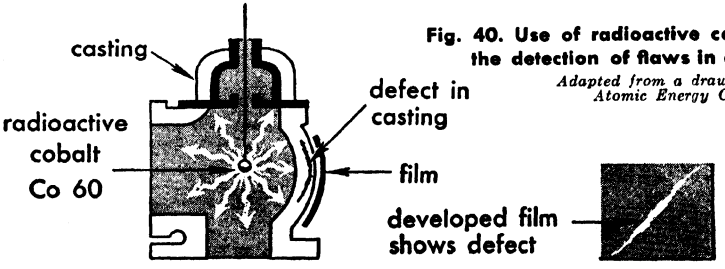


Fig. 40. Use of radioactive cobalt for the detection of flaws in castings.

Adapted from a drawing of the Atomic Energy Commission

of power are already well under way. Atomic power plants "burning" nuclear fuel will supply electricity, not only in our own country but later on also, it is to be hoped, in those areas of the world which are poor in coal, petroleum, and natural water power. Nuclear furnaces may be built by private industry with uranium supplied by the Atomic Energy Commission. The plutonium manufactured during the process will be turned back to the United States Government.

Radioisotopes, first produced artificially by Madame Curie's daughter. In 1934, Irene Joliot-Curie (zhô'lyō') and her husband, Frédéric Joliot-Curie, by bombarding boron with alpha particles, produced a neutron and a radioactive isotope of nitrogen. Here was another case of modern alchemy.

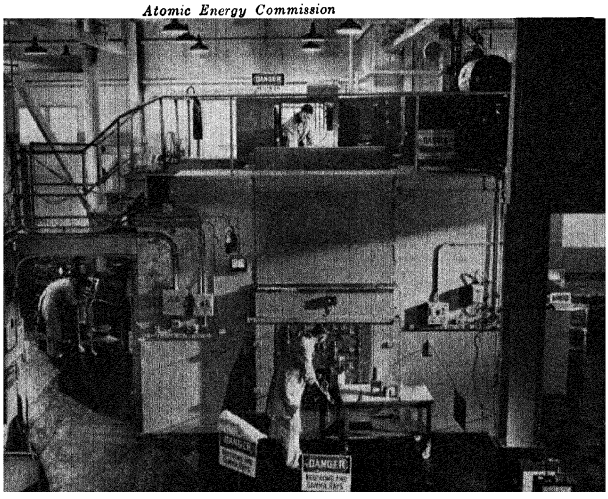
Boron + helium → radioactive nitrogen + neutron
mass 10 + mass 4 → mass 13 + mass 1

Since then, scientists have made more than 700 new and different radioisotopes in cyclotrons and nuclear reactors. For example, when a bit of ordinary iodine (atomic weight 127) is placed in an atomic pile where it is bombarded with neutrons, it changes to a radioisotope of iodine of mass 131. The Atomic Energy Commission supplies hundreds of radioisotopes to research groups all over the world.

A new "tracer technique" uses radioisotopes. Research in medicine, biology, agriculture, and many other fields has been helped tremendously by this new method. Radioactive iodine, for example, is being used in thyroid diagnosis and therapy. A person suffering from hyperthyroidism is fed with a trace of sodium iodide containing I^{131}. With the aid of a Geiger counter, the rate at which this iodine compound collects in the thyroid gland can be accurately determined.

Radioactive cobalt, Co^{60}, loses radioactivity in five days and is used

Atomic Energy Commission



Materials may be made radioactive by exposure within a nuclear reactor such as this water-boiler reactor. Such radioisotopes have many uses in industry, agriculture, and medicine.

in cancer therapy as a substitute for radium and x-ray treatments. Radioactive carbon, C^{14}, is a wonderful tool in the study of photosynthesis and such problems of human health as sugar metabolism. Radioactive phosphorus, P^{32}, is used in agricultural research dealing with the accumulation, utilization, and action of phosphate fertilizers. Industry is using radioisotopes in the improvement of steel, in studying the action of catalysts, in measuring the flow of underground water, oil, and gas, and in the detection of leaks.

Nuclear energy in the future? So far, nuclear energy has been used mainly as a military weapon, and for research. No one knows what the peaceful use of nuclear energy will bring. It seems likely that nuclear science will give higher standards of living to all peoples.

The unlocking of almost unimaginable stores of energy should teach man important lessons. Nuclear energy may transform the world by improving the health and raising the standards of living of millions of persons. But this same instrument in the form of a Hydrogen-bomb can destroy civilization as the A-bomb wiped out much of Hiroshima and Nagasaki. Therefore, the nations of the world must find a way of preventing a war with nuclear weapons from ever taking place.

The H-bomb, based on the *fusion* of the heavy isotopes of hydrogen into helium and triggered by the 100,000,000°C. temperature of an A-bomb explosion, could be made of unlimited size. This *thermonuclear* reaction may be expressed as follows:

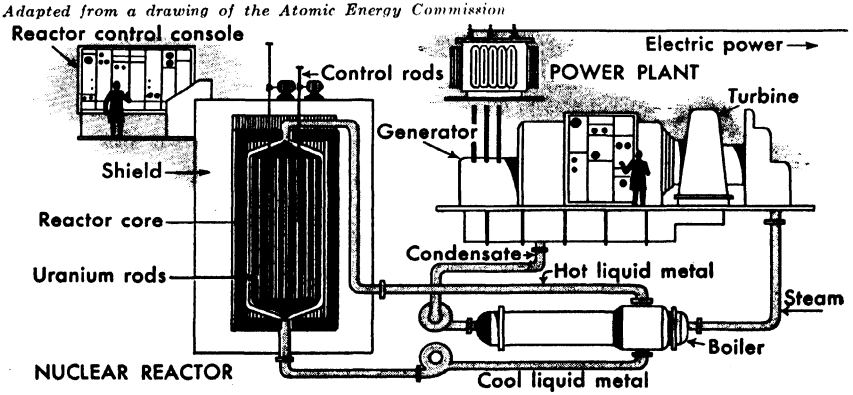
Deuterium + tritium → helium + neutron + energy

$$H^2 + H^3 \rightarrow He + n$$

The sudden conquest of nuclear energy demonstrated that science in a democracy is strong and tremendously creative. By constant vigilance, we must strive to keep it so.

Fig. 41. Simplified drawing of the use of nuclear energy for generating electricity.

Adapted from a drawing of the Atomic Energy Commission





YOU WILL ENJOY READING

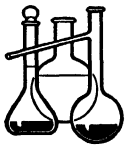
Curie, Eve. *Madame Curie.* Garden City Publishing Co., New York, 1943. In this intimate portrait of her mother, Eve Curie tells an entrancing story of the discovery and isolation of radium.

Glasstone, Samuel. *Sourcebook on Atomic Energy.* D. Van Nostrand Company, New York, 1950. This book, written at the request of the United States Atomic Energy Commission, brings together in readable narrative the important facts about the past history, recent status, and possible future of nuclear energy.

Fermi, Laura. *Atoms in the Family.* The University of Chicago Press, Chicago, 1954. A simple, intimate account of the events surrounding the conquest of a controlled nuclear chain reaction, written by the wife of Enrico Fermi.

Dean, Gordon. *Report on the Atom.* Alfred A. Knopf, New York, 1953. An account of the role of nuclear energy by the former head of the U. S. Atomic Energy Commission.

Smyth, Henry D. *Atomic Energy for Military Purposes.* Princeton University Press, 1945. This is the so-called Smyth Report released by the Army a few days after the first atomic bomb was dropped on Japan. It is semitechnical in nature and not easy reading.



USEFUL IDEAS DEVELOPED

1. X-rays consist of vibrations shorter than those of light. They are produced by bombarding metals with a stream of rapidly moving electrons. These x-rays have great penetrating power.

2. Certain elements break down naturally, or disintegrate, forming lighter elements including helium nuclei. This property is called *radioactivity.*

3. Radium gives off alpha particles, beta particles, and gamma rays, which are similar to x-rays.

4. The simplest units of matter thus far identified are the electron, proton, neutron, positron, and meson.

5. The positron has the same mass as the electron; it has a positive charge; and it can be formed during the disintegration of radioactive nitrogen.

6. Mesons have masses between the mass of an electron and the mass of a proton; they have either a negative charge, a positive charge, or are neutral; they are produced by the bombardment of atoms with cosmic rays or with rays of 100-million electron-volts from the betatron.

7. Modern alchemy, or artificial transmutation, is an accomplished fact.

8. Artificially radioactive elements were first obtained by the Joliot-Curies by bombarding boron with alpha particles. Hundreds of new radioisotopes have since been produced.

9. The age of nuclear energy was ushered in by the controlled fission of U–235 and plutonium in 1945.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) Who discovered x-rays? (b) How are they produced? (c) How do they differ from light?

2. How did Becquerel's discovery lead to the discovery of Ra?

3. List some of the properties and uses of Ra.

4. What is meant by the half-life of an element?

5. What are the alpha, beta, and gamma rays emitted during the disintegration of Ra?

6. Describe the construction and operation of a Geiger counter.

7. Name five different particles that have been expelled from the nucleus of atoms during bombardment.

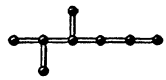
8. Name several known facts concerning the mesons.

9. (a) Has the dream of transmutation come true? (b) Explain your answer.

10. Show by a diagram how Rutherford changed N into H.

11. (a) Write the Einstein equation for the conversion of mass and energy. (b) Illustrate the meaning of this equation in terms of the change of lithium into helium.

12. What is meant by a chain reaction?



13. How does artificial radioactivity differ from the natural radioactivity of Ra?

14. Describe some of the events since 1938 leading up to the final conquest of nuclear energy.

15. By means of three equations, explain the production of plutonium from uranium.

16. By means of equations, explain how nuclear energy was released in 1945.

17. Describe the construction of a nuclear pile.

18. By means of an equation, explain the explosion of a hydrogen bomb.

Group B

19. "The conception of the structure of the atom makes it possible for present-day scientists to explain the riddle of transmutation." Explain this statement.

20. Make a diagram of the heaviest known element showing the composition of the nucleus and the positions of all its electrons. Consult your teacher or a recent edition of some college chemistry textbook.

21. Scientists believe that in releasing about four kilowatt-hours of energy in burning one pound of coal, a very small part of the coal is converted into energy. Why has this fact not been proved by experiment?

22. Describe briefly the future of the peacetime uses of nuclear energy.

23. (a) Would you buy stock in a company organized to exploit nuclear energy? (b) Give reasons for your answer.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

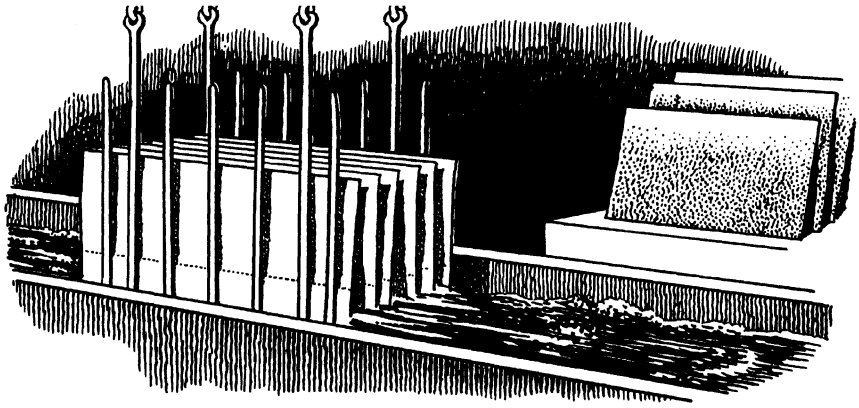
1. Make a small model of an electrical power plant utilizing nuclear fuel. Consult your bibliography on page 192.

2. Visit your dentist or doctor and ask him to show you his x-ray machine. Make a report on its construction and operation, using diagrams.

3. Consult your teacher of economics on the question: "What would the effect of commercial transmutation of iron into gold be on the financial structure of the world, if it were accomplished tomorrow?" Write a report on this subject.

4. Compare the effects of the Industrial Revolution and the possible effects of use of nuclear energy. Ask your social science teacher for help.

5. Write a two-page report on the construction and operation of a cyclotron or other particle accelerator now in use.



13. ACIDS:
HYDROCHLORIC ACID, A TYPICAL ACID

. . . To one man science is a sacred goddess to whose service he is happy to devote his life; to another she is a cow who provides him with butter.
Liebig, 1803–1882

Gunfire in the American wilderness helped us to learn more about digestion. In 1822 at a remote fort on Mackinac Island between Lake Huron and Lake Michigan, a French-Canadian, Alexis St. Martin, was brought in for medical treatment. An accidentally discharged musket had sent a bullet through the wall of his stomach. Dr. William Beaumont, an army surgeon, patched him up.

Despite great effort, it was impossible to get the wound to close, and on healing, a flap covering an opening into St. Martin's stomach was left. Through this opening Beaumont could reach directly into St. Martin's stomach. Beaumont got a strange idea. This freak "lid" over the hole into St. Martin's stomach would enable him to perform experiments to discover the digestive action of the juices of the stomach. St. Martin was agreeable and Beaumont tied pieces of food to a string, inserted them into St. Martin's stomach and, after several hours, removed what was left of the food.

In this way Beaumont gave science the first accurate facts concerning the relative digestibility of foods and the composition of gastric juice. He found gastric juice to contain a small amount of *hydrochloric acid* (about 0.3 percent), which helps to digest certain foods, especially proteins.

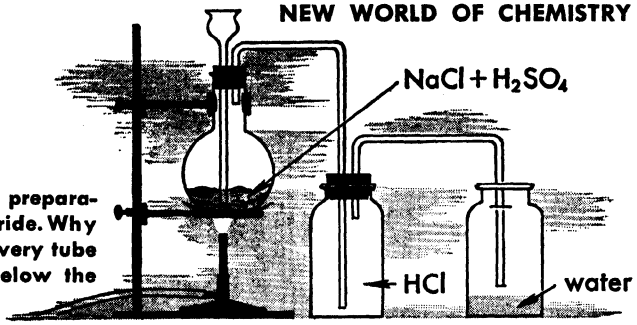


Fig. 42. Laboratory preparation of hydrogen chloride. Why is the end of the delivery tube above rather than below the level of the water?

How hydrogen chloride is prepared in the laboratory. To prepare hydrogen chloride in the laboratory, concentrated sulfuric acid is added to sodium chloride in a flask, as shown in the illustration above. This mixture is heated, and hydrogen chloride gas, which is liberated readily, is collected by the displacement of air. In this chemical change, a double replacement occurs, as indicated in the following equation:

$$H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4 \text{ (sodium bisulfate)}$$

At the outset, we must distinguish clearly between HCl (hydrogen chloride gas) and HCl (hydrochloric acid). When hydrogen chloride gas is dissolved in water, hydrochloric acid is obtained. Both are represented by the same formula, but their physical and chemical properties are entirely different.

How hydrogen chloride is prepared commercially. When a jet of hydrogen is burned in chlorine, hydrogen chloride gas is formed (see Chapter 10).

$$H_2 + Cl_2 \rightarrow 2HCl$$

This is one commercial method of manufacturing HCl. A second commercial method is similar to the laboratory one but at a somewhat higher temperature producing Na_2SO_4 instead of $NaHSO_4$.

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4$$

Chemical properties of hydrochloric acid. Hydrochloric acid is one of the most common and useful laboratory chemicals, or *reagents.* Some of its important properties are:

1) *Taste.* Dilute hydrochloric acid has a sour taste.

2) *Action on indicators.* Hydrochloric acid reacts with a group of substances known as *indicators,* causing a color change. For example, hydrochloric acid turns *blue* litmus *pink.* It also turns reddish-purple *phenolphthalein* (fē-nōl-thăl'ēn) colorless.

3) *Action with metals.* When hydrochloric acid is in contact with most metals, a reaction takes place. Hydrogen is liberated (recall the laboratory method for the preparation of hydrogen), and chlorides are formed. Note that the metal replaces the hydrogen of the HCl.

$$2HCl + Zn \rightarrow H_2\uparrow + ZnCl_2 \text{ (zinc chloride)}$$
$$2HCl + Fe \rightarrow H_2\uparrow + FeCl_2 \text{ (ferrous chloride)}$$

4) *Action with bases,* or *hydroxides of metals.* Hydrochloric acid reacts with a base, forming a neutral compound that possesses the qualities of neither acid nor base (bases are discussed in Chapter 14). Pure water is the only other product of this reaction. For example, when hydrochloric acid and sodium hydroxide react, the products are common salt and water.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Why hydrochloric acid is a typical acid. The chemical properties of hydrochloric acid are characteristic of the whole group of compounds known as *acids.* We may now define an acid as a water solution of a compound with the following characteristic properties:

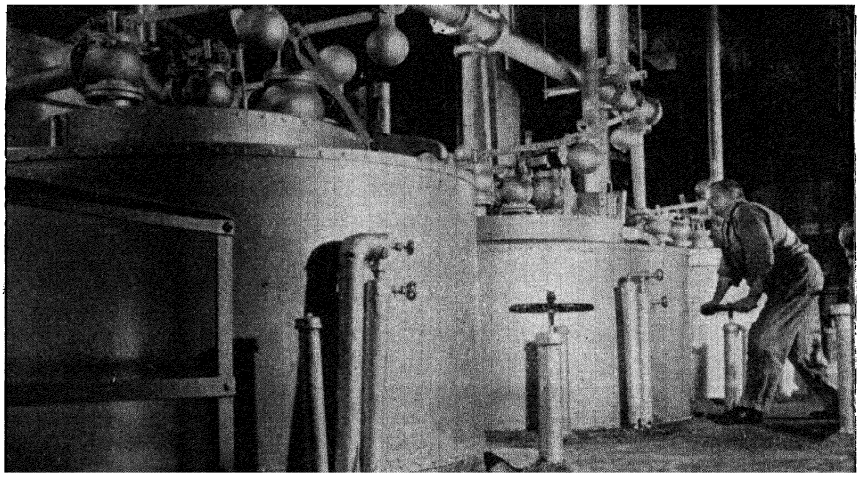
1) *An acid has a sour taste.* The sour taste, or tartness, of fruits is caused by certain acids, such as citric acid, which is found in lemons, limes, and grapefruit.

2) *An acid turns blue litmus pink, reddish-purple phenolphthalein colorless,* and acts with other indicators in the same way as hydrochloric acid.

3) *An acid contains hydrogen that can be replaced* by most metals, forming compounds known as *salts.* This does not mean that all compounds containing hydrogen are acids. Sugar, for example, contains hydrogen, but it is not an acid, because its hydrogen cannot be replaced by metals. *A compound in which the hydrogen of an acid has been replaced by a metal is known as the salt of an acid.* Thus sodium chloride, NaCl, is a salt of hydrochloric acid, and sodium nitrate, $NaNO_3$, is a salt of nitric acid, HNO_3.

4) *An acid neutralizes any base,* forming water and a salt whose composition depends on both the acid and the base used.

In general, an acid consists of hydrogen and a nonmetallic element, or hydrogen and a radical. The hydrogen of the acid can be replaced by a metal. Strictly speaking, while certain substances show acid properties only in water solution, they are commonly called *acids* even when dry. Thus, perfectly dry H_2SO_4 is called *sulfuric acid,* even though it exhibits acid properties only when it is in a



Corn Industries Research Foundation, Inc.

In these convertors, corn starch is changed, under heat and pressure, into corn sugar, or *dextrose*. Hydrochloric acid serves as a catalyst in the process. Because the process simulates human digestion, dextrose is, in effect, a predigested food and is readily assimilated by the body.

water solution. Bases also exhibit their characteristic basic properties only when water is present. Certain characteristics of acids or bases in solution are discussed in Chapter 16.

The general method for the preparation of an acid. Sulfuric acid is one of the most important acids, because it is used as a raw material in the manufacture of most of the other acids. Sulfuric acid has two special characteristics that make it well suited for this purpose: (1) its low cost, and (2) its high boiling point (338°C.). The manufacture of sulfuric acid is discussed on page 309.

The preparation of hydrochloric acid illustrates the *general method used in preparing acids* from sulfuric acid. First, a salt of the acid to be prepared is chosen as a source of the nonmetallic element of the acid. Common salt is the least expensive and most abundant source of chlorine. Many other chlorides can be used, but they are more expensive. Sulfuric acid supplies the hydrogen.

The salt of the acid to be prepared, NaCl, and sulfuric acid are heated together gently. Hydrogen chloride gas is produced by the reaction and is driven off and dissolved in water in the receiving vessel, forming the acid. The higher boiling points of the other compounds taking part in the reaction prevent their vaporizing and thus keep them from passing over into the receiving vessel.

Many other acids are manufactured by treating their least expensive and most abundant salts with sulfuric acid. The acid formed is

usually separated from the reacting substances by methods based on the differences in their boiling points.

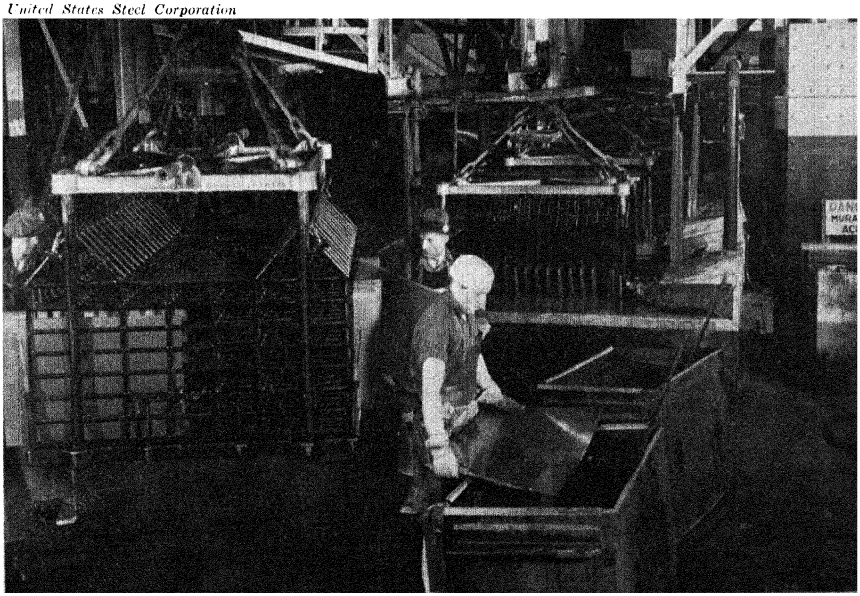
Physical properties of hydrochloric acid. Hydrochloric acid is a colorless liquid, heavier than water. That is, its specific gravity is greater than one. It possesses an irritating odor. Both the boiling point and the specific gravity of hydrochloric acid are determined by the weight of hydrogen chloride gas dissolved in the water. Hydrochloric acid containing 20 percent hydrogen chloride gas by weight boils at 110°C. Impure hydrochloric acid is called *muriatic acid* and is usually yellow in color. In this form it was known for many years before Priestley, in 1772, first isolated pure hydrochloric acid.

Hydrochloric acid cleans metals. Before coating metals, such as iron and steel, with plates, films, or coatings of other metals, including chromium, silver, tin, and zinc, the surface of the metal must be clean and free of oxides. Removing oxides and otherwise cleaning the surface of a metal to be plated or coated is a process known commercially as *pickling*. One of the chief industrial uses of hydrochloric acid is in the pickling of metals, especially before coating with tin in *tinning*, or zinc in *galvanizing*, or with the materials that, after firing, result in enamelware.

Small quantities of hydrochloric acid, usually muriatic acid, are used in removing rust stains from vitreous washbasins and lavatories. Plumbers often use muriatic acid as a *flux* before soldering.

Racks of sheet steel emerge from the pickler. The worker in the foreground is dipping the sheets in water to remove the acid.

United States Steel Corporation



Hydrochloric acid is used in making other chemicals. Chlorides of many metals, including magnesium chloride, aluminum chloride, and zinc chloride, are made by the reaction of hydrochloric acid and a carbonate or oxide of the metal. For the most part, such chemicals are of very high quality, and are used chiefly by manufacturing chemists and drug houses, and by druggists. Zinc chloride is used to impregnate wood to prevent decay, in soldering, and in flame-proofing.

Silver chloride, AgCl, one of the several light-sensitive silver compounds used to coat photographic film may be made by the reaction of silver nitrate, $AgNO_3$, and hydrochloric acid. In the manufacture of glucose from starch, hydrochloric acid acts as a catalytic agent. It is used also in large quantities in the manufacture of glue and gelatin, in the purification of boneblack, and in the processing of textiles.

Physical properties of hydrogen chloride gas. Hydrogen chloride gas is colorless, heavier than air, and has a sharp, penetrating odor. It is extremely soluble in water. If a test tube of hydrogen chloride gas is placed mouth downward in water, the water will rise almost to the top, as the gas dissolves. Water dissolves about 500 times its own volume of this gas under normal laboratory conditions. The gas can be liquefied and solidified, just as all other gases.

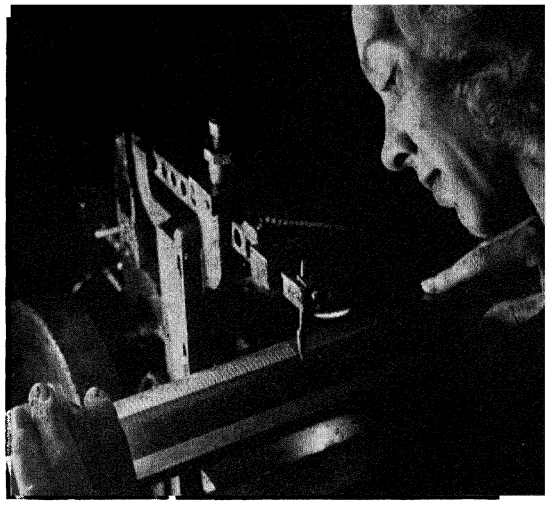
Chemical properties of hydrogen chloride gas. Hydrogen chloride does not show acid properties unless it is dissolved in water or unless some water vapor is present. When dry, it is completely inactive. Its attraction for water is so great that it forms a cloud or mist in moist air of tiny droplets of hydrogen chloride solution.

This property may be used as a test for hydrogen chloride gas. If you blow across the mouth of a bottle containing concentrated hydrochloric acid, a mist will form. This mist is caused by the moisture in your breath combining with the hydrogen chloride vapor that rises from the bottle. Hydrogen chloride does not burn.

Preparation and properties of hydrofluoric acid, HF. The preparation of hydrofluoric acid follows the general method for making an acid. Sulfuric acid reacts with calcium fluoride, CaF_2, the most common salt of hydrofluoric acid, forming hydrofluoric acid. This is the method used by Scheele when he first prepared it in 1771. Calcium fluoride is the chief constituent of the mineral *fluorspar,* found in several parts of the United States.

$$H_2SO_4 + CaF_2 \rightarrow 2HF\uparrow + CaSO_4$$

Pure anhydrous hydrogen fluoride is a colorless gas which boils at room temperature (19.5°C.). It is deadly if inhaled. It dissolves in water, forming a colorless acid that vaporizes at low temperatures.



Calibration marks are carefully scratched through the wax coating on a graduated glass cylinder prior to exposing it to hydrofluoric acid.

Corning Glass Works

Such an acid is called a *fuming* acid. Since hydrofluoric acid reacts with glass, quartz, and most metals, it is distilled in dishes made of lead and must be kept in bottles made of polyethylene or other plastics with which it does not react. This acid produces powerful burns by poisoning the tissues.

How glass is etched with hydrofluoric acid. *Etching* is the biting out of particles of glass or metal by means of chemicals. Hydrofluoric acid etches glass because it unites with the silicon dioxide, SiO_2, of the glass, forming silicon tetrafluoride, SiF_4, which is a gas.

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O$$

In etching glass articles, such as thermometers, electric-light bulbs, and windows, the surface is completely covered with wax and the design to be etched is scratched through the wax. The object is then brought into contact with the vapor of hydrofluoric acid. When the action on the exposed glass has gone as far as necessary, the object is removed from contact with the vapor. In *frosting* the inside of an electric-light bulb, a small amount of hydrofluoric acid is poured into the bulb, shaken for an instant, and poured out, and the bulb is thoroughly rinsed. It is also used in making Freon refrigerants, and as a catalyst in the manufacture of high octane gasoline.

The other halogen acids. Theoretically, both hydrobromic acid, HBr, and hydriodic acid, HI, may be prepared by the general method used in preparing acids.

$$H_2SO_4 + KBr \rightarrow HBr\uparrow + KHSO_4$$
$$H_2SO_4 + NaI \rightarrow HI\uparrow + NaHSO_4$$

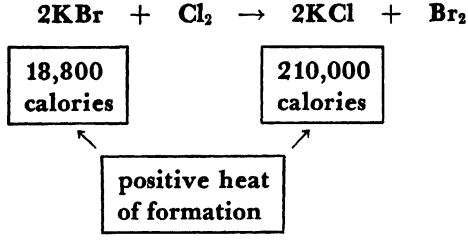
When first formed they are colorless gases with strong irritating odors, but are almost immediately oxidized by the oxygen of the air, forming free bromine and free iodine. In water solution, hydrobromic and hydriodic acids are unstable; on exposure to air they decompose as a result of oxidation.

$$4HBr + O_2 \rightarrow 2H_2O + 2Br_2$$

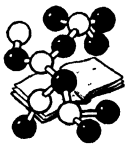
Heat of formation and chemical stability. When hydrogen and chlorine react, forming hydrogen chloride, a great deal of heat is produced. A reaction in which heat is liberated is called an *exothermic reaction* (*ex* — out, *therme* — heat). Exothermic reactions continue after they are first started by external heat. On the other hand, when hydrogen and iodine unite, heat is continuously absorbed and heat must be added if the reaction is to continue. A reaction in which heat is absorbed is an *endothermic reaction.*

The number of calories of heat absorbed or liberated, during the formation of a mole (see page 130) of an element or compound, is called its *heat of formation.* A substance which liberates heat during its formation is said to have a *positive* heat of formation; a substance which absorbs heat is said to have a *negative* heat of formation. A compound such as sodium chloride, NaCl, whose *positive* heat of formation is very great (97,800 calories) is *very stable.* Hydrobromic acid, HBr, whose *positive* heat of formation is small (8400 calories) is *somewhat unstable.* Hydriodic acid, HI, which has a *negative* heat of formation, is *very unstable.*

A knowledge of the heats of formation is very useful to chemists. For example, we can tell whether a certain compound will form and how easily it can be prepared. A compound formed by replacement has a higher positive heat of formation than the compound from which it is formed and hence is more stable.



By similar reasoning we can see why bromine will not replace chlorine from KCl.

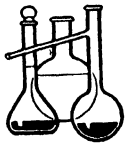


YOU WILL ENJOY READING

Clendening, Logan. *The Human Body,* pp. 74–75. Alfred A. Knopf, New York, revised edition. 1945. An amusing story of Dr. William Beaumont's experiments with Alexis St. Martin.

Jaffe, Bernard. *Men of Science in America,* pp. 157–158. Simon and Schuster, New York, 1944. The dramatic story of the pioneer investigations of the American doctor, William Beaumont, and of John R. Young, which resulted in our knowledge of the presence of hydrochloric acid in the gastric juice.

Lowry, T. M. *Historical Introduction to Chemistry,* pp. 12–16. The Macmillan Co., London, 1915. The discovery of the common acids and their chemical and physical properties are reviewed.



USEFUL IDEAS DEVELOPED

1. An acid is a substance whose water solution (1) has a sour taste, (2) turns blue litmus pink, (3) contains hydrogen that can be replaced by each of many metals with the formation of a salt and the liberation of hydrogen, and (4) neutralizes bases, forming a salt and water.

2. Chemical reactions in which heat is liberated are called *exothermic reactions;* those in which heat is absorbed are called *endothermic reactions.*

3. The heat of formation of a compound is the number of calories of heat liberated or absorbed in the formation of 1 gram-molecular weight of the compound.

4. Compounds with high positive heats of formation are stable; compounds with low positive heats of formation are unstable; compounds with negative heats of formation are very unstable.



USING WHAT YOU HAVE LEARNED

Group A

1. Describe the laboratory method of preparing HCl.

2. (a) What are the two methods of preparing hydrogen chloride commercially? Write an equation for each method. (b) What type of chemical reaction does each method represent?

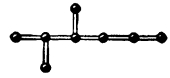
3. Give the properties of HCl as to (a) taste, (b) action on indicators, (c) action on metals, (d) action on oxides, (e) action on hydroxides of metals.

4. (a) What is a salt? (b) Give three examples.

5. (a) What are the salts of HCl called? (b) Name three.

6. (a) What are salts of HNO_3 called? (b) Name one.

7. (a) What is an acid? (b) Name five acids.



8. Make a list of the properties of hydrogen chloride gas.

9. What is the percentage of hydrogen chloride in a solution that has a fixed boiling point of 110°C.?

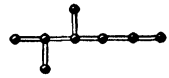
10. What weight of pure salt is needed to prepare 292 lb. of hydrochloric acid containing 15 percent HCl by weight?

11. Compare the solubility of hydrogen chloride in H_2O with the solubility of air, O_2, H_2, CO_2, and N_2.

12. What causes the fuming of hydrogen chloride in moist air?

13. What test or tests would you use in showing the presence of HCl in a liquid?

14. (a) What are the uses of HCl? (b) What process in the human body depends in part upon HCl?

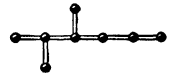


15. (a) State the general method of preparing acids. (b) Why is H_2SO_4 so generally used?

16. Scheele was the first to prepare HF. His method is still used today. Describe it.

17. By means of an equation, explain the etching action of HF.

18. Explain how HF is stored.



19. Compare the properties of the other halogen acids with those of HCl.

20. (a) What is a calory? (b) What is heat of formation?

21. (a) What is the difference between an exothermic reaction and an endothermic reaction? (b) Give an example of each.

22. Explain the relationship between the heat of formation and the stability of a substance.

23. The positive heat of formation of H_2S is 2730 calories. (a) Is H_2S a stable compound? (b) Explain.

24. Write balanced equations for the following:

a) Copper oxide + hydrochloric acid →
b) Hydriodic acid + oxygen →
c) Sulfuric acid + sodium bromide →

Group B

25. What is the effect of chlorine water on litmus?

26. When HCl is boiled, what passes off? Explain.

27. A bottle of HI turns brown. Explain.

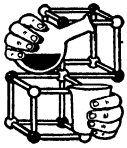
28. What chemical tests would you use in identifying each of the halogen acids?

29. Why is muriatic acid used in the soldering of metals?

30. Water may be considered an acid. Explain.

31. Why is the general method for preparing acids not used in the preparation of HI?

32. In the electrolysis of HCl, the volumes of Cl_2 and H_2 collected are not the same. Explain.

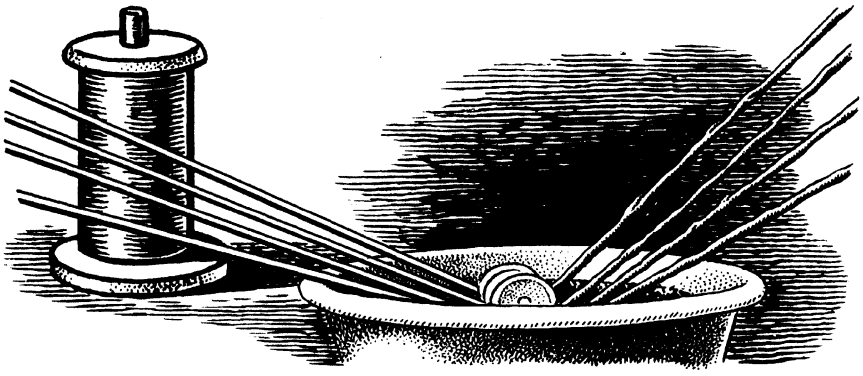


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Take home some strips of litmus paper and test various foods and other substances found at home for the presence of acids. Report your findings to the class. Make a list of common foods that react to your test as acids; as bases. What do you conclude from your tests?

2. Prepare a report on the experiments performed by Beaumont with Alexis St. Martin which dealt with the discovery of HCl in gastric juice.

3. Consider carefully the quotation at the beginning of this chapter. Prepare a report for the class on the meaning of this quotation. Illustrate with examples from the lives of great scientists and inventors.



14. BASES: SODIUM HYDROXIDE, A TYPICAL BASE

. . . Rouelle [the teacher of Lavoisier], to whom we owe the term base, described how natural salts had been restricted at first to salts formed by the union of acids with alkalies which are soluble in water, and impart on the tongue a saline taste.
T. M. Lowry, 1915

How sodium hydroxide is prepared in the laboratory. The laboratory preparation of hydrogen by the action of sodium on water was discussed in Chapter 3. Each sodium atom replaces one of the atoms of hydrogen in the water molecule.

$$2Na + 2HOH \rightarrow 2NaOH + H_2 \uparrow$$

After the water evaporates, a white solid, sodium hydroxide, is left.

Chief properties of sodium hydroxide. Sodium hydroxide is a common and useful substance. Some of its important properties are:

1) *Action on indicators.* Sodium hydroxide turns *pink* litmus *blue* and colorless phenolphthalein reddish-purple.

2) *Action with acids.* Sodium hydroxide reacts with an acid, forming a salt, thus causing the original properties of the acid to disappear along with its own. For example, sodium hydroxide unites with hydrochloric acid, forming common salt and water. The presence of the salt may be proved by evaporating the water and tasting the solid left behind.

3) *Feel.* A water solution of sodium hydroxide has a slippery, soapy feeling.

Why sodium hydroxide is a typical base. The chief properties of sodium hydroxide are characteristic of the whole group of compounds known as *bases*. We may now define a base as a compound (1) that contains the *hydroxyl group* (OH), (2) whose water solution is soapy to the touch, (3) whose water solution turns pink litmus blue and colorless phenolphthalein reddish-purple, and (4) whose water solution reacts with acids, forming water and a salt of the acid used.

In general, then, *a base consists of a metallic element or radical and one or more hydroxyl groups (OH)*.

Strong bases, such as sodium hydroxide and potassium hydroxide, are often known as *alkalies*. Three other important bases are calcium hydroxide (slaked lime), ammonium hydroxide (ammonia water), and magnesium hydroxide (milk of magnesia).

How bases react with acids. When a base reacts with an acid, the hydrogen of the acid combines with the hydroxyl radical of the base, forming water, and the metal or metallic radical of the base unites with the nonmetal or acid radical of the acid, forming a salt. Such a chemical change is called *neutralization*. All neutralization reactions are double replacements.

$$HCl + NaOH \rightarrow HOH + NaCl \text{ (a salt)}$$
$$HNO_3 + KOH \rightarrow HOH + KNO_3 \text{ (a salt)}$$
$$H_2SO_4 + Ca(OH)_2 \rightarrow 2HOH + CaSO_4 \text{ (a salt)}$$
$$HBr + NH_4OH \rightarrow HOH + NH_4Br \text{ (a salt)}$$

Neutralization is the reaction of an acid with a base, forming water and a salt. A salt, then, is a compound made up of a metal or a metallic radical and a nonmetal or an acid radical.

Titration and the use of molar and normal solutions. It is sometimes necessary to know how much of an acid, a base, or a salt is present in a solution. For example, we may want to know how much acetic acid is present in a given sample of vinegar. One way is to neutralize a given volume of this liquid with a solution of a base whose composition is known. This process of determining the strength of an acid or a base with the help of neutralization reaction is called *titration*. It is carried out in long tubes (burettes) which are measured off in milliliters so that volumes can be read off directly. A definite volume of the acid solution to be tested is neutralized with a *standard* solution of a base, that is, one whose composition is known. The point at which neutralization is reached (end point) is determined by the use of an indicator such as phenolphthalein which suddenly changes color.

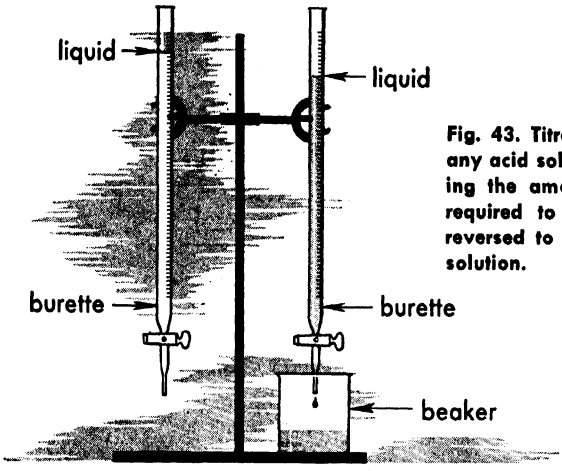


Fig. 43. Titration. The degree of acidity of any acid solution is determined by measuring the amount of normal basic solution required to neutralize it. The process is reversed to find the strength of any basic solution.

There are two kinds of standard solutions used, namely, *molar* solutions and *normal* solutions. *One liter of a molar solution contains one mole or gram-molecular weight of dissolved substance.* For example, a molar solution of NaCl contains 23 + 35.5, or 58.5, grams of NaCl in one liter of this solution. A molar solution of $Ca(OH)_2$ contains 74 g.

One liter of a normal acid solution contains one gram of replaceable hydrogen. One liter of a normal basic solution contains 17 grams of the OH group, and one liter of a normal salt solution contains the equivalent of one gram of replaceable hydrogen. For example, one liter of a normal solution of H_2SO_4 contains 98 ÷ 2, or 49, grams H_2SO_4 since this acid contains two replaceable hydrogen atoms. One liter of a normal $Ca(OH)_2$ solution contains 74 ÷ 2 grams $Ca(OH)_2$. One liter of a normal $AlCl_3$ solution contains 133.5 ÷ 3 grams $AlCl_3$ since this salt contains three hydrogen equivalents. Decimal fractions are used in referring to both molar (M) and normal (N) solutions. Thus a 0.1M solution of HCl contains 36.5 ÷ 10, or 3.65, grams HCl per liter of solution.

PRACTICE WORK ON MOLAR AND NORMAL SOLUTIONS

1. How much NaCl per liter of solution does a 0.3M solution of NaCl contain?

2. How much acid, base, or salt per liter of solution do the following solutions contain: 0.1N $AgNO_3$, 0.3N $MgBr_2$, 1.5N H_3PO_4, 0.125N $CuCl_2$?

3. How would you prepare the following solutions: 0.8N HNO_3, 3.0N KOH, 0.25N $Mg(OH)_2$, 1.3N $Al(OH)_3$?

Heat of neutralization. All neutralization reactions are exothermic. When any strong acid and strong base react, a definite quantity of heat is liberated, 13,700 calories per gram-molecular weight, or mole, of water formed. This heat is called *heat of neutralization.* When 36.5 grams of hydrochloric acid react with 40 grams of sodium hydroxide, 18 grams of water and 58.5 grams of sodium chloride are formed with the liberation of 13,700 calories. In the case of the action of sulfuric acid on potassium hydroxide, 2 × 13,700 calories are produced, because two moles of water are formed.

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$

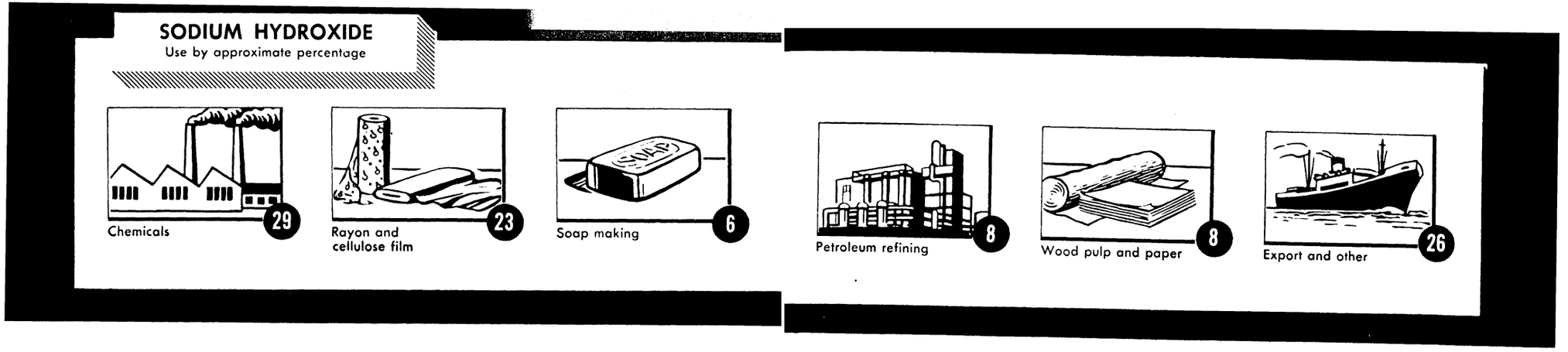
Important uses of neutralization. After petroleum has been purified with the aid of sulfuric acid, the excess acid is removed by neutralizing it with a base, usually sodium hydroxide. Much of the soil in the United States is sour (acid). Four-fifths of the cultivated land in the central western states is sour and therefore not fully productive. These acid soils may be neutralized by the addition of lime, CaO, which combines with water, forming a base. Calcium carbonate, $CaCO_3$, is used also. Soil with excess lime is neutralized with ammonium sulfate, $(NH_4)_2SO_4$.

The destructive effect of acid stains or burns may be minimized by the prompt application of either a weak base or sodium bicarbonate, which neutralizes the effect of the acid. Similarly, an alkali burn is treated by application of a mild acid, such as boric acid or vinegar. An excessive *acid mouth* condition is sometimes treated by using small amounts of milk of magnesia, $Mg(OH)_2$, a mild base, or *antacid.*

Normal blood is slightly alkaline. *Alkaline reserve* refers to the amount of base present as bicarbonate in the blood. Even slight changes in the normal alkalinity of the blood result in serious body disturbances. Such disturbances may, in some cases, be corrected by using neutralizing chemicals administered by a physician.

Existence of an alkaline reserve (a scientific fact) is, unfortunately, used by some advertisers as a reason for selling to the public huge quantities of "alkalizers" to dose ailments that are best treated by *other* methods administered by a competent physician. This is an excellent example of the abuse of scientific knowledge, against which intelligent persons must always be on guard.

Physical properties of sodium hydroxide. The white solid, sodium hydroxide, is very soluble in water. On exposure to moist air, it absorbs large quantities of water and changes into a pool of sodium hydroxide solution. This property of deliquescence makes sodium



hydroxide useful as a drying agent. Usually it is sold in pellets that must be kept in well-sealed bottles which exclude moisture.

Chemical properties of sodium hydroxide. In addition to typical properties of bases already mentioned, sodium hydroxide has other chemical properties. When exposed to air, it unites with carbon dioxide, forming sodium carbonate.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The common name for sodium hydroxide is *caustic soda,* given to it because of its caustic, or burning, action upon the skin. It dissolves wool but has little effect upon cotton, rayons, or nylons. Because of this fact, it is used in determining the amount of wool in a cotton-wool mixture.

Potassium hydroxide (*caustic potash*) closely resembles sodium hydroxide in both chemical and physical properties.

Sodium hydroxide helps clothe us. Sodium hydroxide is one of the most useful compounds known. It serves man in many ways, chief among which is in the manufacture of rayon and cellulose films similar to *cellophane.* Approximately one-fifth of the 3 million tons of sodium hydroxide produced in a recent normal year in this country was consumed in this way. The chemistry of the production of rayon and cellulose films is discussed in detail in Chapter 37.

Many fabrics are made of cotton that has been treated with sodium hydroxide. When cotton fibers are placed in a solution of sodium hydroxide, they lose part of their natural twist and acquire a gloss that is considered very desirable by many persons. Cotton so treated is known as *mercerized cotton.*

Sodium hydroxide helps keep us clean. Until very recently sodium hydroxide and potassium hydroxide were used in making almost all the cleansing agents for both industrial and home use. When sodium hydroxide or potassium hydroxide reacts with a fat, soap and glycerin are formed. Each year the soap industry uses thousands of tons of sodium hydroxide and considerable amounts of potassium hydroxide.

Another important use of sodium hydroxide is in the form of *lye* which contains about 94 percent sodium hydroxide. It is a useful household cleansing agent because it dissolves grease. Lye produces painful burns if it comes in contact with the skin. It should be used cautiously and stored out of the reach of small children.

When kitchen or bathroom plumbing becomes clogged, a strong solution of lye is sometimes poured down the pipes. In this way greasy, fatty accumulations are *saponified* and become soluble in water. "Drano" and other common plumbing cleaners sold under various trademarks contain percentages of impure sodium hydroxide.

Sodium hydroxide helps peel fruits and vegetables. Many fruits and vegetables are peeled before canning or dehydration by the use of sodium hydroxide, or lye. Most of the large lye peelers are of the moving conveyor type, and the fruits or vegetables are immersed in a 20- to 25-percent lye solution for from two to five minutes. During this time, the lye solution reacts with the *pectins,* or binding materials, between the individual cells. The skins become loose and may be removed by washing which also removes all traces of lye.

This process is an outgrowth of the making of old-fashioned lye hominy, a staple in the diet of American pioneers. In the making of lye hominy, grains of corn are soaked in a lye solution until the hard, tough skin of the corn grain becomes loosened. Washing with fresh water removes the skin and also the lye.

Other uses of sodium hydroxide. Large quantities of sodium hydroxide are used in reclaiming aluminum and salvaged rubber, in the processing of many vegetable oils, and in the production of gasoline. In the refining of petroleum, large quantities of this "basic

heavy chemical" are used to neutralize the sulfuric acid with which petroleum is purified. Of only slightly less importance is the use of sodium hydroxide in digesting and purifying the cellulose of wood pulp that is used in manufacturing paper. Potassium hydroxide is the electrolyte in certain types of storage batteries such as the Edison, and Ni-Cd batteries. Lithium hydroxide is used in submarines to absorb CO_2.

How sodium hydroxide is prepared for industrial use. Chlorine, hydrogen, and sodium hydroxide are all formed at the same time during the electrolysis of brine (see Chapter 10). Both chlorine and sodium hydroxide are prepared industrially by this method. If chlorine is the chief product desired, then sodium hydroxide is the *byproduct.* That is, it is a substance formed incidentally during the preparation of another substance. If sodium hydroxide is the compound being manufactured, then chlorine is the byproduct.

The apparatus that is commonly used in the industrial preparation of sodium hydroxide by the electrolytic process is the Hooker cell. The Nelson diaphragm cell, Vorce cell, and mercury cell are also used. The graphite anodes (see Fig. 44) are covered by a sodium chloride solution and are separated from the cathode by an asbestos diaphragm, which prevents the chlorine from mixing with the sodium hydroxide. Chlorine gas escapes through an outlet in the dome at the top of the cell, and hydrogen gas passes through an outlet from the steel screen cathode. Because the sodium hydroxide solution is heavier than the salt solution, it concentrates with it at the bottom of the cell. It is drawn off, and evaporated to dryness during which almost all of the NaCl crystallizes out. This process

Based on a diagram by Hooker Electrochemical Company

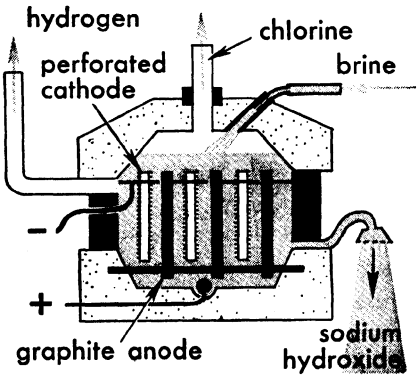


Fig. 44. Hooker cell used in the production of sodium hydroxide and chlorine. Hydrogen is a byproduct.

is continuous, and more brine is added as the strength of the sodium chloride solution diminishes.

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2\uparrow + Cl_2\uparrow$$

An older method, still very widely used, depends upon the conversion of the cheaper base, calcium hydroxide, into sodium hydroxide by means of a solution of sodium carbonate. Until 1940, more sodium hydroxide was produced by this process than by electrolysis.

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaOH$$

Since calcium carbonate is insoluble, it is separated from the soluble sodium hydroxide by filtration.

Methods of preparing a salt. Most inorganic compounds, such as sodium chloride, sodium nitrate, copper sulfate, and so forth, are salts. We have already had occasion to refer to six of the seven methods of preparing salts. A list of these seven methods follows:

1) Neutralization:

$$HCl + NaOH \rightarrow H_2O + \underline{NaCl}$$

2) Action of an acid on a metal:

$$2HCl + Zn \rightarrow H_2\uparrow + \underline{ZnCl_2}$$

3) Union of a metal and a nonmetal:

$$Fe + S \rightarrow \underline{FeS}$$

4) Action of an acid on the oxide of a metal:

$$2HCl + CuO \rightarrow H_2O + \underline{CuCl_2}$$

5) Action of an acid on a salt of a more volatile acid:

$$H_2SO_4 + 2NaCl \rightarrow 2HCl + \underline{Na_2SO_4}$$

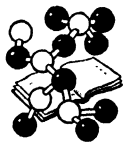
6) Action of one salt on another salt:

$$AgNO_3 + NaCl \rightarrow AgCl + \underline{NaNO_3}$$

7) Action of the oxide of a metal (basic oxide) on the oxide of a nonmetal (acidic oxide):

$$CaO + SO_3 \rightarrow \underline{CaSO_4}$$

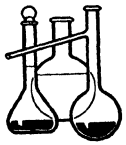
The horizontal lines under certain formulas indicate salts.



YOU WILL ENJOY READING

Fabre, Jean H. *The Wonder Book of Chemistry,* pp. 154–170. Albert & Charles Boni, New York, 1922. Salts and neutralization are discussed in a captivating manner.

Jaffe, Bernard. *Chemical Calculations,* pp. 96–102. World Book Co., Yonkers, New York, 1947. Normal and molar solutions and problems involving them are included.



USEFUL IDEAS DEVELOPED

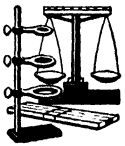
1. A base is a substance that contains a metal or metallic radical and one or more hydroxyl groups. Its water solution is soapy to the touch, turns pink litmus blue, and reacts with acids, forming water and a salt.

2. Neutralization is the action of an acid with a base, forming water and a salt. The hydrogen of the acid unites with the hydroxyl radical of the base, forming water.

3. When a strong acid and a strong base react, forming a mole of water, 13,700 calories of heat are liberated. This amount of heat is called *heat of neutralization.*

4. A salt is a compound made up of a metal or a metallic radical and a nonmetal or an acid radical.

5. The seven methods of preparing salts are: (1) neutralization, (2) action of an acid on a metal, (3) union of a metal and a nonmetal, (4) action of an acid on a metallic oxide, (5) action of an acid on a salt of a more volatile acid, (6) reaction between two salts, and (7) reaction of a basic oxide on an acidic oxide.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) Write an equation illustrating the method of preparing NaOH in the laboratory. (b) How can the NaOH formed be changed into a solid?

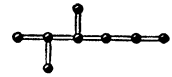
2. (a) What other base can be made in the same way? (b) Write the equation for the preparation of this other base. (c) What is its common name?

3. (a) What is a base? (b) List the four properties by which a base can be recognized.

4. Give the names and formulas of three bases other than NaOH that are often found at home.

5. (a) What is a salt? (b) What is neutralization? (c) How is mercerized cotton prepared?

6. A soil is found to be acid. To obtain the best results with certain crops a neutral soil is required. How would a farmer correct the acid condition of his soil?



7. Write four equations illustrating neutralization.

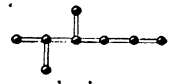
8. (a) What is a molar solution? (b) What weight of acid, base, or salt do the following solutions contain:

(1) 3M NaOH, (2) 0.1M H_2SO_4 (3) 0.5M $AlBr_3$, and (4) 1.8M HNO_3?

9. (a) What is a normal solution? (b) What weight of acid, base, or salt do the following solutions contain:

(1) 0.1N $Mg(OH)_2$, (2) 0.5N H_3PO_4, (3) 2.5N $AgNO_3$, and (4) 1.5N $AlCl_3$?

10. What is meant by titration?



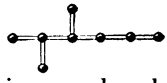
11. Describe the electrolytic process for making NaOH, illustrating your description with a diagram.

12. In a process of the kind mentioned in exercise 11, what determines which is the product and which the byproduct?

13. Write the equation for a method of preparing sodium hydroxide other than the electrolytic method.

14. (a) What is the annual consumption of NaOH in the United States? (b) What are the three chief uses of NaOH?

15. (a) What is lye? (b) Why is it useful in the home? (c) What cautions should be exercised in its use?



16. A sample of fabric was placed in a test tube containing a solution of NaOH, and boiled for a few minutes. Half of the fabric disappeared. What can you say about its composition?

17. Copy and complete the following table, inserting the correct formulas for the salts formed. Do not write in this book.

	HCl	HNO_3	H_2SO_4	H_2CO_3
NaOH	NaCl			
$Ca(OH)_2$				
NH_4OH				$(NH_4)_2CO_3$

18. Classify as acids, bases, or salts: $Al(OH)_3$, K_2CO_3, $CuSO_4$, $Pb(OH)_2$, $HC_2H_3O_2$, $CaCl_2$, $BaSO_4$, HCN, H_2S.

19. Which will produce a greater weight of alkali, 45 g. of Na or 50 g. of K?

20. A piece of Na is thrown in H_2O. The NaOH formed exactly neutralizes 24.5 g. of H_2SO_4. What weight of Na was used?

Group B

21. (a) Write the equations for the neutralization of sodium hydroxide with (1) hydrochloric acid, and (2) sulfuric acid. (b) The heat of neutralization for the first reaction is 13,700 calories; for the second reaction, 2 $\times$ 13,700 calories. Inspect the two equations. Explain why the heat of neutralization is twice as large in the second reaction.

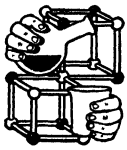
22. What volume of a 0.1N KOH solution is needed to neutralize 50 ml. of a 0.5N solution of H_2SO_4?

23. What is the reason for adding limewater to milk that is to be fed to an infant?

24. $NaHCO_3$ is frequently used to neutralize an acid. (a) Is it a base? (b) Explain your answer.

25. A glass bottle with a glass stopper contained solid NaOH. When an attempt was made to open the bottle, it was found that the glass stopper was firmly cemented to the neck of the bottle. Explain.

26. In making cream of tomato soup, a pinch of $NaHCO_3$ is added to the tomato puree before the milk is added. Explain the reason for this practice.

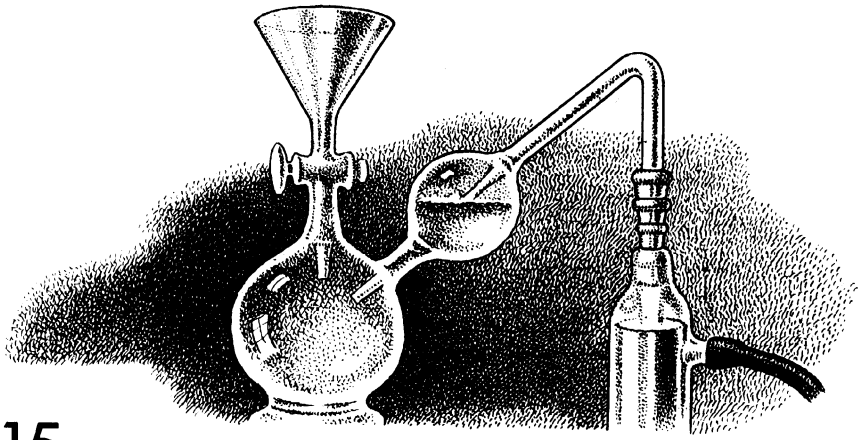


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Take home some pieces of litmus paper and test the following substances for acidic, basic, or neutral properties: vinegar, milk of magnesia, ammonia water, table salt solution, soap solution, sugar solution, and the liquid in an automobile battery. What do you conclude about the importance of acids and bases in everyday living?

2. With the help of your chemistry teacher, perform the following experiment: Pour an excess of NH_4OH on a solution of $FeCl_3$. You will get a brown, sticky precipitate of $Fe(OH)_3$. Boil thoroughly, then filter. Wash the insoluble $Fe(OH)_3$ several times with distilled water. What properties of soluble bases are not possessed by this insoluble base?

3. Using litmus paper as indicator, neutralize (with constant stirring) a known volume of vinegar with some household ammonia. Report to your class on the relative strength of these solutions.



15. SOLUTIONS: WATER, THE UNIVERSAL SOLVENT

. . . The sea is the chemist that dissolves the mountains and the rocks, pulverizes old continents and builds new, forever redistributing the solid matter of the globe. Ralph Waldo Emerson, 1803–1882

Is chemically pure water found in nature? The purest form of water in nature is rain water. Although it is perfectly safe for drinking purposes, rain water is not pure water, for it is mixed with the gases of the atmosphere and with small amounts of dust and other impurities, which it has washed down from the air.

Eventually all water finds its way to the ocean, the great reservoir. Rain may fall upon busy streets and flow through sewers to the sea. It may fall on the ground and furnish the water so necessary to growing plants. Water evaporates from the leaf-surfaces of plants and from the surfaces of streams, lakes, and oceans only to fall again as rain. Without this *water-cycle,* life as we know it could not exist.

Water that flows over the ground (*surface water*) collects fine particles of solid material. The size and the weight of this material depend on the speed with which the water flows, for fast-moving water can carry much heavier material than a slow-moving stream.

Water that soaks into the ground (*ground water*) carries almost no load of this type, since the soil acts as a filter and holds the solid particles back. But ground water is still not pure water, no matter how clear and sparkling it may be, for it contains minerals that have been dissolved out of the soil.

What is a solution? When a teaspoonful of sugar is dissolved in a glass of water, the sugar completely disappears from view, and we say that we have made a *solution* of sugar and water. The substance that is dissolved is called the *solute;* the substance in which the solute dissolves is called the *solvent.* Thus, when we make a solution of sugar and water, the sugar is the solute and the water is the solvent.

If we taste a sample of this solution of sugar and water, we find that it tastes the same, no matter whether we have taken our sample from the top or the bottom of the solution. This indicates that a solution has the same composition throughout; that is, it is *homogeneous.* If we take care not to let any of the water evaporate, the sugar will not settle to the bottom; the solution will remain the same. Of course, different amounts of sugar will dissolve in a glass of water — the solution may be very sweet or it may be only slightly sweet. Thus a solution differs from a compound, for we can vary the composition of a solution. The composition of a compound does not vary.

A uniform mixture of solute and solvent that does not conform to the law of definite proportions is called a solution. The kinetic theory of matter helps to explain the mechanism of solution. According to this theory, the solute breaks down into molecules which distribute themselves between the molecules of the solvent. For this reason, *a solution* is sometimes called a *molecular dispersion of a solute in a solvent.* If the solute is colorless (for example, sugar), it can no longer be identified by sight when it is in solution.

Difference between dilute and concentrated solutions. A pinch of salt in a gallon of water makes a very *dilute solution.* Half a pound of salt added to the same amount of water makes a *concentrated solution.* When only a small amount of solute is dissolved in a solvent, we have a dilute solution; when the amount of solute dissolved is considerable we have a concentrated solution.

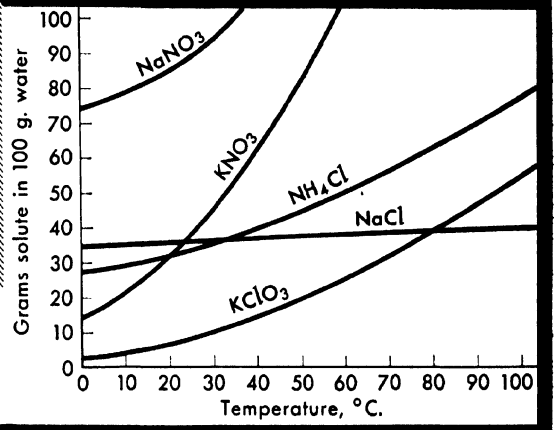
What determines the amount of solute that will dissolve? There is a limit, of course, to the amount of a solute that will dissolve in a given volume of a solvent. Several factors determine the amount of solute that will enter into solution. The most important factors are the *nature of the solvent* and the *nature of the solute.* Large amounts of certain substances, such as salt, dissolve in water, but the amount of gold that dissolves in water is extremely minute. Iodine dissolves only slightly in water, but it is very soluble in alcohol, forming an alcohol solution known as a *tincture.* Just why a substance dissolves in one solvent and not in another is not thoroughly understood.

Temperature has a great deal to do with the amount of a solute that will enter into solution. More sugar will dissolve in hot tea than

in iced tea. In general, most solids dissolve in larger amount in warm liquids than in cold liquids. This is not true of gases, for the higher the temperature of a liquid, the smaller the amount of gas that will dissolve in it. You are familiar with this fact if you have ever noticed that gas from a warm bottle of soda pop escapes more rapidly than gas from an ice-cold bottle of the same beverage.

TABLE 9.
SOLUBILITY CURVES

Solubility varies with temperature. A nearly straight line indicates that an increase in temperature produces a regular increase in solubility.



Another important factor that determines the solubility of a gas is *pressure*. The higher the pressure, the greater the amount of gas that will dissolve. For this reason, when we want to make a concentrated solution of carbon dioxide in water (the *carbonated water* you see at every soda fountain), we add the gas to the water under high pressure and at low temperature. The weight of gas that dissolves is proportional to the pressure on the gas (*Henry's law*). In other words, if we double the pressure, twice as much gas will dissolve.

Two factors that help to determine the amount of solute that will dissolve in a definite period of time (speed of solution) are the degree of subdivision of the solute and the extent to which particles of solute and solvent are closely intermingled by stirring. As you know, the finer the particles and the more vigorous the stirring, the quicker the solid will dissolve. However, while these two factors affect the speed at which a solute dissolves, they do not affect the maximum amount of solute that will dissolve.

What is a saturated solution? If we add a salt, such as alum, to a given volume of water at a definite temperature and under fixed

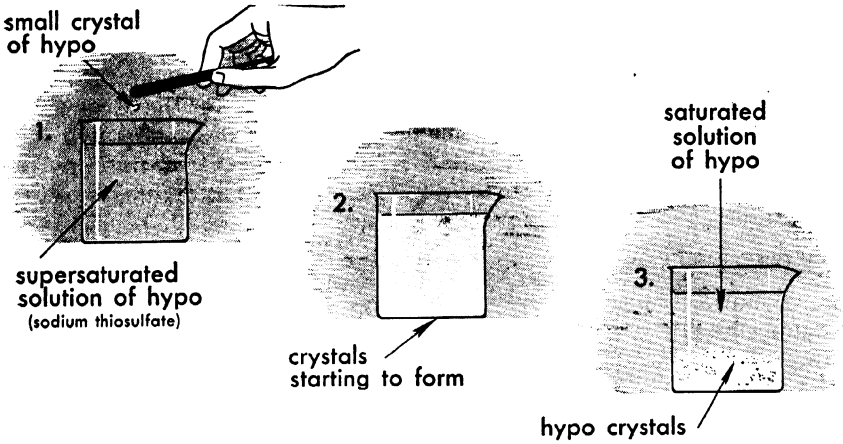


Fig. 45. Formation of hypo crystals from a supersaturated solution.

conditions of pressure, the water will continue to dissolve the salt until it has dissolved a certain amount. After this amount is dissolved, no more alum will dissolve, and any additional alum that is added will settle to the bottom of the water and remain there. *A solution in which no more of the solute will dissolve, at that particular temperature and pressure, is a saturated solution. As long as the solvent will dissolve more solute, the solution is said to be unsaturated.*

The addition of another crystal of the solute to a solution will indicate saturation or unsaturation. If the crystal added does not dissolve, the solution is saturated. From the point of view of the kinetic theory of matter, some of the crystals added to a saturated solution do dissolve, but just as many molecules of the solute come out of solution. Thus the crystals added do not appear to dissolve.

How supersaturation is used in purifying solids. It may sound contradictory to say that it is possible to prepare a *supersaturated solution,* that is, a solution which contains more of the solute than a saturated solution. But it is possible. For example, to prepare a supersaturated solution of hypo ($Na_2S_2O_3 \cdot 5H_2O$), we first make a saturated solution of this salt in boiling water, and then slowly cool the solution. The excess hypo does not come out of solution, as we would expect, but remains in solution. *Because this solution contains more solute than it normally holds at the lower temperature when saturated, it is called a supersaturated solution.*

Supersaturation is an unstable condition, and if the solution is disturbed by adding a tiny crystal of the solute, all of the *excess* salt separates out and the solution becomes saturated. Since only pure

crystals will separate out, this method is often used commercially in preparing chemically pure (C.P.) salt crystals. Because impurities are present to a small degree as a rule, they separate out later.

The effect of a solute on freezing and boiling points. As you know, the addition of salt to water lowers the freezing point of the solution. In general, a solute raises the boiling point and lowers the freezing point of a solvent a definite number of degrees. This principle is used in preparing *antifreeze mixtures,* which freeze at temperatures much lower than 0°C., the freezing point of pure water. A water solution that is 50 percent grain alcohol does not freeze until it reaches −31°C. Hence, solutions containing alcohol or other solutes are used in automobile radiators in cold weather.

All substances do not have the same effect on freezing and boiling points. Certain acids, bases, and salts raise the boiling point and lower the freezing point two or three times as much as other substances including sugar, alcohol, and glycerin. This singular behavior has an important relation to dissociation (see Chapter 16).

The difference between a solution and a suspension. If a substance does not actually dissolve but becomes mixed somewhat uniformly with a solvent and then separates on standing, the mixture is not a true solution but a *suspension.* Fine clay or other fine materials intimately mixed with water is a suspension.

The chief differences in behavior between a true solution and a suspension depend upon differences in the size of the particles of the solute in solution compared with the size of the particles in suspension. Particles of solutes in solution are in the molecular state of subdivision. But even the finest particles in suspension are much larger than molecules; hence, they settle out.

Particles in suspension may be separated by filtration; those in a solute cannot be separated by filtration. The solute of a true solution has a greater effect upon the boiling and freezing points of the solvent than the particles in suspension have on a suspension.

In the borderland between true solutions and suspensions is another condition of matter called the *colloidal state.* This condition of matter is so important that all of Chapter 38 is devoted to it.

How we purify water. Even before the germ theory of disease was proved, several methods were in use for the purification of water. In ancient times, water was made more fit to drink by filtering, boiling, or by allowing suspended impurities to settle out. Laws were passed to guard against the contamination of river water used for drinking purposes by prohibiting the washing of clothes and the disposal of refuse and sewage in it.

In a chemical sense most drinking water is not pure, for it contains dissolved minerals and gases. It is pure in a biological sense, which means that it is comparatively free from bacteria and other organic matter harmful to health.

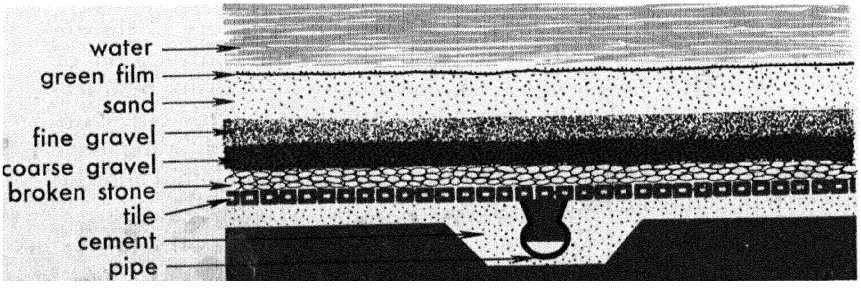
Water used for drinking purposes may be put through one or more of the following processes of purification, depending upon the nature of the impurities it contains:

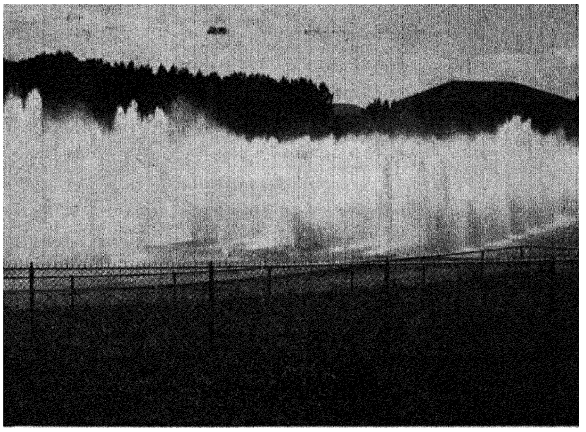
(1) *Aeration* consists of spraying the water into the air or letting it flow down a series of steps in thin sheets so that sunlight and oxygen may kill most bacteria present. (2) *Filtration* consists of straining the water through a suitable sieve (filter), thus separating substances either in suspension or afloat. Sand filtration dates as far back as 1829, when London purified its drinking water by passing the water through beds of fine sand. (3) *Chlorination,* discussed in Chapter 10. (4) *Ozonation,* discussed in Chapter 2. (5) *Coagulation* consists of adding alum or other chemicals that cause the organic matter containing bacteria and other suspended material to settle out. Coagulation is discussed more fully on page 396. (6) *Chloramination,* another process of water purification using both chlorine and ammonia is discussed on page 253. (7) *Demineralization* by means of synthetic resins (see page 491).

Modern sewage disposal. Closely related to the problem of maintaining an adequate supply of safe drinking water is the problem of disposing of the domestic and industrial wastes that are produced especially under the crowded living conditions of modern cities.

Sewage, as these wastes are called, includes chiefly the organic wastes that may be disposed of by *putrefaction,* a process that consists of a combination of bacterial action and oxidation. In some communities, sewage is discharged directly into streams which carry the sewage away. The dissolved oxygen in the water of the stream eventually oxidizes sewage; but, as a result, the dissolved oxygen

Fig. 46. Water filtration. As the water passes through the filtering layers, solid matter and many germs are removed.





An effective and relatively inexpensive method of purifying water is to aerate it by spraying it into the air.

is used up and all the fish and other higher plant and animal life normally found in the stream are unable to live in the water because they cannot obtain oxygen. Only a few of the lower forms of life, such as certain algae and bacteria, can live in the polluted stream, and the water is unfit for almost all purposes. Oxygen-consuming factory wastes are sometimes handled in disposal wells. Fortunately, the oxygen of the air cleanses the polluted stream in the course of its meanderings. The distance necessary to cleanse the stream depends upon several factors — the amount of sewage discharged, the size of the stream, its rate of flow, and so forth.

Most modern cities dispose of sewage by more modern and less harmful methods of treatment such as the *activated sludge process.* The sewage, which flows to the modern treatment plant in great quantities of flushing water, is first run into closed tanks where the solids settle as a *sludge,* or is run through sieves and screens that remove the suspended solids. Certain bacteria present in the sewage decompose the sludge, liberating both nitrogen and methane gas, and convert the sewage into a nontoxic, humus-like waste that may be used as a fertilizer. The partially purified water may be further purified by one of the methods of purification already discussed, or it may be discharged into a neighboring stream or body of water. In certain types of installations, the methane gas produced during the digestion of the sludge is burned in gas engines to produce the energy necessary to operate the sewage-treatment plant.

How water can be made chemically pure by distillation. None of the methods mentioned removes *all* impurities from water. Not one of them completely removes substances *dissolved* in water. Dissolved substances are completely removed from solution both in industry and in the laboratory by *distillation.* Because the boiling points of substances differ, it is possible to separate solute from

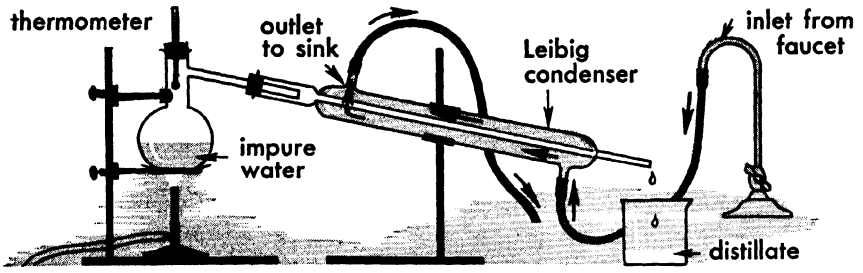


Fig. 47. Distillation of water using a Liebig condenser. Why should cold water enter the jacket at the lower end?

solvent. In general, solids that are dissolved in water have higher boiling points than water, and remain behind after the water has been boiled off. Certain liquids, including glycerin, have higher boiling points than water; others, as alcohol, have lower boiling points. Hence two or more liquids in solution may be separated by distillation. Gases in solution are driven off soon after the water is heated.

During distillation, water is first boiled, or evaporated, and then the steam, or water vapor, is cooled. This cooling condenses it into water again. Distillation is thus a double process, including both evaporation and condensation. The first portion of the *distillate,* the liquid that results from the condensation of the vapor, may contain small amounts of dissolved gases. The final portion of the distillate may contain small amounts of liquids or even dissolved solids whose boiling points are close to that of water. If these two portions are discarded, the rest of the distillate will be free of all impurities.

Stills used for industrial purposes are made of such material as copper, steel, lead-lined steel, and fused silica (SiO_2).

How water is distilled in the laboratory. The laboratory apparatus for water distillation consists of a flask, a Liebig condenser made popular in 1850 by Justus von Liebig (fôn lē'bĭĸ), a German chemist famed for his contributions to organic and agricultural chemistry, and a receiver. Impure water, which, for the purpose of the experiment, may contain small amounts of ammonia, salt, and red ink, is boiled in a sidearm flask, as shown in Fig. 47. A thermometer indicates the boiling point of the solution. The steam and water vapor pass into the inner glass tube of the Liebig condenser, which is surrounded by a glass jacket having a glass inlet and outlet for water. To condense the water vapor before it escapes from the inner glass tube, cold water is circulated through the outer tube of the condenser. As a result of this cooling, distilled water collects as the distillate.

Fractional, partial vacuum, and high vacuum distillation. When the boiling points of the impurities are very close to the boiling

point of the solvent, simple distillation is not very effective. For example, the boiling point of grain alcohol is 78°C., and if separated from water by a single distillation, the distillate is not pure.

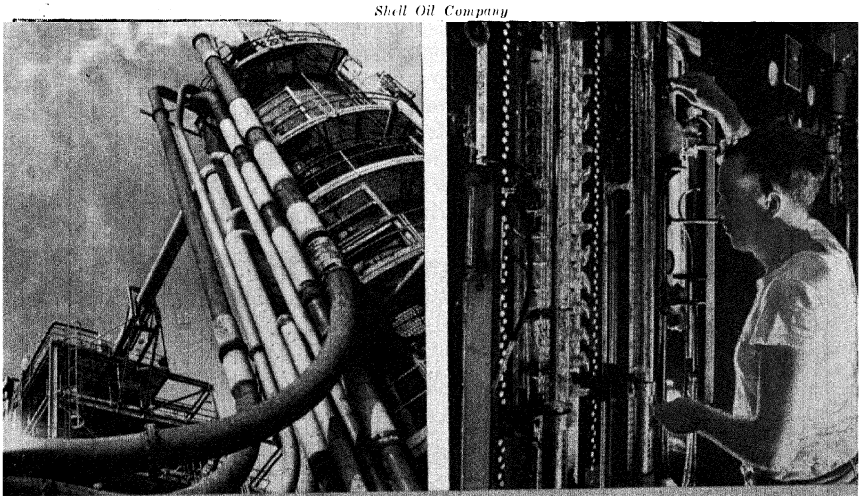
Oil refiners face a difficult problem in separating the liquids that make up crude petroleum. The boiling points of these liquids are so close together that he must resort to *fractional distillation.* This consists of heating the mixture carefully and separating it into its various liquid fractions, which boil off at different temperatures. For example, the first fraction might boil off below 200°C., the next between 200°C. and 220°C., and so forth. In each case, it is necessary to purify each fraction further by additional distillations.

It often happens that liquids cannot be separated by fractional distillation, because the high temperature required may char or otherwise decompose the solute. In such cases *partial vacuum,* or even *high vacuum distillation* is used. By reducing the pressure over the solution, its boiling point is also lowered.

According to the kinetic theory of matter, the molecules of water leave the liquid and become water-vapor molecules much more easily when the pressure over them is decreased. Water, for example, under normal atmospheric pressure boils at 100°C. If this pressure is lowered to one-half normal, water will boil at 82°C., and the process of distillation can be carried through at this lower temperature. Thus, water is removed from milk in making evaporated milk by partial vacuum distillation. Water is removed from sugarcane sap in making granulated sugar by reduced pressure distillation. High vacuum distillation is used in making vaccines, serums, antibiotics, blood plasma, frozen orange juice, and for coating metals.

The principle of distillation is used in both the huge petroleum "cracker" (left) and the laboratory fractionating equipment (right).

Shell Oil Company



Distilled water has many uses. Because distilled water is free from dissolved gases from the air, it is flat and insipid in taste. Its properties are those of chemically pure water (see page 65). Ordinarily, distilled water is not used for drinking purposes on land. However, at sea, drinking water is commonly prepared from sea water by distillation. The economic production of drinking water from sea water, which contains about 3.5 percent of dissolved salts, is very old, dating back at least to the time of Aristotle (about 350 B.C.).

Today, ships of nearly all kinds obtain drinking water by distilling sea water under reduced pressure. Seagoing vessels also produce water for use in boilers by distilling sea water under reduced pressure. In this way, all salts are removed, and subsequent treatment removes all traces of dissolved gases. Consequently, the operation of the boilers is not reduced in efficiency by the formation of large quantities of boiler scale (see page 489).

Today, aviators who are forced down at sea, and all abandon-ship equipment of warships and merchant vessels, carry small kits that may be used to prepare safe drinking water from sea water easily and simply. Such kits produce drinking water by chemical means. Their chemistry is discussed on page 491.

Distilled water is used in storage batteries, in which ordinary drinking water should not be used because of the harmful effect of its impurities on the plates of the battery. Distilled water is indispensable in many scientific and industrial operations. In the preparation of vaccines, pharmaceuticals, certain dyed textiles, and C.P. chemicals, distilled water is commonly used.

Heavy water, a powerful tool of research. The heavier hydrogen isotopes, deuterium and tritium (see page 56), may be represented respectively by the symbols *D* and *T*. It has been determined that the nucleus of deuterium contains one proton and one neutron. Therefore its atomic weight is two. The nucleus of tritium contains one proton and two neutrons and it has an atomic weight of three.

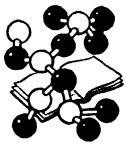
When water is formed from oxygen and one of the two heavy hydrogen isotopes, its molecular weight is greater than 18, the molecular weight of ordinary water. This water is called *heavy water*. Heavy water can also be formed from deuterium or tritium and any one of the three heavy isotopes of oxygen. Deuterium oxide, D_2O, is present in ordinary water to the extent of about one part of D_2O in 5000 parts of water. Tritium is seldom found in nature but is ordinarily made in an atomic pile.

Deuterium oxide has been prepared in large quantities. It differs to a small extent from ordinary water in both freezing and boiling

points. Its maximum density occurs at 11.6°C. rather than at 4°C., as is the case with H_2O. Heavy water is used in atomic piles as a moderator.

Deuterium oxide appears to arrest the growth of seedlings; tadpoles die prematurely in it; it is, however, not toxic to man and the higher animals.

Heavy hydrogen has been substituted for ordinary hydrogen in certain fats, and the course and changes which these "tagged" fat molecules have undergone on their way through the animal body have been studied by the tracer technique.



YOU WILL ENJOY READING

Cerna, Wendell W. "Industrial Water Conditioning Processes." *Journal of Chemical Education,* March, 1943, pp. 107–115, and April, 1943, pp. 191–197.

Ellis, Cecil B. *Fresh Water from the Ocean.* Ronald Press Company, New York, 1954. This is a conservation study dealing with water for cities, industry, and irrigation.

Goldblatt, L. A., Ed. *Collateral Readings in Inorganic Chemistry.* D. Appleton-Century Co., New York, 1937 (2nd series, 1942). No. 8 of the 31 articles in this collection deals with "Factors Contributing to Quality of Public Water Supplies." Written by H. E. Jordan.



USEFUL IDEAS DEVELOPED

1. A solution is a uniform mixture of solvent and solute which does not conform to the law of definite proportions.

2. A dilute solution contains very little solute in comparison with the solvent; a concentrated solution contains a large amount of solute.

3. Some of the factors which determine the amount of solute that will dissolve in a solvent are: (1) the nature of solute and solvent, (2) temperature, and (3) pressure. The speed of solution depends upon (1) the state of subdivision of the solute, and (2) how thoroughly the solute and solvent are intermingled.

4. All solutes raise the boiling point and lower the freezing point of the solvent. The amount of solute determines the number of degrees of change. Acids, bases, and salts in solution affect boiling and freezing points to a greater degree than do other substances, including alcohol, sugar, and glycerin.

5. Solutions and suspensions differ in the following respects: (1) In a suspension, the mixture separates on long standing. (2) The particles in suspension are much larger than the particles of a solute in a solvent (which are in the molecular state of subdivision). (3) The particles of a suspension may be separated out by filtration; the particles of a solution cannot be so separated. (4) A solute has greater effect on the freezing and boiling points than has a material in suspension.

6. The colloidal state of matter is in the borderland between true solutions and suspensions.

7. Distillation consists of evaporation and condensation. Impurities can be removed by distillation because of the difference in the boiling points of a solvent and its solute.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) What is the purest form of H_2O found in nature? (b) What property of H_2O makes it almost impossible to find pure H_2O in nature?

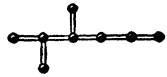
2. (a) What is a solution? (b) In a solution of NaCl in H_2O, which is the solvent and which the solute? (c) What is a tincture?

3. Distinguish a dilute solution from a concentrated solution.

4. Name four factors that determine the degree and the speed of solubility of a substance.

5. Why is more sugar or more stirring required to sweeten iced coffee than hot coffee?

6. Why should sealed bottles of H_2O heavily charged with CO_2 be kept cold?



7. How would you proceed to prepare a saturated water solution of washing soda, Na_2CO_3?

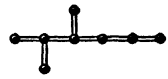
8. How could you change a saturated solution of $CuSO_4$ to an unsaturated solution having the same volume?

9. Without changing the temperature or volume of a solution of CO_2 in H_2O, how could you change an unsaturated solution of this gas into a saturated one?

10. How could you determine whether a solution is saturated, unsaturated, or supersaturated?

11. Mention one commercial use of supersaturation.

12. What is the effect of a solute on the freezing and boiling points of a solvent?



13. What principle is involved in the use of an antifreeze mixture in an automobile radiator?

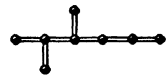
14. How do true solutions and suspensions differ?

15. What is the name given to the state of matter that is on the borderland between true solutions and suspensions?

16. What are seven methods used to purify drinking water?

17. How is sewage disposed of in modern sewage-disposal plants?

18. What may be the results of ineffective methods of sewage disposal?



19. Which method or methods of purifying H_2O produce chemically pure H_2O?

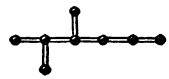
20. (a) What is distillation? (b) Upon what fact does the separation of impurities by distillation depend?

21. Why is the middle portion of a distillate the purest?

22. Make a diagram of the apparatus used in the laboratory distillation of H_2O.

23. (a) Is the drinking water of a large city, such as Chicago or New York, distilled? (b) Give reasons for your answer.

24. Petroleum is refined by fractional distillation. Why?



25. Why are liquids often distilled under reduced pressure?

26. State the physical properties of distilled water.

27. For what is distilled water used?

28. What are the desirable characteristics of drinking water?

29. What is the difference between *wholesome water* and *chemically pure water*?

30. (a) What is heavy water? (b) How does it differ from ordinary water? (c) Name two uses of heavy water.

Group B

31. Devise an experiment to show that perfectly clear spring water contains impurities.

32. Small filters attached to household faucets sometimes become a menace to health. Explain this statement.

33. What would be the effect of the continued use of rain water in storage batteries?

34. Is water obtained by melting ice from a lake purer than the water of that lake? Explain your answer.

35. If a liquid is colorless, odorless, and clear, how could you determine whether it is a solution or a pure compound?

36. How does a solution of NaCl in water differ from a mixture of NaCl and sugar?

37. Can a dilute solution be a saturated solution also? Explain.

38. Explain the operation and principle of the pressure cooker.

39. (a) Explain solution by means of the kinetic theory of matter. (b) According to the kinetic theory, explain why it is easier to evaporate or distill a liquid under reduced pressure.

40. Would there be any advantage or disadvantage in making solutions of (a) table salt, (b) calcium hydroxide, with hot water instead of cold? (c) Explain each answer.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

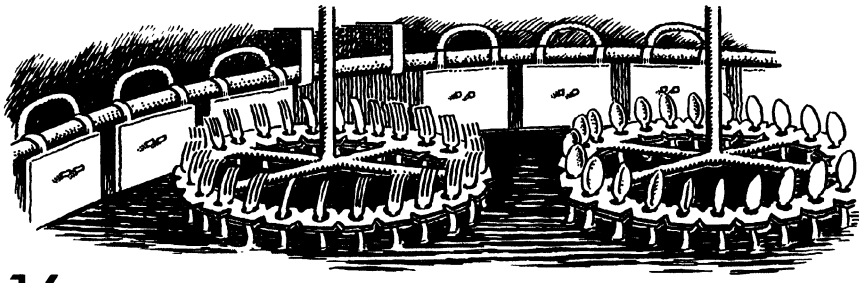
1. Visit your local sewage-disposal plant, and study its operation. Make a report on this visit to your class.

2. Obtain some Rochelle salt (U.S.P.) from your teacher or druggist and prepare pure crystals from it. Bring them to class and explain the process you used. (As a substitute, you may prepare "rock candy" crystals.)

3. Harold C. Urey, discoverer of heavy water, in a lecture in 1938, made the following statement, "I believe I speak for the vast majority of all scientific men. Our object is not to make jobs and dividends. These are a means to an end, merely incidental. We wish to abolish drudgery, discomfort and want from the lives of men, and bring them pleasure, comfort, leisure and beauty. Often we are thwarted but in the end we will succeed." Write a short report either for or against this view, or organize a class discussion on this subject.

4. Study the methods of water purification in your own community. Report to your class on this subject. Find out, if you can, the mineral content of the water and the amount and kind of suspended solids present both before and after treatment.

5. Using *hypo* (sodium thiosulfate) prepare 10 ml. of a supersaturated solution. Allow the solution to cool slowly to room temperature. Then add a crystal of hypo. Repeat this before your class if it can be arranged.



16 IONS AND DISSOCIATION

. . . I heard Clève say: "Do you believe sodium chloride is dissolved into sodium and chlorine? In this glass I have a solution of sodium chloride. Do you believe there are sodium and chlorine in it?" "Oh, yes," Ostwald replied, "there is some truth in that idea." . . . Clève threw a look at Ostwald which clearly showed that he did not think much of his knowledge of chemistry.

Svante Arrhenius, 1925

Two eternal questions: How? and Why? Science is constantly trying to answer two questions — *how* and *why*. Often it is not too difficult to answer the *hows* but the *whys* — well, that is a different story. Theories must be formulated, tested, and adapted to keep them in accord with *all* the observed facts, and that is a big job.

At least two great theories underlie much of chemistry: the electron theory and the theory of dissociation. In a sense, the theory of dissociation is but an aspect of the electron theory, for the theory of dissociation is explained in terms of the electron theory. These two great theories explain some of the *hows* and *whys* of chemistry.

A Swedish boy tackles some puzzling questions. Why is distilled water a nonconductor of electricity? Why do water solutions of some substances conduct electricity yet water solutions of other substances do not? What causes some acids and bases to be strong while others are weak?

These were some of the unsolved problems that confronted chemists when Svante Arrhenius (ȧr-rā'nĭ-ŭs) was still at school in Sweden.

Arrhenius not only wondered about these problems but set to work to solve them. He had some unusual notions of his own about the

way in which electricity passes through solutions. Day after day, and often far into the night, he worked in his laboratory with hundreds of different solutions. For two years he toiled ceaselessly.

Arrhenius attempted to formulate a theory that would explain what he had observed. In those days his whole world, both of waking and sleeping hours, was one of solutions, electric currents, and formulas. For him the rest of the world did not exist. One night he sat up very late. Suddenly, like a flash, he saw the answer to the great riddle. "I got the idea," he wrote, "in the night of the 17th of May in the year 1883, and I could not sleep that night until I had worked through the whole problem."

He went to his teacher of chemistry. "I have a new theory of electrical conductivity," Arrhenius told him. The professor looked at this boy and said: "You have a new theory? That is very interesting. Good-by." But Arrhenius did not lose heart. He wrote to the leaders in chemistry. Most of them were hostile to his revolutionary theory. After a long struggle, however, they were forced to admit its probable truth and later saw Arrhenius awarded the Nobel prize in chemistry. And so it happened that a mere boy, with the clear insight and the creative imagination of a truly great scientist, stepped in and cleared away an obstacle that had stood squarely in the path of chemical progress.

How Arrhenius explained the conductivity of solutions. The theory proposed by Arrhenius is known as the *theory of ionization,* or *dissociation.* Arrhenius assumed that when an electrolyte, such as sodium chloride, dissolves in water, it tends to *dissociate,* or *ionize.* That is, it tends to break apart into electrically charged atoms or groups of atoms (radicals). Arrhenius used the term *ion,* meaning *wanderer,* to refer to an atom or group of atoms carrying an electric charge. He represented the dissociation of the sodium chloride molecule into ions when it dissolves in water thus:

$$NaCl \rightarrow Na^+ \text{ (sodium ion)} + Cl^- \text{ (chloride ion)}$$

He represented the dissociation of the sodium nitrate molecule thus:

$$NaNO_3 \rightarrow Na^+ + (NO_3)^-$$

Arrhenius could not see the ions in solution. They are far too small to be seen. He advanced the theory that they were present because he could account for what he observed *only by assuming* such ions to be present. To him, when an electrolyte dissolves, a certain number of its molecules immediately split up into ions. Thus an electrically

neutral compound tends to dissociate into a number of positively and negatively charged particles, or ions. They move about in all directions until the passage of an electric current draws each ion to the electrode bearing an opposite charge.

It is the ions that carry an electric current, or flow of electrons. Hence a substance that does not dissociate into ions is a nonelectrolyte, and a substance of which a large proportion dissociates in water solution is a good electrolyte. Arrhenius' theory of ions and of electrolytic dissociation is today, with certain modifications, universally accepted as the correct explanation of the conductivity of solutions.

How an ion differs from an atom. There are two main differences between an atom and an ion: (1) An atom is electrically neutral; an ion is positively or negatively charged. (2) An atom always consists of a single element; an ion may consist of one or more than one element, as in the case of the ammonium ion, $(NH_4)^+$. A sodium atom is quite different from a sodium ion. The former is a silvery metal particle that reacts violently with water; the latter is a colorless particle that has no noticeable reaction with water.

The dissociation of zinc chloride may be represented thus:

$$ZnCl_2 \rightarrow Zn^{++} + 2Cl^-$$

Note the change from Cl_2 in $ZnCl_2$ to 2 Cl^- when the zinc chloride is dissociated into ions. The number of positive or negative charges on the ion is equal to the valence of the element or radical.

PRACTICE WORK ON DISSOCIATION EQUATIONS. Write equations showing what happens when the following electrolytes dissociate:

a) Nitric acid, HNO_3.
b) Lithium hydroxide, LiOH.
c) Potassium hydroxide, KOH.
d) Ammonium hydroxide, NH_4OH.
e) Barium hydroxide, $Ba(OH)_2$.
f) Aluminum chloride, $AlCl_3$.
g) Sulfuric acid, H_2SO_4.
h) Potassium carbonate, K_2CO_3.
i) Sodium phosphate, Na_3PO_4.
j) Potassium chlorate, $KClO_3$.
k) Magnesium bicarbonate, $Mg(HCO_3)_2$.
l) Calcium nitrate, $Ca(NO_3)_2$.

Where and how are free ions formed? Most commonly, dissociation takes place in a water solution. However, it also occurs in compounds such as sodium hydroxide, NaOH, when they are heated until they melt, or *fuse*. Such compounds are made up, *not of molecules,* as was previously supposed, but of *ions* in a definite pattern (see

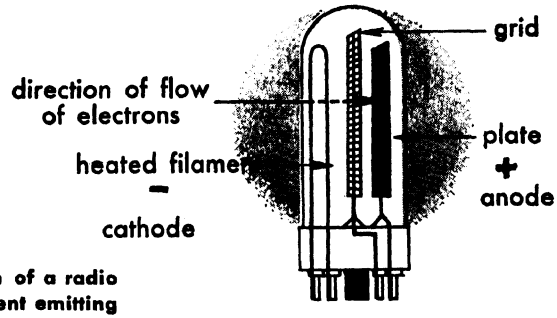


Fig. 48. Simplified diagram of a radio tube showing the hot filament emitting a stream of electrons.

page 631). As the compound is heated, its ions vibrate more rapidly and eventually tear apart, leaving them free to carry an electric current. Gases, too, at very high temperatures dissociate into ions, thus becoming conductors of electricity. Flames, x-rays, and radioactive elements ionize the air around them.

A metal, when heated to incandescence, boils off electrons from the outer rings of its atoms. This principle is used in the *electron* tubes so familiar to us in radios, television sets, and other electronic instruments. Certain types of electron tubes are filled with a gas or mixture of gases at low pressure. Electrons from the hot cathode of the tube strike the molecules of the gas, ionizing them.

The positive ions move toward the negative electrode, or cathode, and the negative ions and electrons move toward the positive electrode, or anode. In a radio tube, the anode is the plate, and the cathode may be the hot filament. Thus a stream of electrons or electric current flows through the tube. Because a gas-filled tube contains more molecules that can be ionized than does a vacuum tube from which most of the molecules have been removed, relatively large currents can flow through a gas-filled tube. The *thyratron* tube, often employed as a rectifier, is a common example of a gas-filled electron tube.

How Arrhenius explained the action of acids. All acids in water solution contain free hydrogen ions. These hydrogen ions determine the typical properties of acids. It is the free hydrogen ion that turns blue litmus pink, has a sour taste, is replaceable by a metal, and neutralizes a base by combining with its hydroxyl ion.

The number of hydrogen ions present determines the strength of an acid. A *strong acid* is one that *dissociates easily,* and thus produces a large number of hydrogen ions. The most commonly used strong acids are hydrochloric, nitric, and sulfuric acids. Carbonic acid, H_2CO_3, sulfurous acid, H_2SO_3, and boric acid, H_3BO_8, are *weak acids,* because they do not dissociate easily, and thus form only a *small number of hydrogen ions* in solution.

How Arrhenius explained the action of bases. What has been said about strong and weak acids refers equally well to strong and weak bases, except that the determining factor here is the number of free hydroxyl $(OH)^-$ ions present. In water solution, a *strong base,* such as sodium hydroxide, NaOH, potassium hydroxide, KOH, or lithium hydroxide, LiOH, forms *large numbers of hydroxyl ions.* A *weak base,* such as ammonium hydroxide, NH_4OH, produces a comparatively *small number of* $(OH)^-$ *ions.*

Some bases, like copper hydroxide, $Cu(OH)_2$, and aluminum hydroxide, $Al(OH)_3$, are extremely weak, because, in addition to the fact that they form a relatively small number of ions, they are also only sparingly soluble. The properties of bases are caused by the presence of free hydroxyl ions. Hence dry, solid sodium hydroxide has no basic properties; that is, it does not react as a base.

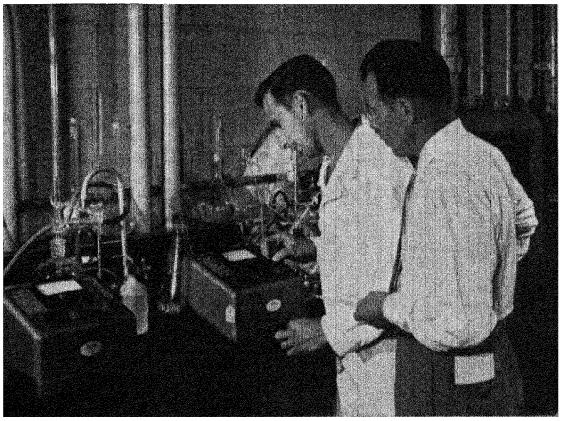
How the theory of Arrhenius explained neutralization. The hydrogen ion and the hydroxyl ion are responsible for acidic and basic properties respectively. If these free ions are removed, acidic and basic properties are destroyed. This is exactly what happens in neutralization. The hydrogen ion of the acid unites with the hydroxyl ion of the base, forming water, a nonelectrolyte.

$$Na^+ + (OH)^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + HOH$$

Hydrogen-ion concentration (*p*H) and how it is measured. It is frequently important to know whether complete neutralization has been produced, or what the degree of acidity or alkalinity (basicity) of a substance is. Sugar-refiners, brewers, paper-makers, electroplaters, sanitary engineers, and bacteriologists must have a working knowledge of the acidity or alkalinity of many substances.

Chemists make use of a *hydrogen-ion scale* in which the unit is the *p*H *value* (pronounced by reading the letters p, H), just as the unit of temperature is a degree. A *p*H value of seven is considered

The Dow Chemical Company



Chemists in professional laboratories use special equipment to determine the pH value of solutions.

true neutralization. Pure water has such a value. A *p*H value less than seven indicates an acid condition. Thus, saliva has a *p*H value of about 6.9 and is slightly acid. A *p*H value greater than seven indicates an alkaline condition. Thus, normal blood has a *p*H value of about 7.3 and is slightly alkaline. A value higher than 7.5 represents a condition of *alkalosis.* Since the human blood is normally slightly alkaline, a *p*H below 7.2 indicates a condition of *acidosis.* A *p*H value of five represents an acidity 10 times as great as a *p*H of six.

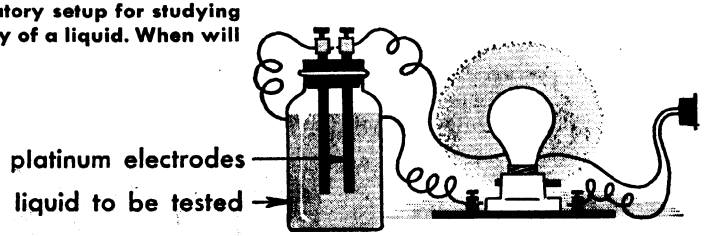
Litmus may be used as an indicator only with those solutions whose *p*H is not less than four or greater than eight. Other indicators have wider or narrower ranges. By comparison with standard color tubes for each indicator, the degree of acidity or alkalinity of a liquid can be determined accurately.

Several types of indicator papers have been developed for determining the *p*H values of solutions. The use of such papers containing water-soluble dyes is very convenient and is much quicker than referring to standard color tubes. One such paper is known as "Hydrion Paper."

How the degree of dissociation was determined. We have seen that some substances produce a large percentage of ions and other substances produce a small percentage of ions. In other words, compounds differ in the extent to which they form ions in solution, that is, in their degree of dissociation. *The degree of dissociation of a solution depends upon (1) the solute, (2) the solvent, (3) the concentration of the solution, and (4) the temperature.*

The degree of dissociation is measured by *electric conductivity,* that is, the ease with which an electric current passes through a solution. This may be determined roughly by setting up an apparatus as shown in the illustration below (Fig. 49). When the bottle contains carbonic acid (a weak acid) the electric-light bulb glows faintly. When it contains a dilute solution of hydrochloric acid (a strong acid), the light bulb glows brightly, showing that little resistance is being offered to the passage of the current. A solution of sugar in water, when placed in the bottle, does not produce a glow in the bulb, and thus shows that a sugar solution is a nonelectrolyte.

Fig. 49. Laboratory setup for studying the conductivity of a liquid. When will the bulb light?



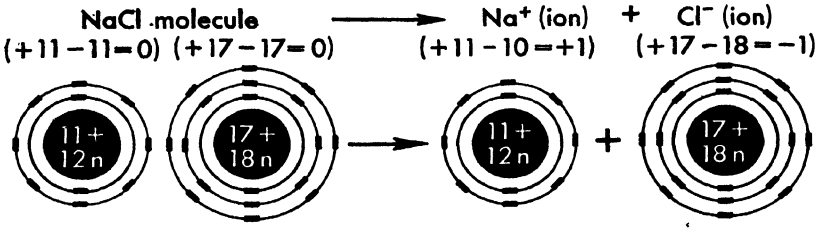
Arrhenius determined the *apparent* percentage of dissociation of many compounds by this method. He found that in one-tenth normal water solution (0.1N) the *apparent* dissociation of hydrochloric acid, nitric acid, and sodium hydroxide was about 92 percent (strong electrolytes); that of sulfuric acid about 61 percent; that of potassium chloride about 86 percent; and that of acetic acid, ammonium hydroxide, and mercuric chloride only about 1 percent (weak electrolytes). Later it was found that this method had certain limitations.

How Arrhenius explained abnormal boiling and freezing points of solutions. The theory of ionization also explains why certain acids, bases, and salts raise the boiling points of their water solutions to an abnormally high degree, though sugar does not to the same extent. The acid dissociates and produces two or three times as many particles (ions) as there are molecules of undissociated sugar. The higher percentage of dissociation of the acid produces a greater increase in the boiling point, since it is the actual number of particles (ions or molecules) in solution that determines both the boiling and freezing points of a solution.

How the theory of ionization fits in with the electron theory. When Arrhenius proposed his theory of dissociation, the electron was still undiscovered, and the electron theory of matter had not yet been formulated. Ions, however, fit in beautifully with our present electron concept of matter. *Atoms become ions by gaining or losing electrons.* For example, if an electrically neutral atom of sodium ($Na\pm$) *loses 1 electron,* it becomes a positively charged particle, and we represent it Na^+. This is a sodium ion ($Na^0 - \epsilon \rightarrow Na^+$). Similarly, if an electrically neutral atom of chlorine ($Cl\pm$) *gains 1 electron,* it becomes a negatively charged particle, and we write it Cl^-. This is a chloride ion ($Cl^0 + \epsilon \rightarrow Cl^-$).

The compound made up of these elements (NaCl) is really composed of both of these ions held strongly together, making what is known as an *ion-molecule* that is electrically neutral. However, when these ion-molecules are placed in water, they are split into two parts, and so long as water is present, we have separate sodium ions and chloride ions. Dissociation, then, may be represented as shown below.

Fig. 50. Dissociation of a sodium chloride molecule, according to the electron theory.



The charge on the ion is thus seen to be the same as the valence of the element.

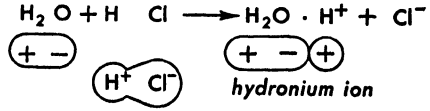
How the theory of Arrhenius was later modified. In general, Arrhenius' theory has stood the test of time very well. In three respects, however, it has been modified slightly.

1) The Swedish chemist thought that water simply kept the ions apart, but today we have a better understanding of the important role of the solvent. The covalent water molecule is pictured as a tiny magnet with a *plus* hydrogen end and a *less positive* oxygen end. Such a molecule is called a *dipole.*

When crystals of the polar compound, NaCl (made up of a lattice of Na and Cl ions — see page 630), are added to water, the positive end of the dipole molecule attracts the negative Cl ion; the other end of the dipole attracts the positive Na ion. The Na and Cl are thus dissociated and free sodium and chloride ions are produced in solution. When the water is evaporated, the ions recombine forming ion-molecules of NaCl crystals. NaCl and other ionic compounds are *strong* electrolytes.

2) The Brønsted-Lowry theory has added to what Arrhenius believed about the ionization of acids. According to this theory, an acid is a proton (hydrogen ion) donor; that is, any compound *that tends to lose a proton* (H+) to another substance is an acid.

For example, in the case of a water solution of HCl, the water molecule combines with the positive hydrogen ion end (proton) of the HCl, forming a hydrogen (hydronium) ion, leaving the chlorine negatively charged, thus:



As HCl dissolves in water, heat is liberated, indicating a chemical change is taking place. The hydronium ion is an *acid* since it may give up its proton. It is also written as H_8O^+.

A base is a proton *acceptor.* A base is any substance which combines with a hydrogen ion or proton. Thus the water molecule which will accept a proton is a base, though not an active one. Bases are often negative ions such as OH^-, which is an active one.

3) Insofar as weak electrolytes are concerned, the theory expressed by Arrhenius is still correct. They are *not* completely dissociated. In the case of strong electrolytes, however, it is now believed that they dissociate *completely.* The fact that the heat of

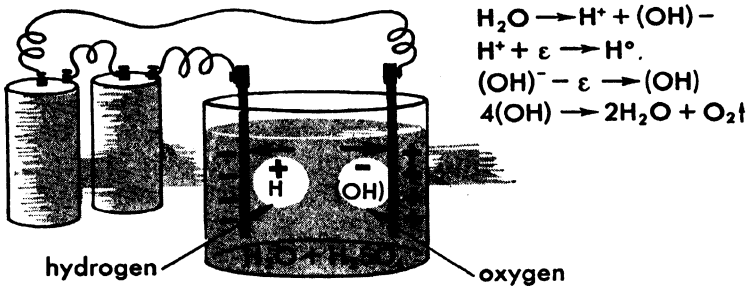


Fig. 51. Action during the electrolysis of water.

neutralization of all strong acids and bases is the same is one evidence in support of this belief. The fact that when dilute solutions of strong electrolytes are mixed there is no trace of heat is further proof. The degree of dissociation of weak electrolytes can be determined accurately, but that of strong electrolytes cannot because of the disturbing electrical effects of a large concentration of ions. In such a high concentration, ions do not behave as "free ions" and only an *apparent* ionization is obtained.

The theory of dissociation as stated by Arrhenius is still useful. Other new ideas have added to the accuracy of our concept of dissociation. For example, we know that molecules of compounds such as carbon dioxide do not dissociate in solution and are nonelectrolytes because they are nonpolar. However, these new ideas are of value chiefly in dealing with phenomena which are beyond the scope of this book. For this reason, we shall follow the theory of ionization as Arrhenius originally presented it.

What happens during the electrolysis of water? So far we have considered pure water a nonelectrolyte. Roughly speaking, this is true, since in about 1 billion grams of water only about 1 gram of free hydrogen ions is present. Yet this very slight dissociation of water [$H_2O \rightarrow H^+ + (OH)^-$] is important. Water is such a poor conductor that acid must be added to conduct the current. Nevertheless, the hydrogen and oxygen that are products of electrolysis come from the water. How?

The positive hydrogen ions travel to the negative cathode. The cathode, connected to a battery, is supplied with electrons. When the hydrogen ion reaches the cathode, an electron, ϵ, from the cathode is given up to the hydrogen ion, which changes to a neutral hydrogen atom. This atom immediately joins another hydrogen atom and is liberated as a molecule of gas, thus:

$$H^+ + \epsilon \rightarrow H^0; \quad H^0 + H^0 \rightarrow H_2\uparrow$$

The negative sulfate ions, and hydroxyl ions from the water, travel to the positive anode. The hydroxyl ion gives up its electron more readily than does the sulfate ion. Having lost its electron, it becomes the hydroxyl radical, which breaks down, forming water and oxygen. The sulfate ions remain in solution. The concentration of the acid remains unchanged.

$$(OH)^- - \epsilon \rightarrow (OH); \quad 4(OH) \rightarrow 2H_2O + O_2 \uparrow$$

What is hydrolysis? We should expect neutral salts to show neither acid nor basic properties, since they contain neither hydrogen nor the hydroxyl radical which might form ions. Yet when we add blue litmus to a solution of copper sulfate, the litmus turns pink, indicating an acid. Where are the free hydrogen ions to account for this behavior? The answer lies in the fact that water is slightly dissociated.

$$Cu^{++} + (SO_4)^{--} + 2HOH \rightleftarrows 2H^+ + (SO_4)^{--} + Cu(OH)_2$$

Since the copper hydroxide formed is only very slightly dissociated, there will be some union of Cu^{++} and $(OH)^-$, thus forming this very weak base, and liberating an excess of hydrogen ions that form the strong acid, sulfuric acid. Therefore, the solution is slightly acid. This reaction is the reverse of the neutralization of sulfuric acid by the base $Cu(OH)_2$. *Hydrolysis of a salt is the action between the ions of water and the ions of a dissolved salt, forming an acid and a base.*

Hydrolysis also explains the basic nature of Na_2CO_3, thus:

$$2Na^+ + (CO_3)^{--} + 2HOH \rightleftarrows 2Na^+ + 2(OH)^- + H_2CO_3$$

Since the H_2CO_3 is a weak acid, there will be some union of H^+ and $(CO_3)^{--}$, thus forming the slightly dissociated H_2CO_3, and liberating an excess of OH ions which form the strong base, NaOH.

A solution of sodium chloride and water is perfectly neutral, since it is made from a strong acid and a strong base. A solution of a salt made from a strong base and a weak acid, or from a weak base and a strong acid, does not show a neutral reaction.

PRACTICE WORK ON EQUATIONS REPRESENTING THE HYDROLYSIS OF COMPOUNDS

Complete the following equations, and tell whether the solution in each case will be acidic, basic, or neutral toward litmus:

a) $K_2CO_3 + 2HOH \rightarrow$
b) $ZnSO_4 + 2HOH \rightarrow$
c) $AlCl_3 + 3HOH \rightarrow$
d) $Na_2SO_4 + 2HOH \rightarrow$
e) $KNO_3 + HOH \rightarrow$
f) $K_2SO_4 + 2HOH \rightarrow$

What are reversible reactions? Most reactions we deal with are reactions that take place in water solutions and, hence, are reactions between ions. The presence of free ions facilitates chemical changes. If we dissolve sodium chloride, NaCl, and potassium nitrate, KNO_3, in water, these salts immediately dissociate, forming free Na^+, Cl^-, K^+, and $(NO_3)^-$. These swiftly moving ions constantly meet and form molecules of KNO_3 and NaCl. The entire reaction, therefore, is said to be *reversible,* that is, it goes in both directions.

$$KNO_3 + NaCl \rightleftarrows KCl + NaNO_3$$

A reversible reaction always reaches a point at which change is no longer apparent. In other words, the reaction has reached a point of balance or *equilibrium.* This does not mean that nothing is happening. On the contrary, the equilibrium is *dynamic,* or moving, for the substances are breaking up as rapidly as they are being formed.

Reversible reactions and equilibrium. The dissociation of an electrolyte is a reversible reaction. Thus, when acetic acid, $HC_2H_3O_2$, is dissolved in water, free hydrogen ions and free acetate ions are formed. These ions meet and form acetic acid.

$$HC_2H_3O_2 \rightleftarrows H^+ + (C_2H_3O_2)^-$$

Finally a time is reached when the rate of change from free ions to $HC_2H_3O_2$ will just equal the rate of change from $HC_2H_3O_2$ to free ions. This will happen, in the case of a 0.01N acid solution, when 98.7 percent of the $HC_2H_3O_2$ is in the form of free ions and 1.3 percent is in the form of $HC_2H_3O_2$. When this condition is reached, it would appear that the $HC_2H_3O_2$ is no longer dissociating and that a condition of stable equilibrium has been reached. In reality the equilibrium is not stable but dynamic, or changing. Changes go on even after the 98.7 : 1.3 ratio is attained, but while new $HC_2H_3O_2$ is being formed, more is being ionized, keeping the same ratio.

When do reactions go to completion? Substances that do not dissociate cannot react readily with other substances that do. If even one of the products of a reaction is unable to dissociate to any great extent, the backward action cannot take place. The reaction is then said to *go to completion.* Advantage is taken of this to secure reactions that complete themselves.

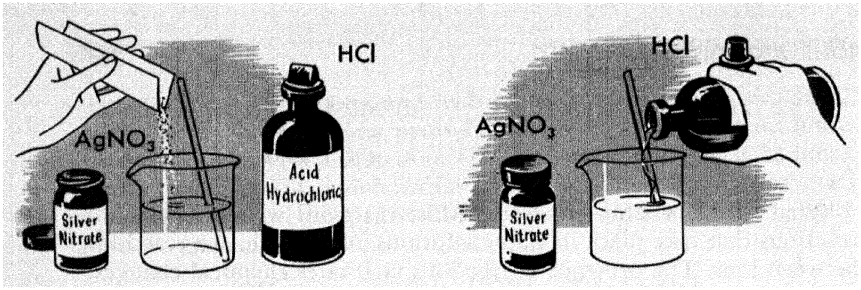


Fig. 52. Action of silver nitrate and dilute hydrochloric acid. Does this reaction go to completion? Why? Under what conditions do reactions go to completion?

Insoluble substances, called *precipitates,* gases liberated under normal temperature conditions, and pure water are practically incapable of dissociation. Hence a reaction will go to completion whenever one of the products formed is (1) a precipitate, (2) a gas, or (3) water. Examples of such reactions follow:

1) *Formation of a precipitate.* Chemists use as tests reactions in which precipitates are formed. Thus, in testing for a chloride, silver nitrate, $AgNO_3$, is added. The formation of insoluble silver chloride, AgCl, prevents the reaction from reversing itself.

$$Ag^+ + (NO_3)^- + Na^+ + Cl^- \rightarrow AgCl \downarrow + Na^+ + (NO_3)^-$$

2) *Formation of a gas.* In the laboratory preparation of hydrogen chloride, a mixture of sodium chloride and sulfuric acid is heated, and the hydrogen chloride gas that is liberated leaves the field of action. Hence the reaction does not reverse itself.

$$Na^+ + Cl^- + H^+ + (HSO_4)^- \rightarrow HCl \uparrow + Na^+ + (HSO_4)^-$$

3) *Formation of undissociated water.* During neutralization, water is always one of the products formed. Therefore the neutralizing reaction is complete, since water, which is practically undissociated, may be considered as having left the field of chemical action.

$$Na^+ + (OH)^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + HOH$$

This is strictly true only when the salt formed is not hydrolyzed.

PRACTICE WORK ON EQUATIONS REPRESENTING REACTIONS THAT GO TO COMPLETION

1. Complete and balance the following equations:

a) $KNO_3 + NaCl \rightarrow$
b) $BaCl_2 + K_2SO_4 \rightarrow$
c) $NaOH + PbCl_2 \rightarrow$
d) $KOH + H_2SO_4 \rightarrow$

e) $Na_2SO_3 + H_2SO_4 \rightarrow SO_2 + H_2O +$
f) $FeS + HCl \rightarrow$
g) $CaCO_3 + HNO_3 \rightarrow CO_2 + H_2O +$
h) $CaCl_2 + NaNO_3 \rightarrow$
i) $Na_2SiO_3 + Ca(OH)_2 \rightarrow$

2. Examine the foregoing equations and, in each case, see whether any of the products formed are gases or precipitates. Mark them with the appropriate arrows, ↑ or ↓. Remember that SO_2, H_2S, and CO_2 are gases.

3. Finally, with the aid of the following table of solubilities, tell whether *each* of the reactions goes to completion or not, stating your reason in each case.

TABLE 10. SOLUBILITY OF COMMON COMPOUNDS

All *nitrates*, *chlorates*, and *acetates* are soluble in water.
All *chlorides*, *bromides*, and *iodides* are soluble, except those of Ag, Pb, and Hg.
All *sulfates* are soluble, except $PbSO_4$, $BaSO_4$, $CaSO_4$, $HgSO_4$, and Ag_2SO_4.
All *hydroxides* are insoluble, except those of Na, K, NH_4, Ca, and Ba.
All *sulfides* are insoluble, except those of Na, K, NH_4, Ca, and Ba.
All *oxides* are insoluble, except those of Na, K, and Ca.
All *carbonates*, *silicates*, and *phosphates* are insoluble, except those of Na, K, and NH_4.

The law of mass action and equilibrium. The quantity of a substance in a unit volume of solution is a measure of the *concentration* of a solution. As early as 1803, the French chemist Claude Berthollet (who first made use of the bleaching action of chlorine) noticed that the direction of a chemical reaction is dependent upon the concentrations of the substances involved in the reaction.

He noticed that, in general, the greater the concentration, the greater the speed of the reaction. For example, a match burns quietly in ordinary air which contains about 21 percent oxygen. In pure oxygen, however, the match burns much more quickly, since the concentration of the oxygen (one of the reacting substances) has been increased almost fivefold. A greater concentration of oxygen means more molecules of oxygen per unit volume of gas, and, therefore, a greater possibility for oxygen molecules to come in contact with molecules of carbon and carbon compounds. This causes an increase in the speed of the chemical reaction involved in burning.

Sixty-four years later, Guldberg and Waage, professors of mathematics and chemistry at the University of Oslo, Norway, demonstrated that the speed of a chemical reaction is *directly proportional* to the concentrations of the reacting substances. They also made an interesting discovery concerning the point of dynamic equilibrium

of a chemical reaction — that is, the point at which the reaction in one direction just balances the reaction in the opposite direction. They found that a chemical reaction which is normally reversible can be forced to go in one direction with small reversal. This is accomplished by manipulating the concentrations of the reacting substances.

Guldberg and Waage expressed this phenomenon in the form of the *law of mass action,* which implies that *a change in the quantity of the reacting substances* results in a change in the equilibrium point of the reaction. In the manufacture of chemicals, the direction of a reaction is so controlled that large yields are produced.

How the addition of a common ion forces a reaction to go to completion. In the light of the law of mass action, let us consider a saturated solution of sodium chloride. We may express the reaction that is taking place as:

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

In such a reaction, *the product of the concentrations of the free sodium ions and the free chloride ions is a constant.* If, by any means, we *increase* the number of chloride ions, the number of sodium ions must *decrease.* The number of sodium ions can decrease only if some of the sodium chloride comes out of solution.

To increase the chloride ions, we add to the solution a compound of chlorine that dissociates to a high degree. Hydrochloric acid is such a compound. Therefore, if hydrochloric acid is added to a saturated solution of sodium chloride, some of the sodium chloride will be precipitated. We call this shifting of the equilibrium point the *common-ion effect.* In this case, the common-ion effect is caused by the addition of the chloride ion, which is common to HCl and NaCl.

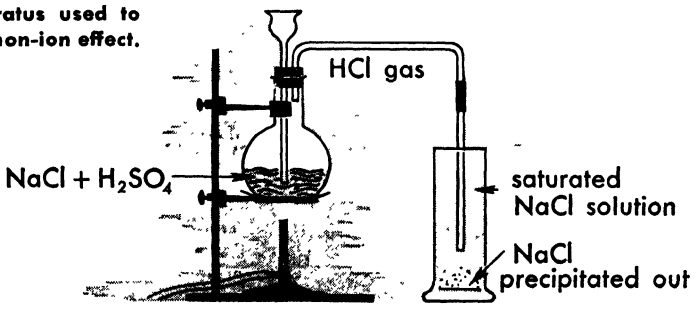
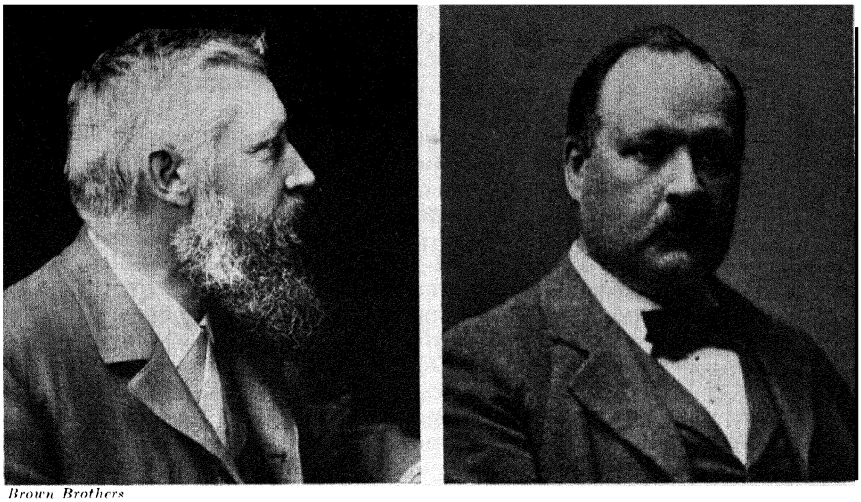


Fig. 53. Apparatus used to show the common-ion effect.

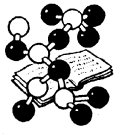


Brown Brothers

Svante Arrhenius (right) and his close friend, Wilhelm Ostwald. Each was awarded a Nobel prize for chemistry, Arrhenius in 1903, Ostwald in 1909.

Almost insoluble salts, such as silver chloride, AgCl, may be completely precipitated by adding a common ion. Thus, the addition of an excess of NaCl increases the concentration of the few dissociated chloride ions from the silver chloride, and causes some more AgCl to precipitate.

A weak acid may be weakened by adding a salt of the weak acid. Thus the addition of sodium citrate to citric acid weakens that acid, because the addition of the common ion (the citrate ion) forces more of the citric acid to the undissociated form.



YOU WILL ENJOY READING

Jaffe, Bernard. *Crucibles: The Story of Chemistry*, pp. 219–241. Simon and Schuster, New York, 1948. The story of the life and work of Arrhenius.

Sammis, Constance S. "How Annabella Learned the Facts about *pH*." *Journal of Chemical Education*, Oct., 1942, pp. 490–494. A delightful, cleverly illustrated treatment of a very important topic.



USEFUL IDEAS DEVELOPED

1. Science must always answer at least two questions — how? and why?

2. Two great theories underlie much of chemistry: (1) the electron theory and (2) the theory of dissociation.

3. The theory of ionization was advanced to explain electrolysis, nonelectrolytes, strong and weak acids and bases, and other puzzling facts.

4. An ion is an atom or radical that carries an electric charge.

5. When an acid, base, or salt goes into solution, it dissociates, partially forming free ions. When a current is passed through such a solution, the ions are attracted to the electrodes having a charge opposite their own.

6. Free ions are formed in greatest numbers in water solutions of electrolytes. Free ions occur also in molten substances, in heated gases, and in the air surrounding radioactive substances. Atoms of glowing metals throw off electrons; if the electrons come in contact with a gas, as in a radio tube, the molecules of the gas become ionized.

7. In terms of ionization, an acid is a substance that produces free hydrogen ions; a base is a substance that produces free hydroxyl ions.

8. A strong acid is one that dissociates easily, forming large numbers of hydrogen ions. A weak acid forms only a small number of hydrogen ions. Strong bases form a large number of hydroxyl ions; weak bases form few. A compound, such as water, whose molecule acts like a tiny magnet, is called a dipole. The molecules of nonpolar compounds, such as CO_2, do not dissociate in solution, are nonelectrolytes and nonconductors of electricity.

9. Neutralization is the union of the hydrogen ions of an acid with the hydroxyl ions of a base.

10. The acidity or alkalinity of a solution is measured in *p*H values. Water, with a *p*H of seven, represents neutrality. A substance with a *p*H greater than seven is basic; one with a *p*H less than seven is acidic.

11. Substances dissociate to different degrees, depending on the (1) solute, (2) solvent, (3) concentration of the solution, and (4) temperature.

12. All water solutions of acids, bases, and salts are electrolytes; that is, they dissociate and conduct an electric current.

13. Electrolytes raise the boiling points and lower the freezing points of solutions to a greater degree than nonelectrolytes do, because they dissociate, forming larger numbers of ions.

14. The electron theory upholds the theory of dissociation. The charge on an ion is the same as the valence of the element.

15. Hydrolysis of a salt is the action between the ions of water and the ions of a dissolved salt, forming an acid and a base. It is the opposite of neutralization. Salts formed by the

reaction of a strong acid and a weak base are acidic; by the reaction of a weak acid and a strong base are basic.

16. A reversible reaction is one that will go in two directions depending upon the conditions of the reaction. Since most chemical reactions are reactions between free ions, if the ions are neutralized or removed, the reaction goes to completion.

17. Reactions go to completion when one of the products formed is (1) a precipitate, (2) a gas, or (3) water.

18. The common-ion effect is caused by adding an ion identical with one of the ions of a compound in solution. It results in a partial precipitation of that compound.



USING WHAT YOU HAVE LEARNED

Group A

1. To what questions did Arrhenius seek an answer?

2. (a) What is an electrolyte? (b) What three classes of compounds are electrolytes? (c) Give three examples of nonelectrolytes.

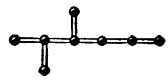
3. How could you find out whether a solution contained an electrolyte?

4. Explain in terms of the dissociation theory what happens when NaCl is dissolved in H_2O.

5. Name two ways in which ions differ from atoms.

6. In terms of the theory of dissociation define (a) an acid, (b) a base.

7. (a) On what do the properties common to bases depend? (b) to acids?



8. Why do we always use *dilute* acid in preparing hydrogen by displacement of hydrogen from that acid by a metal?

9. Why will a thoroughly insoluble hydroxide not turn pink litmus blue?

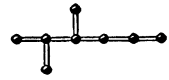
10. Explain neutralization in terms of ions.

11. Define strong acid and strong base in terms of the dissociation theory.

12. What are (a) three common strong acids, (b) two common weak acids, (c) three common weak bases, and (d) two common strong bases?

13. A solution has a *p*H value of six. What does this mean?

14. Normal blood has a *p*H of about 7.3. Is it acid or alkaline?



15. How does the degree of dissociation of NH_4OH compare with that of NaOH in equivalent solutions?

16. (a) What happens to a metal atom when it becomes an ion? (b) Explain the dissociation of NaCl in terms of electrons.

17. Explain the difference in physical and chemical properties of the potassium atom and the potassium ion.

18. By means of diagrams, show the difference between the chloride ion and the chlorine atom.

19. Change the following equations into ionic equations. Consult the table of solubilities on page 243.

a) $AgNO_3 + KCl \rightarrow AgCl + KNO_3$
b) $2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4$
c) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

20. (a) What is a concentrated acid? (b) Would a concentrated acid necessarily be a strong acid? Explain.

21. Insoluble bases are very weak bases. Explain.



22. Complete and balance the following equations.

a) $Na_2CO_3 + CaCl_2 \rightarrow$
b) $Zn + H_2SO_4 \rightarrow$
c) $AgNO_3 + NaBr \rightarrow$
d) $NaCl + H_2SO_4 \rightarrow$
e) $NaCl + Zn(NO_3)_2 \rightarrow$
f) $Pb(NO_3)_2 + NaCl \rightarrow$
g) $BaCl_2 + K_2SO_4 \rightarrow$
h) $NaNO_3 + CuCl_2 \rightarrow$
i) $Pb(NO_3)_2 + H_2S \rightarrow$
j) $NaOH + NH_4Cl \rightarrow$

23. Which of the reactions in exercise 22 are reversible and which go to completion?

24. (a) Which of the following salts are neutral in solution? (b) Which give an acid reaction? (c) basic reaction? (d) Explain.

(1) NaCl (2) Na_2CO_3 (3) $AlCl_3$ (4) KNO_3 (5) Na_3BO_3 (6) K_2SO_4 (7) $ZnSO_4$ (8) Na_2SO_3

25. What is the percentage composition of sodium acetate, $NaC_2H_3O_2$?

26. Explain the electrolysis of H_2O in terms of ions and electrons.

Group B

27. Why does cold dilute H_2SO_4 attack Zn, although cold concentrated H_2SO_4 does not?

28. Dry cobalt chloride ($CoCl_2$) is blue in color. A solution of this salt in water is pink. Explain why this color change occurs.

29. In what three respects has the original theory of dissociation been modified?

30. Concentrated H_2SO_4 is a poorer conductor of electricity than dilute H_2SO_4. What does this indicate with reference to ions?

31. Explain how the study of the freezing points of solutions led to the theory of dissociation.

32. (a) State the law of mass action. (b) Explain how it works, using a suitable reaction as an example.

33. What is a dipole? Illustrate your answer.

34. What weight of "Prestone," $C_2H_4(OH)_2$, should you use in a $3\frac{1}{2}$ gallon auto radiator to protect it against 5°F. weather? One mole of $C_2H_4(OH)_2$ lowers the freezing point of one liter of water from 0°C. to −1.87°C. Density of $C_2H_4(OH)_2$ is 1.13.

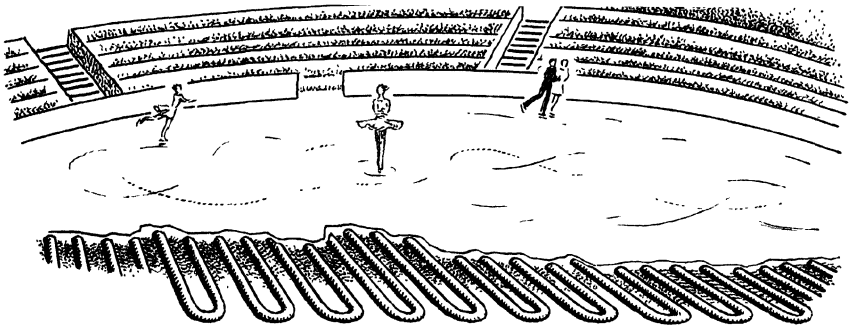


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Write a report or organize a class discussion on the importance of *p*H measurements to a soil (agricultural) chemist or to a medical research man. Consult your teacher of agriculture or your family doctor.

2. Construct a laboratory setup as shown on page 239. Plate some copper onto a piece of steel. The steel object should be the cathode and the copper strip the anode. The electrolyte should be a copper sulfate solution.

3. Take an old radio tube apart and demonstrate to the class how electrons are liberated from the heated filament, and how the flow of electrons passes through the grid toward the positive plate. Consult your teacher of physics or a radio engineer in connection with this project.



17 AMMONIA
AND REVERSIBLE REACTIONS

The men of experiment are like the ant: they only collect and use; the reasoners resemble spiders who make cobwebs out of their own substance. But the bee takes a middle course; it gathers its material from the flowers of the garden but transforms it by a power of its own. Francis Bacon (1561–1626) in *Novum Organum*

The electron structure of ammonia. At high temperatures, nitrogen combines with hydrogen, forming ammonia, NH_3. Nitrogen acts like a nonmetal with a valence of three. Since its outer ring is short three electrons, it combines with three hydrogen atoms, forming a nonionic compound.

The three-dimensional, or *cubic,* diagram (Fig. 54) is another method of showing the arrangement of electrons around the nucleus of an atom. This diagram represents the formation of ammonia. Note that the electrons of the three hydrogen atoms are shared by the nitrogen atom in forming the ammonia molecule. Since NH_3 bears two unshared electrons, it can accept, or combine with a proton (H^+) to form NH_4^+. Hence, it is a base.

How ammonia is prepared in the laboratory. When ammonium chloride is heated with calcium hydroxide, ammonia gas is liberated and may be collected by the displacement of air (Fig. 55).

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3\uparrow + 2H_2O$$

Since the only function of the ammonium chloride is to furnish the ammonium group, NH_4, almost any other ammonium salt may be

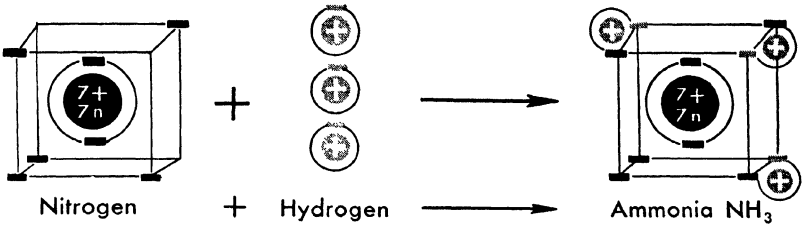


Fig. 54. Formation of ammonia, showing electron transfer.

substituted for it. Since any soluble base can supply the OH radical, we can use any soluble base instead of calcium hydroxide. The general method for preparing ammonia is, therefore, by the reaction of an ammonium salt with any soluble base.

Physical properties of ammonia. Priestley collected ammonia over mercury, because it is soluble in water. At room temperature 1 volume of water will dissolve more than 700 volumes of this gas, NH_3.

The extreme solubility of ammonia may be shown by the *ammonia fountain.* This setup consists of a flask and a tube (Fig. 56). The flask is filled with dry ammonia gas, and inverted over water. As soon as the tube enters the water, some ammonia dissolves in it, reducing the pressure inside the flask. The air pressure outside then forces the water up into the tube, and as it issues from the top of the tube it forms a fountain of ammonia water. Why?

The characteristic pungent odor of ammonia was known to Priestley. It is reported that as he bent over the fireplace where he prepared the gas by the method we use today, its vapor made his eyes fill with tears and drove the occupants of his house out of doors.

Ammonia gas is about half as heavy as air. It may be readily liquefied, using only 70 pounds of pressure per square inch at ordinary temperatures. The colorless liquid NH_3 is kept in steel cylinders and shipped in tank cars.

Fig. 55. Laboratory preparation of ammonia. Why is the generating tube tilted downward?

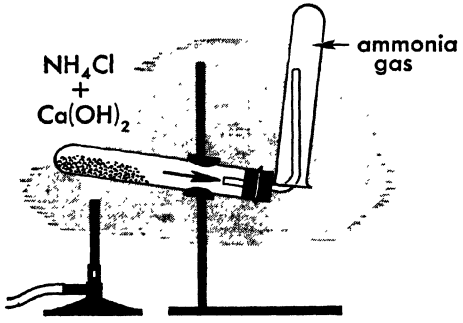
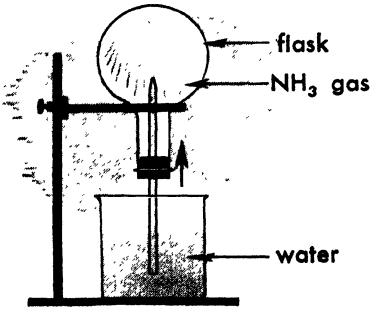


Fig. 56. The ammonia fountain.



Chemical properties of ammonia. Ammonia reacts with water, forming ammonium and hydroxyl ions. The latter ions account for the basic characteristics shown by the water solution of ammonia, *aqua ammonia.*

$$NH_3 + H_2O \rightleftarrows (NH_4)^+ + (OH)^-$$

Ammonia gas does not burn in air, but it does burn in pure oxygen with a pale greenish flame.

$$4NH_3 + 5O_2 \rightarrow 6H_2O + 4NO$$

Dry ammonia does not unite with dry hydrogen chloride, but the presence of a trace of water causes the two to combine, forming a white cloud that settles out as ammonium chloride powder.

$$NH_3 + HCl \rightleftarrows NH_4Cl$$

Ammonia unites with the very active metals. When passed over hot magnesium, for example, magnesium nitride and hydrogen are formed.

$$2NH_3 + 3Mg \rightarrow 3H_2 + Mg_3N_2$$

Ammonia is a very useful compound. Liquefied ammonia gas, or *anhydrous ammonia* as it is called, is a widely used compound. In a recent normal year, more than 2,000,000 tons were produced in this country for use in the chemical industries.

More than 75 percent of all chemical nitrogen products are produced from ammonia. Ammonia is the chief raw material from which nitric acid and *nitrates,* or salts of nitric acid, are made. Combined with acids to form ammonium sulfate, $(NH_4)_2SO_4$, ammonium nitrate, NH_4NO_3, and monoammonium phosphate, $NH_4H_2PO_4$, ammonia is one of the chief sources of nitrogen in fertilizers. Urea, used as a fertilizer, is also made from ammonia. The manufacture

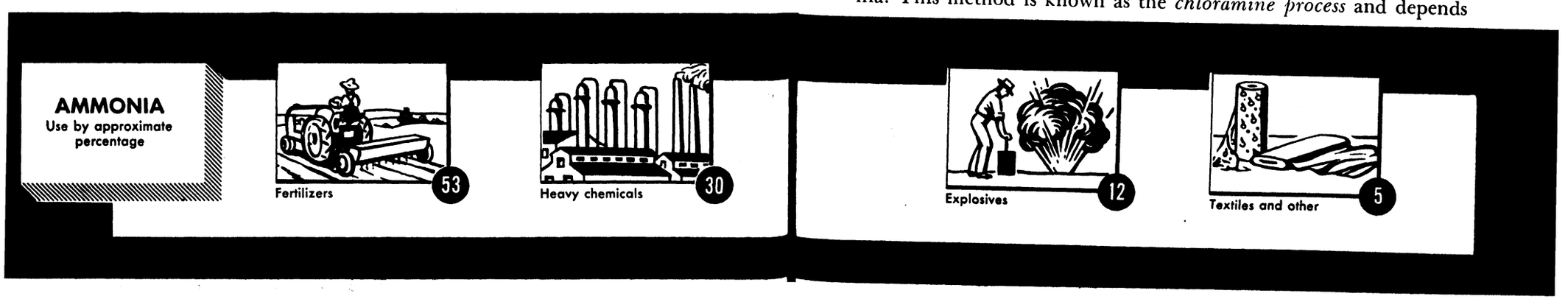
of sodium bicarbonate by the Solvay process, using ammonia, is discussed on page 474.

In recent years, there has been an increasing use of anhydrous ammonia as a primary fertilizer. Sometimes the ammonia is added to irrigation water which effectively spreads it throughout the soil. A more widespread practice is to inject liquid anhydrous ammonia directly into the soil through tubes mounted on a plow-like applicator. Upon release, the ammonia, which has been kept under pressure, reverts to a gas and unites chemically with the soil particles. Greatly increased crop yields have resulted from treating the soil with anhydrous ammonia.

Ammonia is widely used as a refrigerant. Dry ammonia gas is used extensively in commercial refrigeration because of the ease with which it can be liquefied. In making artificial ice, ammonia gas is placed in a closed system of pipes and coils. By means of a pump, the gas is compressed until it changes to a liquid; the heat evolved in the process is removed by a spray of cold water. Then, as cold liquid ammonia, it is passed through pipes into the freezing chamber, which contains brine or a water solution of calcium chloride, $CaCl_2$.

As fast as the liquid ammonia enters the pipes in the chamber through a needle valve, it expands suddenly and vaporizes as a result of the reduced pressure, and in so doing absorbs a great amount of heat from the brine. So cold does the brine become that the pure water in the tanks that are immersed in the brine changes to blocks of ice. The ammonia gas returns to the pumping chamber, where it is again compressed for reuse. The process is continuous, and the same ammonia gas is used over and over again.

Ammonia gas also helps purify water. One method of water purification of increasingly wide use employs both chlorine and ammonia. This method is known as the *chloramine process* and depends



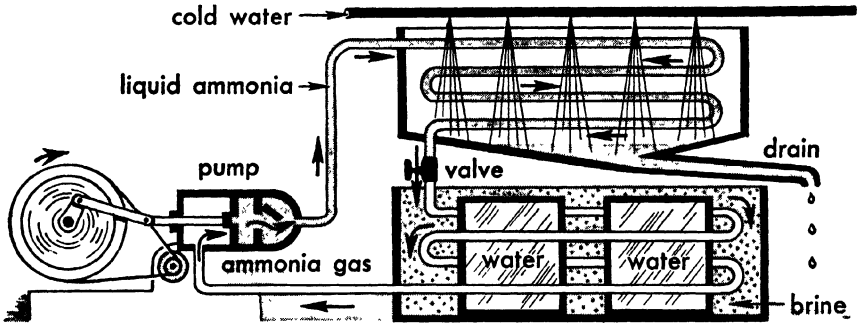


Fig. 57. Ammonia refrigeration equipment.

on the fact that when ammonia and chlorine react, chloramine, NH_2Cl, is formed. One of the reactions is:

$$2NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$$

Chloramine is a very effective killer of bacteria, or *bactericide*, but is less active chemically than chlorine and produces less of the typical taste of chlorinated water. The process is somewhat less expensive than chlorination, and is especially well adapted to communities whose water supplies have musty or swampy tastes.

Preparation and properties of ammonium hydroxide. Care must be taken to distinguish between ammonia, NH_3, and the ammonium ion, NH_4^+. In the laboratory preparation of ammonia, the nitrogen compound first formed might be thought of as ammonium hydroxide, which breaks down into ammonia and water.

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + [2(NH_4)^+ + 2(OH)^-]$$
$$\downarrow$$
$$2NH_3 + 2H_2O$$

A water solution of NH_3 is often called *ammonium hydroxide* even though the compound probably does not exist. The solution really consists of some dissolved NH_3, some NH_4 ions, and some OH ions. A saturated solution of ammonia is lighter than water (sp. gr. 0.88), and contains about 36 percent NH_3 by weight at room temperatures. The ammonia may be expelled by boiling. Household ammonia is a water solution of NH_3 containing about 6 percent oleic acid.

A water solution of ammonia is a weak base, since NH_3 reacts with water to form only a few (one percent) hydroxyl ions. Because it is a base, it dissolves grease and hence removes dirt. Since this ammonia water gives off vapor, or *volatilizes*, rapidly and completely without leaving a solid, it is useful as a household cleansing agent.

The ammonium radical and ammonium salts. The ammonium radical, because of its positive valence, is considered metallic. Its presence may be detected by adding the salt to be tested to a base, such as sodium hydroxide, and heating the mixture. If the suspected substance is an ammonium compound, ammonia gas will be liberated, and can be identified by its odor. Moist pink litmus paper held in the gas turns blue. Why must the litmus be wet?

$$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + 2NH_3 \uparrow$$

One of the most common of the ammonium salts is ammonium chloride, or *sal ammoniac.* This salt, first produced in Egypt, was known to the early alchemists. It is a white, crystalline substance, readily soluble in water. It is decomposed by heat into two gases, NH_3 and HCl, which reunite on cooling.

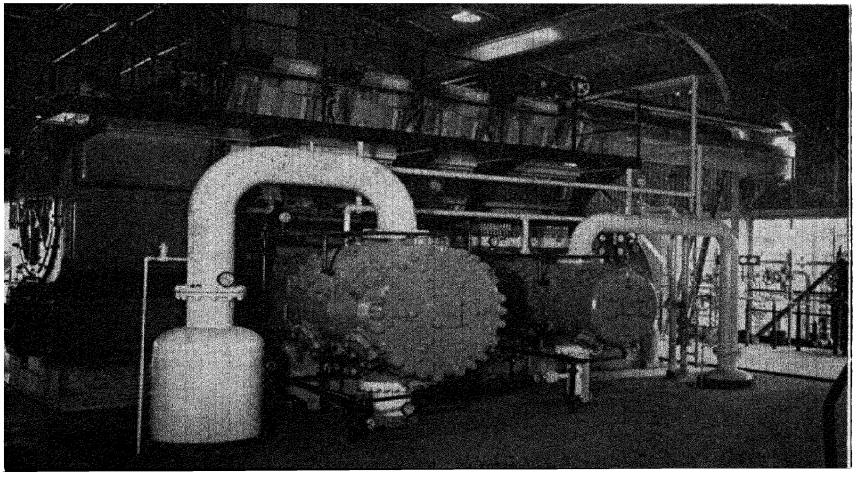
$$NH_4Cl \rightleftarrows NH_3 + HCl$$

Sal ammoniac is used extensively in dry batteries as an electrolyte and in *soldering* in which the hot iron dissociates the salt. The hydrogen chloride and ammonia liberated remove the rust that covers the surface of the metal to be soldered, the hydrogen chloride by dissolving the rust, and the ammonia by reducing it.

Fritz Haber makes the synthesis of ammonia a commercial success. Minor quantities of ammonia are still made by an old process — the destructive distillation of coal. This process, in which ammonia is produced as a valuable byproduct, is discussed on pages 362–363. Synthetic methods have superseded the method of preparing ammonia from coal. The most successful synthesis of ammonia is based

A compressor used in the manufacture of ammonia. The hydrogen is made from natural gas produced in nearby oilfields.

Shell Chemical Corporation



on the process first worked out on a commercial basis by Fritz Haber (hä'bĕr) in 1913 and known as the *Haber process.*

The first real test of this great achievement came during World War I, partly as a result of the desperate need of the German government for nitrogen compounds. Haber's process made agriculture in blockaded Germany independent of Chile saltpeter and also gave the German military machine a new source of nitrates for high explosives. The Haber process enabled Germany to fight hunger, and stave off defeat much longer than the Allies expected. Fritz Haber was later forced into exile by the Nazis and died in Switzerland.

The Haber process. This process, with its many modifications, is the most important single process for the *fixation of nitrogen,* that is, the combining of the free nitrogen of the air with other elements to form useful compounds. The process is based upon what appears to be a very simple reaction, the union of hydrogen and nitrogen gases.

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

The nitrogen and hydrogen for this reaction are obtained from air, coke-oven gas, water gas, natural gas, and some petroleum refinery gases. Although this chemical reaction has been known for a long time, it was not industrially practicable until the reversible reaction could be controlled. The laws of chemical equilibrium had to be used, so that some of the ammonia gas formed would not be immediately decomposed into its elements.

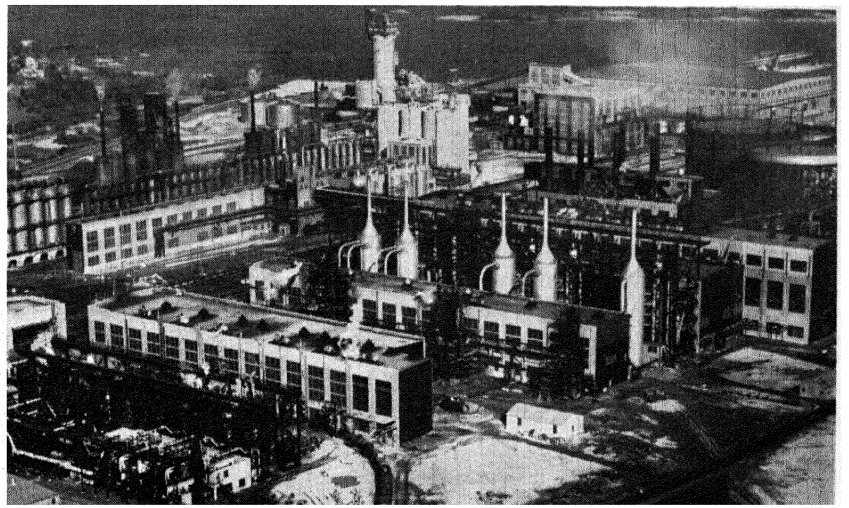
What factors can be used to control the point of equilibrium? Most chemical reactions are reversible. In the synthesis of ammonia, the first equilibrium ratio was about two percent ammonia to 98 percent of a mixture of nitrogen and hydrogen. In other words, most of the ammonia formed during the union of nitrogen and hydrogen decomposed into its constituent gases.

The point of *equilibrium, however, can be controlled to some extent.* The factors that help to control it are (1) *temperature,* (2) *pressure,* and (3) *concentration of the substances involved in the reaction.* Catalytic agents increase the speed of a reaction and, hence, enable the point of equilibrium to be reached more rapidly. It is not probable that catalysts alter the point of equilibrium.

Thus, in the case of the preparation of ammonia in America by a modified Haber process, the reaction

$$3H_2 + N_2 \rightarrow 2NH_3 \uparrow + 24{,}000 \text{ calories}$$

has been forced to go to the right, producing as much as 30 percent NH_3, instead of only two percent of the theoretical yield.



Nitrogen Division, Allied Chemical and Dye Corporation

Aerial view of a large plant for the synthesis of ammonia and the manufacture of fertilizer.

The conditions that made the American process a success were (1) the use of a specially prepared iron oxide as catalyst, (2) a temperature of about 475°C., (3) a reaction pressure of about 300 atmospheres (atm.), that is, 300 times atmospheric pressure, and (4) a rapid removal of the NH_3 formed. Since heat is evolved during the synthesis of ammonia, the higher the temperature, the less the yield, and consequently too high a temperature is avoided. Since there is a diminution of volume (three volumes of hydrogen unite with one volume of nitrogen, forming only two volumes of ammonia), the yield is increased by an increase in pressure. The manufacturing conditions represent the most effective compromise between largest yield, shortest time, and most profitable rate.

Another synthetic process for making ammonia. In 1916 the United States built a large nitrogen-fixation plant at Muscle Shoals, Alabama, where ammonia was to be prepared by the *cyanamide process*. This project was later abandoned, although the cyanamide process at Niagara Falls, Canada, has been very successful as a source of calcium cyanamide. The chief chemical changes that take place in the cyanamide process are:

1) The formation of calcium carbide by heating lime, CaO, and coke, C, in an electric furnace.

$$CaO + 3C \rightarrow CO + CaC_2 \text{ (calcium carbide)}$$

2) The union of calcium carbide with free nitrogen, forming calcium cyanamide.

$$CaC_2 + N_2 \rightarrow C + CaCN_2 \text{ (calcium cyanamide)}$$

3) The addition of steam to cyanamide, forming ammonia.

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3\uparrow$$

In dry form, crude, powdered calcium cyanamide containing about 60 percent $CaCN_2$ is sold as a fertilizer under the name of "Cyanamid." All of its nitrogen is available as a plant food.



YOU WILL ENJOY READING

Berl, E. "Fritz Haber." *Journal of Chemical Education,* May, 1937, pp. 203–207. A short biography.

Jaffe, Bernard. *Men of Science in America,* pp. 307–330. Simon & Schuster, New York, 1944. The development of our ideas regarding reversible reactions is tied up with the contribution of America's greatest theoretical scientist, J. Willard Gibbs. His life and work are described here.

Ross, William H.; Adams, J. Richard; Yee, J. Y.; and Whittaker, Colin W. "Preparation of NH_4NO_3 for Fertilizer Use." *Industrial and Engineering Chemistry,* Dec., 1944, pp. 1088–1095.

Slosson, Edwin E., *Creative Chemistry,* pp. 14–36. D. Appleton-Century Co., New York, 1920. "Nitrogen, Preserver and Destroyer of Life."



USEFUL IDEAS DEVELOPED

1. When a substance which ionizes goes into solution, the change that takes place is reversible. The substance dissociates into ions; these ions unite, *re*-forming the original substance. Even when equilibrium is established, this reversible reaction continues. Change is no longer apparent, however, because the rate of dissociation is the same as the rate at which the ions in the solution *reunite,* forming the original substance. The solution is in a state of dynamic equilibrium.

2. The point of equilibrium of a reversible reaction can be controlled to a certain extent by (1) temperature, (2) pressure, and (3) concentration of the substances involved. Catalytic agents increase the speed of a reaction and, hence, enable the point of equilibrium to be reached more rapidly.



USING WHAT YOU HAVE LEARNED

Group A

1. Describe the laboratory preparation of NH_3. Use a labeled diagram.

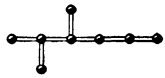
2. (a) How did Priestley first collect ammonia? (b) Why did he use this method?

3. (a) What is the general method of preparing NH_3? (b) Write two equations illustrating two ways of preparing NH_3 from NH_4Cl.

4. Show, by a simple experiment, the extreme solubility of NH_3 in H_2O.

5. Devise a simple experiment to determine whether NH_3 is lighter or heavier than air.

6. Does NH_3 burn? Explain.



7. (a) By means of an equation, give the chief chemical property of NH_3. (b) What type of reaction is this? (c) How can you make the reaction go to the right? (d) to the left?

8. Complete and balance the following equations:

a) $NH_3 + HCl \rightarrow$ c) $(NH_4)_2SO_4 + NaOH \rightarrow$

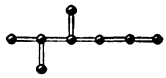
b) $NH_3 + Mg \rightarrow$ d) $NH_3 + H_2SO_4 \rightarrow$

e) $NH_3 + Cl_2 \rightarrow$

9. What are five uses of NH_3?

10. What substances are present in a water solution of NH_3?

11. (a) Is a solution of NH_3 in water a strong base? (b) Explain your answer.



12. (a) Write an ionic equation showing the neutralization of HCl by NH_4OH, (b) also the neutralization of H_2SO_4 and (c) of HNO_3 by the same base.

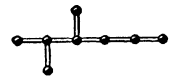
13. Does dry NH_3 affect litmus? Explain.

14. (a) In what group of elements is the ammonium radical placed? (b) Explain.

15. What are two commercial methods of preparing NH_3?

16. What was the difficulty that confronted manufacturers who attempted to make NH_3 by direct synthesis of its elements?

17. What four conditions are met in the improved Haber process?



18. (a) Describe the cyanamide process for making NH_3. (b) What are the three equations?

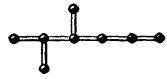
19. Complete and balance the following equations:

a) $NH_3 + HNO_3 \rightarrow$ b) $NH_3 + H_3PO_4 \rightarrow$

20. "Spirits of hartshorn" was the name applied to ammonia water prepared by the alchemists by heating the horns of deer. What elements must have been present in deer horns?

21. In what two ways do liquid ammonia and aqua ammonia differ?

22. What simple test will distinguish NH_4Cl from NaCl? Both of these compounds are white, soluble salts.



23. Compare the laboratory methods of collecting NH_3, N_2, HCl, O_2, Cl_2, and H_2.

24. Explain the action of liquid NH_3 on dry litmus paper.

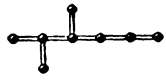
25. Why is ammonia water called the *volatile alkali?*

26. Bottles of household ammonia were formerly closed with rubber rather than with glass or cork. Why?

27. Why is ammonia water, rather than lye, used in removing grease spots from clothing?

28. Compare the ease with which NH_3, N_2, Cl_2, and H_2 are liquefied.

29. Describe the preparation of artificial ice by means of NH_3. (b) What property of NH_3 makes it useful in this process? (c) Of what use is the $CaCl_2$ or brine solution?



30. What weight of NH_4Cl is necessary to make 340 tons of dry liquid NH_3?

31. Determine the percentage of nitrogen in monoammonium phosphate.

32. (a) What is chloramine? (b) How is it prepared?

Group B

33. Bottles of ammonia water and hydrochloric acid are placed within a few inches of each other and their stoppers removed. White fumes are seen. Explain.

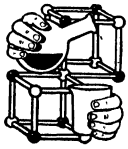
34. Explain how you would determine the strength of a bottle of household ammonia by titration. Give details.

35. How can a knowledge of the laws of equilibrium be used in making the preparation of NH_3 by the Haber process more efficient and more economical?

36. When water is added to magnesium nitride (Mg_3N_2), the odor of NH_3 is detected. Write an equation to explain this.

37. $CaCl_2$ unites with NH_3, forming $CaCl_2 \cdot 8NH_3$. Explain whether you could use $CaCl_2$ in drying ammonia gas.

38. Account for the odor of NH_3 around heaps of garbage and manure.

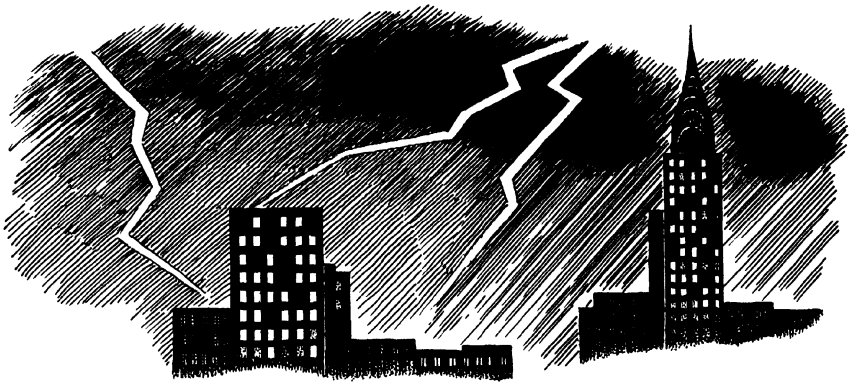


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Take a dry cell apart, and show the various substances that are used in its manufacture. Prove the presence of NH_4Cl by a chemical test. What is the purpose of the NH_4Cl?

2. Write a two- or three-page report on the freedom of the man of science in a democracy compared with the enslavement of science in totalitarian states. Use Haber and, perhaps, Langmuir as examples.

3. Set aside 2 ml. of household ammonia in an open test tube for two weeks. Test for the presence of ammonium hydroxide with pink litmus paper at the end of the time. Explain the results.



18 NITRIC ACID AND NITROGEN COMPOUNDS

. . . For nitrogen plays a double role in human economy. It appears like Brahma in two aspects, Vishnu the Preserver and Siva the Destroyer.
E. E. Slosson, 1919

The revolution brought about by man-made nitrogen compounds. Haber's successful synthesis of ammonia widened man's control over nature by making him less dependent for his raw materials on supplies present in limited or faraway areas of the earth's surface. Synthetic ammonia was soon converted into nitric acid. This, in turn, gave mankind an unlimited supply, not only of fertilizers, but also of high explosives. The synthesis of nitrogen compounds from air and water was a bloodless revolution whose consequences touched the lives of half the people of the world.

Preparation and properties of nitric oxide. Not only does nitrogen unite with hydrogen at high temperatures, but it combines with oxygen also when an electric spark is passed through a mixture of the two gases. Cavendish made this discovery in 1770 when he passed an electric spark through mixtures of hydrogen and air in his synthesis of water. Soon afterward Priestley made a thorough study of the compound formed by the direct union of nitrogen and oxygen.

$$N_2 + O_2 \rightarrow 2NO \text{ (nitric oxide)}$$

Priestley also prepared nitric oxide by the action of copper on *dilute* nitric acid, collecting the gas by the displacement of water,

as shown in the illustration below. This is the *laboratory method* used today.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO \uparrow$$

Nitric oxide is a poisonous, colorless gas, very slightly soluble in water, and about as heavy as air. Chemically, it is very active. When exposed to air or oxygen, it oxidizes at once to nitrogen dioxide, NO_2. This reaction produces much heat; that is, it is decidedly exothermic.

Nitrogen dioxide. The equation representing the oxidation of nitric oxide to nitrogen dioxide is:

$$2NO + O_2 \rightarrow 2NO_2$$

Nitrogen dioxide is reddish brown in color, heavier than air, very soluble in water, and easily liquefied. Its fumes are irritating and poisonous.

In preparing nitric oxide by means of copper and nitric acid, the gas first seen in the generating bottle is brown nitrogen dioxide rather than the colorless nitric oxide. Actually NO is formed first, but combines with the oxygen in the air of the generating bottle to form the brown NO_2. When the mixture of the NO and NO_2 passes through the delivery tube into the collecting bottle, the NO_2 dissolves in the water. Only the colorless nitric oxide displaces the water in the bottle.

As its temperature is lowered, nitrogen dioxide gradually changes into nitrogen tetroxide gas, N_2O_4. The reaction $2NO_2 \rightleftarrows N_2O_4$ is a reversible one. Above 140°C., the reaction goes to completion, as shown by the arrow pointing to the left. At room temperature, the gas obtained is a mixture of the reddish brown NO_2 and the colorless N_2O_4. At very low temperatures, NO_2 changes completely into N_2O_4.

The arc process of making nitric acid from air and water. The union of nitrogen with oxygen in an electric arc, or by the action of an electric spark, was used as the basis of many commercial ventures attempting to produce synthetic nitric acid. In the beginning, they

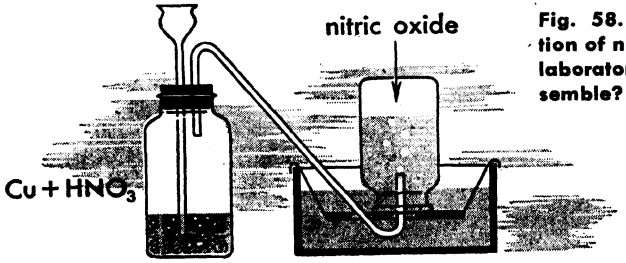


Fig. 58. Laboratory preparation of nitric oxide. What other laboratory setup does this resemble?

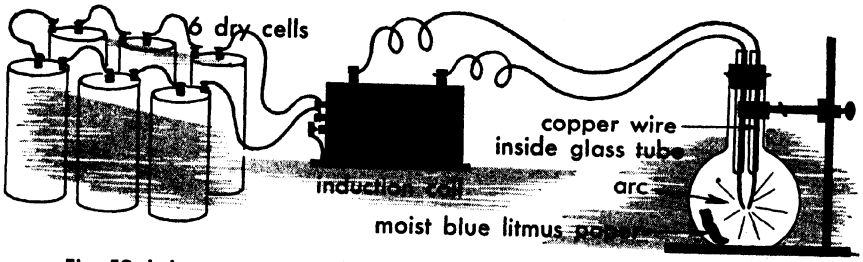


Fig. 59. Laboratory preparation of nitrogen dioxide by the arc process. How can you tell whether NO_2 is formed?

all failed because when a mixture of nitrogen and oxygen was thus treated, the yield of nitric oxide was very small. Because the reaction is reversible, practically all the nitric oxide formed at first was decomposed into its original elements.

$$N_2 + O_2 \rightleftarrows 2NO \uparrow$$

A careful application of the laws of chemical equilibrium finally resulted in larger yields of nitric oxide. This gas combined with the oxygen of the air to form nitrogen dioxide which was then dissolved in water to form nitric acid, HNO_3.

$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \uparrow$$

The Ostwald process, another commercial method of making nitric acid. The arc process because of its higher cost has been superseded by the Ostwald process. No sooner had the synthesis of ammonia been successfully carried out than Wilhelm Ostwald (ôst'vält), a chemist who helped Arrhenius establish the theory of ionization, showed how ammonia gas could be converted into nitric acid on an industrial scale.

The *Ostwald process* consists of oxidizing ammonia gas in the presence of a catalyst, which consists of a specially-prepared platinum or platinum-rhodium gauze heated to a red heat. The two oxides of nitrogen are formed during the process, but the final products may be represented by the following equation:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

Using a pressure of only about six atmospheres, about 95 percent of the ammonia is converted into a water solution of nitric acid of about 50 percent concentration.

Nitrogen fixation. The change of free nitrogen into ammonia by the Haber process and the change of free nitrogen from the air into nitric acid by the arc process are examples of nitrogen fixation.

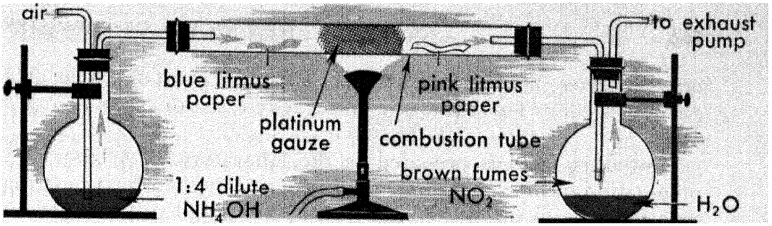


Fig. 60. Laboratory preparation of NO_2 by the Ostwald process.

Nitrogen fixation is the changing of free nitrogen from the air into useful compounds. During electric storms, some nitric acid is formed in the atmosphere by a natural arc process.

Nitrogen-fixing bacteria help the farmer. Most farm crops use part of the valuable salts in soil. On the other hand, certain crops such as peas, beans, and alfalfa, actually enrich the soil in which they are grown. Chemistry explains the fertility of such soil in the following way: Plants require nitrogen in the form of nitrates. These nitrates are soluble in water and can, therefore, be absorbed by the root hairs of plants by *osmosis,* a process by which liquids and gases pass through semipermeable tissues. On the roots of plants such as peas, beans, and alfalfa are little nodules, inside which live billions of *nitrogen-fixing bacteria* (*Rhizobium*). These bacteria and several others have the ability to change the free nitrogen, present in porous soil, into soluble nitrogen compounds, particularly nitrates, that plants use in building living tissues. When such crops are plowed under, this "green manure" adds nitrogen to the soil.

The nitrogen cycle — nitrogen compounds break down into free nitrogen. Various other bacteria break down nitrogen compounds in the soil into simpler compounds and even return considerable quantities of free nitrogen to the air. Such bacteria, called *denitrifying* (dē-nī'trĭ-fī-ĭng) *bacteria,* cause the loss of nitrogen from the soil and thus complete the extremely important *nitrogen cycle.* These bacteria are responsible, in part, for the rapid decay of nitrogen-containing

Nitragin Company



These pea roots are covered with nodules containing nitrogen-fixing bacteria.

organic wastes. They are used widely in the treatment of sewage (see pages 222–223). This series of changes is referred to as *the nitrogen cycle.*

How nitric acid is prepared in the laboratory. The laboratory preparation of nitric acid follows the general method for preparing an acid. Sodium nitrate, mixed with concentrated sulfuric acid, is heated gently in a glass retort. Nitric acid is formed, which, having a lower boiling point than sulfuric acid, evaporates. It is then condensed into a colorless liquid by cooling, as shown in the illustration below. The equation for the preparation of nitric acid is:

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4 \text{ (sodium hydrogen sulfate)}$$

This method is also one of the commercial processes used today in making about 10 percent of the nitric acid consumed by the world's industries. Synthetic $NaNO_3$ supplies the nitrate.

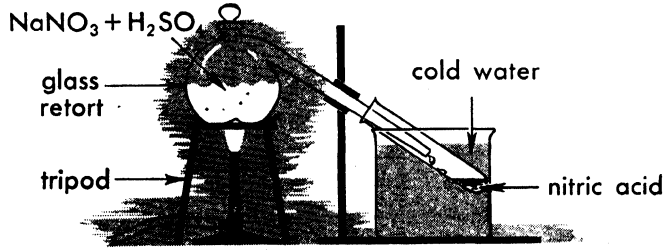
Nitric acid was known to the alchemists more than 1000 years ago. Geber (gā'bĕr), an Arabian physician and alchemist, prepared it about A.D. 800. It was called *aqua fortis,* meaning *strong water.*

Physical properties of nitric acid. When pure, nitric acid is a colorless liquid. Its water solution, containing 68 percent nitric acid by weight (that is, the *concentrated* nitric acid of commerce), has a specific gravity of 1.4, and boils at 120°C. The concentrated acid fumes strongly. The yellowish appearance of the nitric acid prepared in the laboratory is caused by the presence of nitrogen dioxide, formed by the partial decomposition of the nitric acid during the heating.

Chemical properties of nitric acid. Because nitric acid mixes with water in all proportions and dissociates almost completely, thus producing large quantities of hydrogen ions, it is a strong acid. Nitric acid is unstable. In sunlight or when heated, it decomposes into water, oxygen, and nitrogen dioxide.

$$4HNO_3 \rightarrow 2H_2O + 4NO_2 \uparrow + O_2 \uparrow$$

Fig. 61. Laboratory preparation of nitric acid. By what process is the acid collected?



A glowing splint inserted in the vapors of boiling concentrated nitric acid catches fire, thus showing that oxygen is present in the vapors. When an element, such as nitrogen in HNO_3, is in a very highly oxidized state, that is, it has a *high positive charge,* the compound is a strong oxidizing agent.

The action of nitric acid on metals illustrates its oxidizing powers. When hydrochloric acid reacts with many of the metals, hydrogen is liberated even if concentrated acid is used. On the other hand, dilute nitric acid acts on a metal, forming water instead of hydrogen. Nitric oxide gas is also formed. In fact, one of the methods used to prepare nitric oxide depends on this action of nitric acid.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO \uparrow$$

When concentrated nitric acid reacts with a metal, nitrogen dioxide, instead of nitric oxide, is formed. Brown NO_2 is produced by the oxidation of NO to NO_2.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2 \uparrow$$

The electron theory explains the oxidizing power of nitric acid as follows: oxidation is a loss of electrons; therefore, a substance such as chlorine, which borrows electrons, is a good oxidizing agent. HNO_3 may be thought of as containing N^{+++++}, which borrows electrons from the copper in the reaction above, changing to N^{++} (in NO). Thus the copper is said to be *oxidized* and the nitrogen *reduced.*

Nitric acid attacks proteins, forming a yellow compound. The yellow coloration produced on the skin by nitric acid is caused by this chemical reaction (see also Chapter 36). Nitric acid oxidizes both cotton and wool, destroying most of the strength of the fibers.

Aquà regia, the acid mixture that dissolves gold and platinum. Nitric acid, when mixed with hydrochloric acid, oxidizes the latter, liberating atomic chlorine. This mixture of nitric and hydrochloric acids as in the equation below is called *aqua regia,* or royal water.

$$3HCl + HNO_3 \rightarrow 2H_2O + NO + 3Cl$$

This chlorine reacts with gold, forming soluble gold chloride.

$$Au + 3Cl \rightarrow AuCl_3$$

Both gold and platinum are insoluble in any one of the three common *strong acids,* but they are soluble in aqua regia.

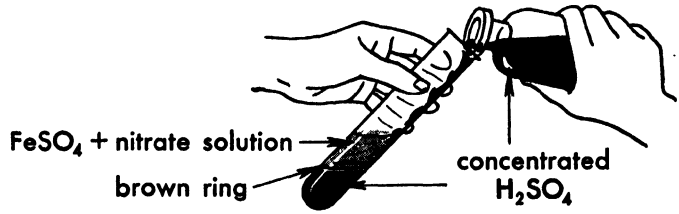


Fig. 62. The brown-ring test for a nitrate.

How do we test for the nitrate ion? The nitrates, salts of nitric acid, are all soluble in water, are decomposed by heat, and may be detected by the *brown-ring* test. This test is made by adding a small amount of freshly prepared ferrous sulfate solution to the solution suspected of containing a nitrate. Concentrated sulfuric acid is then carefully poured down the side of the test tube in such a way that it collects at the bottom without mixing with the solution. If a brown layer forms between the heavy sulfuric acid and the solution floating on top, a nitrate is present. The sulfuric acid produces nitric acid by reacting with the nitrate, and the nitric acid in turn reacts with the ferrous sulfate, forming a brown compound, $FeSO_4 \cdot NO$.

Gunpowder, the earliest explosive. The inactive element nitrogen does not unite easily with other elements. And after it does, the unions so produced are very unstable. In fact, such unions are so extremely unstable that on the slightest provocation the nitrogen breaks away with a bang! Most explosives, except those based on nuclear fission, depend upon this fact.

Nearly all nonfission explosives contain either *nitrate* (NO_3), or *nitro* (NO_2), radicals. In addition, some explosives contain ammonium radicals, NH_4. When compounds that contain nitrate or nitro radicals are mixed with other compounds that can easily use the oxygen of these unstable radicals, an explosive is the result. In certain cases, the compound containing the nitrate or nitro radicals actually supplies the means of its own destruction by furnishing the elements that can use the oxygen readily. When something, such as a shock, starts the reaction, the unstable nitrate or nitro radicals release their oxygen for combination with other elements and liberate free nitrogen gas. Nearly always, most of the other products of the reaction are gases also, and because of the high temperatures produced, terrific pressures result.

The earliest explosive was made thousands of years ago by the Chinese. How the *black powder* came to be produced is not known, but it was made then about as it is now, by mixing approximately 15 parts by weight of potassium nitrate, KNO_3, with three parts of sulfur, and two parts of powdered charcoal. The resulting

black powder, or *gunpowder,* explodes with terrific violence, much fire, and great quantities of acrid smoke. The reaction produced is:

$$2KNO_3 + 3C + S \rightarrow K_2S + N_2\uparrow + 3CO_2\uparrow$$

The Chinese used gunpowder in producing firecrackers and other kinds of fireworks for use in ceremonies and celebrations. But sometime within the past few centuries, no one knows for sure just when, gunpowder was turned to military uses, and, like so many other scientific discoveries, soon created a revolution. The foot soldier with his primitive musket quickly replaced the heavily-armored and beplumed knight with his lance and shield. Turrets and thick stone walls were no defense against powerful cannons, and the picturesque castle of the Middle Ages became obsolete.

Nitrocellulose, nitroglycerin, and some detonators. Today, gunpowder is considered a relatively "tame" explosive. Since its invention, chemists have produced many kinds of explosives chiefly by *nitrating,* or adding NO_3 or NO_2 radicals to, such substances as cotton, glycerin, sugar, starch, and other organic compounds. *Nitrocellulose,* or *guncotton,* was produced by Schönbein (shûn'bīn) in 1846 by nitrating cotton with a mixture of nitric and sulfuric acids. *Nitroglycerin,* made by nitrating glycerin, a common byproduct of the manufacture of soap, was produced in 1847. Both of these compounds are more powerful explosives than gunpowder, but both are much more sensitive to shock and, hence, explode much more easily.

In 1888, Alfred Nobel, a Swedish inventor, produced *dynamite* by absorbing nitroglycerin in a fine clay, or *diatomaceous* earth (see page 506). Dynamite is much less sensitive to shock and, hence,

Standard Oil Company (N.J.)



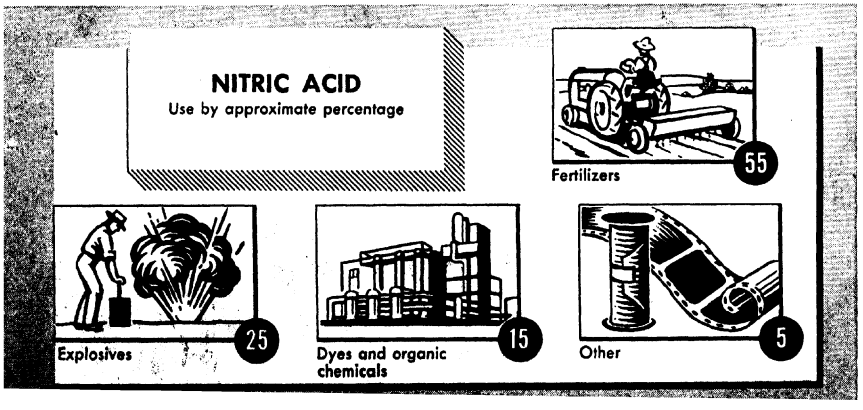
A workman inserts a dynam cartridge into a drilled h during the construction of underground pipeline.

can be used with greater safety than nitroglycerin. American dynamite usually consists of nitroglycerin absorbed in a wood meal that resembles fine sawdust. The substance is packed in sticks composed of parchment paper. So overcome was Nobel by the possible uses of his invention that he dedicated part of its profits to the establishment of the Nobel Peace prize for outstanding contributions to the peace of the nations of the world, and of the Nobel prizes for outstanding contributions to research in physics, chemistry, medicine and physiology, and literature. Peacetime uses of explosives include mining, building dams, and other construction work.

Explosives are set off, or detonated, by means of a shock produced by even more unstable, and thus more sensitive, compounds of nitrogen called *detonators. Fulminate of mercury,* $Hg(CNO)_2$, a widely used detonator, is 11 times as sensitive to shock as *trinitrotoluene,* or TNT, and twice as sensitive as nitrocellulose. *Lead azide,* $Pb(N_3)_2$, another detonator, is half as sensitive to shock as fulminate of mercury. Such substances are used in making the *caps* and other devices with which explosives are set off.

Nitric acid has many peacetime uses. Aside from the production of explosives, a major industry even in peacetime, the chief use of nitric acid is in the production of nitrates of organic compounds, such as nitrocellulose and nitrobenzene. Nitrocellulose is used in making some photographic films, and many quick-drying lacquers and enamels, especially for the automobile industry. Nitrocellulose is used also in the production of many kinds of artificial leathers. Nitrobenzene is the basic raw material of the aniline, or coal-tar dye, industry.

Nitric acid also furnishes the oxides of nitrogen required in the chamber process for the manufacture of sulfuric acid (see page 311). Nitrates for fertilizers and metallic nitrates are made from nitric acid. Sodium nitrate and ammonium nitrate are the chief fertilizers produced. Strontium nitrate is one of the chemicals used in *pyrotechnics,* the production of fireworks, which consist mainly of flares



and shells that give off flames and smokes of various colors. A one percent silver nitrate solution is put in the eyes of newborn babies to prevent infection that may lead to blindness.

Nitric acid plays an important role in the pickling of steel, in the etching of engravers' plates for printing, and in the manufacture of the arsenate insecticides (chiefly lead and calcium arsenates) so widely used against the boll weevil, and in the spraying of fruit trees (see page 453).

The nitrogen situation today represents a chemical revolution. It should be apparent already that the production of nitrogen compounds is a basic industry. The world's normal consumption of manufactured nitrogen compounds is many millions of tons annually. At one time, sodium nitrate from Chile and nitrogen compounds obtained as byproducts from the coal industry and slaughterhouses were the only sources of nitrogen compounds. *Today, the total annual amount of fixed nitrogen produced by chemical methods is many times as great as the total annual consumption of both Chilean nitrate and all byproduct nitrogen taken together.* The story of the nitrogen industry bears testimony to the widespread development of synthetic chemistry. It has changed the economic life of millions.

There are six oxides of nitrogen. In addition to the two oxides of nitrogen already discussed, four other oxides are known. The complete list is: nitrous oxide, N_2O; nitric oxide, NO; nitrogen dioxide, NO_2; nitrogen trioxide, N_2O_3; nitrogen tetroxide, N_2O_4, a powerful oxidizing agent; and nitrogen pentoxide, N_2O_5. They illustrate the law of multiple proportions and the fact that nitrogen has several different valences. Why?

When nitrogen trioxide, N_2O_3, is added to water, nitrous acid, a very unstable acid, is formed.

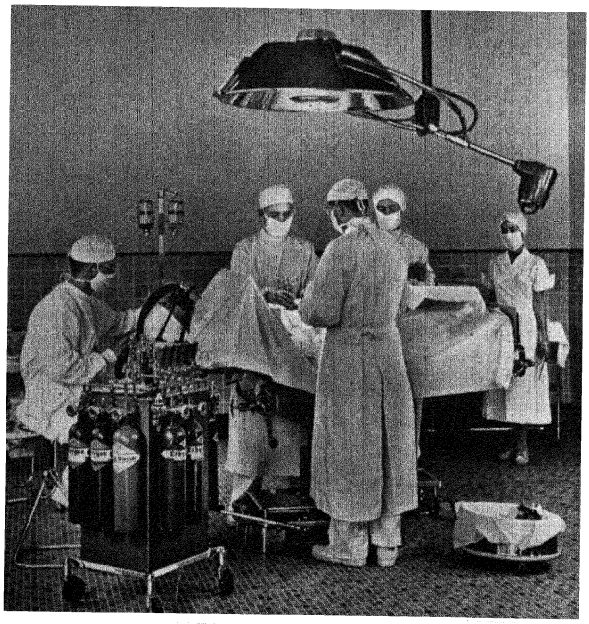
$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

Similarly, the addition of water to nitrogen pentoxide, N_2O_5, produces nitric acid.

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

These two gases may therefore be said to be the *anhydrides* (without water) of nitrous and nitric acids, respectively. *An acid anhydride is an oxide whose water solution is an acid.*

Nitrous oxide, or laughing gas. Priestley was the first to produce nitrous oxide, N_2O, a colorless, heavy gas, slightly sweetish in odor and somewhat soluble in water. This was about two years before he



Ohio Chemical and Surgical Equipment Company

A modern hospital operating room. Suspended from the table in the left foreground are tanks of pure oxygen, carbon dioxide, nitrous oxide and other gases ready for immediate administration when needed.

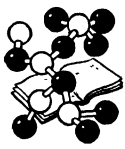
discovered oxygen. He learned that it supported the burning of a candle better than did ordinary air. It decomposes rather easily into oxygen and nitrogen. Just before the close of the eighteenth century, Humphry Davy achieved fame overnight by his discovery of the physiological effects of this gas. He breathed four gallons of it and noticed its power to produce a peculiar intoxication, which included laughing. The poet Samuel Coleridge, as well as other distinguished persons, came to Davy's London laboratory to experience the thrill of inhaling this gas. Nitrous oxide is still prepared as Davy made it, by heating ammonium nitrate.

$$NH_4NO_3 \rightarrow 2H_2O + N_2O$$

In 1842 *ether* was used as the first anesthetic in surgery by Dr. Crawford W. Long, a country doctor of Georgia. William Morton's use of ether at the Massachusetts General Hospital in 1846 introduced this anesthetic to the medical world. Two years earlier, Dr. Horace Wells, a dentist of Hartford, Connecticut, had one of his teeth extracted after he had anesthetized himself with nitrous oxide.

Today nitrous oxide is still used as an anesthetic in many operations, especially those of dentistry. It is usually mixed with about 25 percent oxygen and, in cases of more serious operations, with ether. This mixture of nitrous oxide and oxygen can be breathed for a considerable period without harmful effects on the circulatory

system or on vital organs. Small amounts of nitrous oxide are used in preserving perishable foods and liquids. Easily liquefied, it is sold in cylinders. It is used to eject whipped cream at soda fountains.

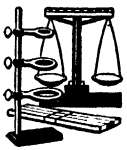


YOU WILL ENJOY READING

Conant, James Bryant. *The Overthrow of the Phlogiston Theory*. Case 2 of the Harvard Case Histories in Experimental Science. Harvard University Press, Cambridge, Mass., 1950. Gives an excellent account of Priestley's confusion between oxygen and nitrous oxide.

Haynes, William. *This Chemical Age,* pp. 78–94. Alfred A. Knopf, New York, 1942. A discussion on explosives and their relation to the dye industry, entitled "Mars: Chemical Dictator."

Slosson, Edwin E. *Creative Chemistry,* pp. 37–59. D. Appleton-Century Co., New York, 1920. A very readable account of nitrogen and nitrogen compounds in relation to plants.



USING WHAT YOU HAVE LEARNED

Group A

1. Explain the arc process of making HNO_3.

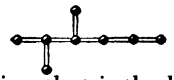
2. Write equations showing two methods of preparing NO.

3. State one chemical and three physical properties of NO.

4. Make a diagram showing the laboratory preparation of NO.

5. (a) What happens when NO comes in contact with air? (b) Explain.

6. Under what conditions does NO_2 change into N_2O_4?



7. Write the equation that is the basis of the Ostwald process for the synthesis of HNO_3.

8. (a) What natural phenomenon results in the formation of certain oxides of nitrogen? (b) Explain.

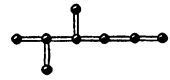
9. (a) What is nitrogen fixation? (b) Illustrate.

10. Make a diagram showing the laboratory preparation of HNO_3.

11. When a mixture of $NaNO_3$ and H_2SO_4 is heated in a retort, HNO_3 is formed a little at a time. (a) What four

substances are in the retort? (b) Which is removed by heat? Why? (c) Why do the other substances remain?

12. (a) What property of HNO_3 makes it possible to prepare the acid by the laboratory method? (b) Why could not HCl be used instead of H_2SO_4?



13. Write the equation for the laboratory preparation of HNO_3.

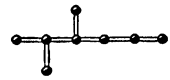
14. State four chemical properties of HNO_3.

15. (a) How is aqua regia prepared? (b) Its power to dissolve gold results from what property? (c) What property of HNO_3 is shown?

16. (a) Why does HNO_3 appear to be yellow when prepared in the laboratory? (b) What property of HNO_3 does this color indicate?

17. (a) What oxide of nitrogen is always formed when HNO_3 decomposes? (b) What oxide of nitrogen is always formed when HNO_3 acts as an oxidizing agent?

18. How would you test for the presence of the nitrate ion?



19. What are the three principal uses of HNO_3?

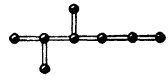
20. (a) Most explosives are based upon what fact? (b) What is a detonator?

21. (a) What is gunpowder? (b) dynamite?

22. Copy and complete the following: The six oxides of nitrogen illustrate the law of .... The anhydride of HNO_3 is ..., and the anhydride of HNO_2 is .... Another name for N_2O is .... N_2O was first used as ... by Dr. Horace Wells. N_2O is prepared by heating ....

23. 120 g. of NO are obtained by the action of Cu on HNO_3. How many grams of $Cu(NO_3)_2$ are formed?

24. How do you explain the fact that the reaction of $N_2 + O_2 \rightarrow 2NO$, although known for more than a century, could not be used in the preparation of HNO_3 until rather recently?



25. Why is N_2O a better supporter of combustion than NO?

26. (a) How does nature restore some of the nitrogen compounds taken from the soil by growing crops? (b) What is "green manure"?

27. In 1898, Sir William Crookes, one of England's most eminent chemists, predicted a future world famine caused by exhaustion of nitrogen compound fertilizers. Why has his prediction not materialized?

28. Make a table showing the properties of the six oxides of nitrogen.

29. How would you separate Au from Cu in a copper-gold mixture?

Group B

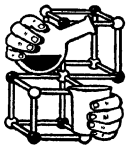
30. Why cannot HNO_3 be used in preparing H_2? Answer this question in the light of the electron theory.

31. (a) Using the electron theory, explain how HNO_3 oxidizes Cu. By inspection of the equation, state how many atoms of Cu are oxidized. (b) How many atoms of nitrogen are reduced? (c) How does the total number of electrons lost compare with the total number gained?

32. How could you determine experimentally whether a gas contained a high percentage of N_2O_4 and a small amount of NO_2, or was composed almost entirely of NO_2?

33. There is less oxygen in nitrous oxide than in nitric oxide. (a) Which would support burning better? (b) Explain.

34. Nitrates are unstable in the presence of heat. What product would you expect $Cu(NO_3)_2$ to yield when heated?

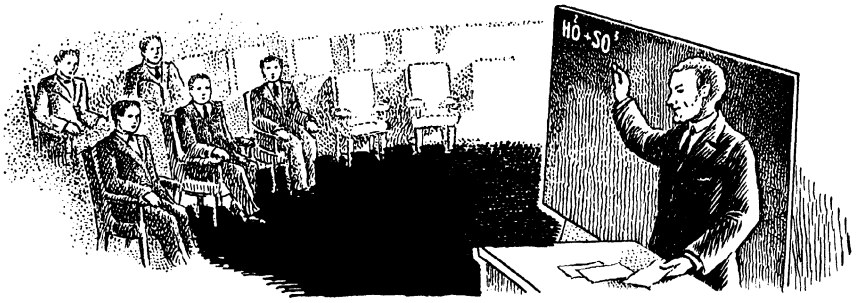


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. At Muscle Shoals, Alabama, there is a huge plant for generating electric power. This plant is capable of producing thousands of tons of nitrogen compounds a year by fixation. The U.S. government spent many millions of dollars on this project. What is the present state of this plant? Consult your teacher of history or economics or write to your Congressman, Senator, or the Tennessee Valley Authority at Knoxville, Tennessee. What do you think should be done? Prepare a debate or discussion of this question.

2. Write a report comparing the changes brought about by the introduction of gunpowder into warfare with the changes that the A- and H-bombs may produce.

3. If available at this time, obtain a fresh sample of some legume such as peas, beans, alfalfa, or soybeans. Examine its roots for nodules of nitrogen-fixing bacteria. Exhibit to class and explain its function.



19 MOLECULES: AVOGADRO'S HYPOTHESIS

. . . In 1858 the atomic theory of Dalton was just 50 years old. Students at this time were generally unfamiliar with the word molecule, for chemists spoke as complacently about an atom of water as about an atom of oxygen. For the most part, also, they had never heard of Amedeo Avogadro. William Tilden, 1921

The battle over the molecules of Avogadro. In 1860, chemical science was in a turmoil caused by a misunderstanding of the terms *atom* and *molecule.* Chemists had spoken of "atoms of water," which is a compound, in the same way in which they mentioned atoms of hydrogen, which is an element. Some used the term *compound atoms.* So great was the confusion that finally a congress of chemists was called at Karlsruhe to decide when to use the term *atom* and when to use the term *molecule,* which up to that time had been used interchangeably.

Among the brilliant men who gathered at Karlsruhe from all parts of the world was a bearded young Italian, Cannizzaro (kän-nêt-sä'rô). He had come to champion the use of the term *molecule* in the sense that it was used in 1811 by Avogadro (ä-vô-gä'drô), a modest professor of chemistry. According to Avogadro, *a molecule is the smallest part of either an element or a compound which has the properties of that substance.*

Avogadro had reached this new meaning of a molecule from his study of the behavior of gases. He had died four years before the congress was held, but Cannizzaro championed his ideas so successfully that they were finally accepted by the congress.

What Boyle and Charles discovered about the behavior of gases. In order to understand the significance of Avogadro's contribution to chemistry, it is necessary to trace the story of the study of gases after 1660. In that year Robert Boyle, revered by Englishmen as the father of modern chemistry, discovered that if the pressure on a gas is doubled — for example, increased from 15 pounds to 30 pounds per square inch — its volume is decreased one-half. Furthermore, he found that this relationship between pressure and volume does not depend upon the nature of the gas; it is true for all gases. Thus we have Boyle's law: *The volume of a gas varies inversely as the pressure exerted upon it if the temperature remains constant.*

In 1785, Charles, a French scientist, noted that under constant pressure the volume of a gas increases $\frac{1}{273}$ of its volume at 0°C. for each centigrade degree of rise in temperature; in other words, if the *absolute temperature* (see page 644) of a gas increases from 273° to 546° (2 × 273°) its volume doubles also. This he found true of any gas. Thus we have Charles' law: *The volume of a gas varies directly as the absolute* (A) *temperature, if the pressure on the gas remains constant.*

Although gases act according to Boyle's and Charles' laws under ordinary temperatures, they do not do so at very high pressures or very low temperatures. However, a discussion of the way in which gases act at low temperatures and under high pressures is beyond the scope of an introductory course in chemistry.

Gay-Lussac finds the law of combining volumes of gases. The next important advance came 23 years later. Gay-Lussac, the Frenchman who collected air samples in a balloon high over Paris, had long been interested in the study of gas volumes. He knew that one volume of nitrogen unites with one volume of oxygen, forming two volumes of nitric oxide. Besides, when he repeated the experiments of Cavendish and Lavoisier, he found that two volumes of hydrogen unite with one volume of oxygen, forming two volumes of water vapor. This was not a new discovery, but Gay-Lussac suspected that "other gases might also combine in simple ratios."

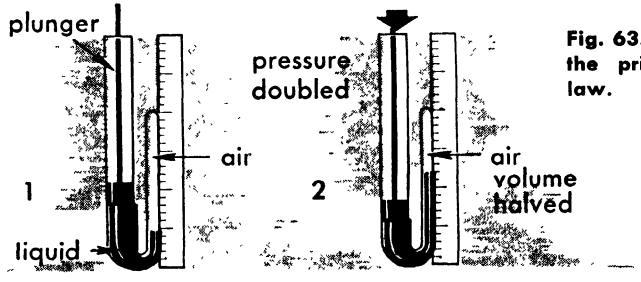


Fig. 63. A demonstration of the principles of Boyle's law.

Resuming his researches, Gay-Lussac discovered that one volume of hydrogen chloride gas when brought in contact with one volume of ammonia gas yielded a white powder, with no residue of either gas. The two gases had combined volume for volume. Furthermore, he had read that one volume of nitrogen combined with exactly three volumes of hydrogen, forming exactly two volumes of ammonia gas. This was an arithmetical simplicity of remarkable significance. Fractions of volumes of gases were not involved.

1 vol. nitrogen + 1 vol. oxygen → 2 vol. nitric oxide
1 vol. oxygen + 2 vol. hydrogen → 2 vol. water vapor
1 vol. HCl + 1 vol. NH_3 → NH_4Cl (a solid)
1 vol. nitrogen + 3 vol. hydrogen → 2 vol. ammonia gas

On the last day of the year 1808, Gay-Lussac formulated from these observations a law, which bears his name. Gay-Lussac's law states that *the relation between the combining volumes of gases and the volumes of their products (if they, too, are gases) may be expressed in small whole numbers.* Why this regularity? On the basis of Dalton's atomic theory, chemists could not explain this law.

When Dalton was faced with this fact, he refused to accept Gay-Lussac's law. "The truth is," Dalton maintained, "that gases do not unite in equal or exact proportions in any one instance. When they appear to do so, it is owing to the inaccuracy of our experiments." Later, however, after further experimentation and study, Dalton accepted Gay-Lussac's law. His acceptance of Gay-Lussac's law, when experimental evidence pointed toward its accuracy, reveals Dalton as a true scientist.

Is the sum of 2 and 1 always 3? The law of Gay-Lussac in particular, and the laws of Boyle and Charles to a lesser degree, suggested a number of interesting problems to Avogadro's inquiring mind. Why, for example, is the behavior of gases so uniform under changing temperature, while the behavior of solids and liquids is so variable? Why do gases combine in simple ratios by volume? Furthermore, why, with respect to gases, is not the sum of two and one always three? For example, why do two volumes of hydrogen unite with one volume of oxygen, making two volumes of water vapor; and, similarly, three volumes of hydrogen combine with one volume of nitrogen, making two volumes of ammonia gas?

Avogadro continues his work with gases. Avogadro tried to answer these questions. In reference to the last question, perhaps he thought: it might be that equal volumes of gases contain the same number of molecules.

But according to this idea, one volume of oxygen ought to combine with one volume of nitrogen, forming one volume of nitric oxide:

$$N + O \rightarrow NO$$

whereas, according to actual experiment, two volumes of nitric oxide are formed. Something was wrong. But wait! Suppose the molecule of nitrogen gas contains two atoms instead of one, that is, is N_2 and not N, and similarly the oxygen molecule is O_2 and not O, what then? According to this idea, the equation would be:

$$N_2 + O_2 \rightarrow 2NO$$

and the conditions necessary for the formation of two volumes of NO would be fulfilled.

How would this idea work out in other cases, for example, in the formation of water? If the molecule of hydrogen contains two atoms, like the molecule of oxygen, we should have the equation,

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

or stated in other words, two volumes of hydrogen unite with 1 volume of oxygen, forming two volumes of water vapor. This agrees with actual measurements of the volumes.

Apparently Avogadro was on the right track. It remained for him only to test his hypothesis further by means of other gas combinations to be able to show that, assuming the molecules of elementary gases to be composed of two atoms each, the volumes corresponded with the equation as he had calculated.

This he actually did and finally was able to establish the accuracy of his hypothesis, that all gases behave alike, because *equal volumes of all gases under the same conditions of temperature and pressure are composed of the same number of molecules* (*Avogadro's hypothesis*). To this professor from Turin, elementary gases, such as hydrogen, oxygen, nitrogen, and chlorine, consist normally of molecules each composed of two atoms instead of one, as Dalton and the rest of the world had supposed. Incidentally, Avogadro's hypothesis reconciled the atomic theory of Dalton with Gay-Lussac's law. How?

Of what value to chemistry was Avogadro's hypothesis? What evidence did Avogadro have to back up so bold an hypothesis? He could not verify it experimentally. No balance was sensitive enough to weigh a molecule. It would take billions of these tiny particles to turn the scales of even the most sensitive balance. He surely had not looked into the molecules of matter and detected the twin

arrangement of atoms, for it would take many millions of molecules placed side by side to make a line one inch long. Only in recent years have methods been developed which can make such a tiny particle visible.

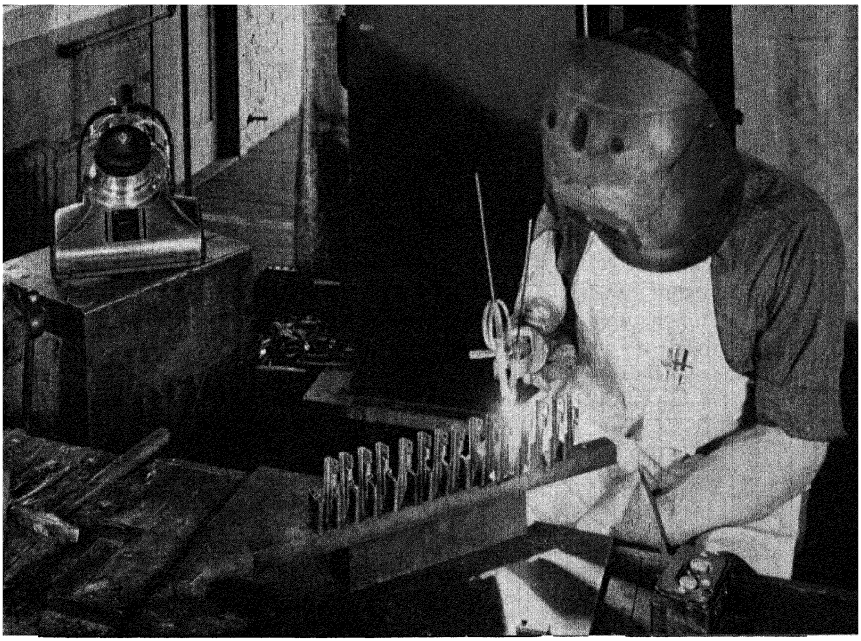
The only evidence Avogadro had was that of clear, accurate reasoning and his own creative imagination. However, this evidence was strong enough to clear the air and allow chemistry to advance. The particles of elementary gases were henceforth considered to be diatomic, that is, composed of two atoms to the molecule. (Later, by other methods, the inert gases of the atmosphere were shown to contain only one atom to the molecule.) Atomic weights and molecular weights were thus clearly differentiated. New methods were made possible for determining the molecular weights of gases and, from these, their atomic weights also.

How Avogadro's hypothesis was actually verified. Since the time of Avogadro, new apparatus and new methods have been devised for verifying his prophetic statement. A number of scientists, Millikan and Perrin (pĕ-răN′) among them, determined by experiment the number of molecules in a given volume of gas. They found that the number of molecules in two grams of hydrogen gas (a gram-molecular weight), for example, is approximately 602,000,000,000,000,000,000,000 (602 sextillion). This number, usually written 6.02×10^{23}, is now called *Avogadro's number.* Approximately this number of molecules is known to be present in equal volumes (22.4 liters) of all gases and vapors under the same conditions of temperature and pressure. This is no idle guess.

Perrin and Millikan, both Nobel prize winners in physics, maintained that we can count the number of molecules in a small volume of a gas with as much accuracy as we can determine the population of a city such as New York. Avogadro's hypothesis has now taken its place as one of the laws of chemistry.

Then came another remarkable verification. Irving Langmuir (lăng′mūr), another Nobel laureate in chemistry, succeeded in breaking up the molecules of hydrogen gas. As a result of his experiments he found that hydrogen gas is made up of molecules each of which consists of two atoms. Langmuir made use of this discovery when he invented the atomic-hydrogen torch.

Principle of the atomic-hydrogen torch. In an atomic-hydrogen torch, hydrogen gas is passed through an electric arc produced between electrodes made of wolfram. The heat of the electric arc splits the hydrogen molecule into hydrogen atoms. Immediately after passing through the arc, the atoms reunite, forming hydrogen molecules,



General Electric Company

Repairing worn parts of vacuum cleaners with an atomic-hydrogen arc welder.

which are oxidized, forming water. Atomic hydrogen cannot be stored.

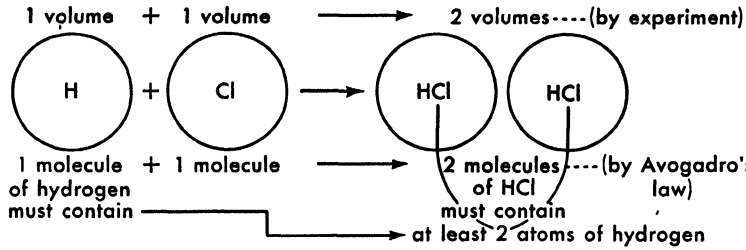
$$H_2 \rightleftarrows H + H$$

All the energy absorbed from the electric arc in splitting the molecule is liberated when the atoms of hydrogen reunite. This energy, as heat, added to the heat normally generated when hydrogen burns, produces a temperature between 4000°C. and 5000°C. (The oxy-acetylene torch gives a temperature of about 3300°C.)

The atomic-hydrogen torch is used for cutting and welding metals. It has the advantage of protecting the object against oxidation, since the jet of burning hydrogen is always surrounded by hydrogen, a reducing agent.

Proof that the molecule of hydrogen contains two atoms. Theoretically, we can prove the formula of hydrogen gas to be H_2 as follows: (1) From experiments, we know that one volume of hydrogen unites with one volume of chlorine, yielding two volumes of hydrogen chloride gas. (2) According to Avogadro's law, equal volumes of all gases contain the same number of molecules. Conversely, equal numbers of molecules of gases occupy equal volumes. Hence,

one molecule of hydrogen and one molecule of chlorine occupy equal volumes, and two molecules of HCl gas occupy twice this volume. We may represent this graphically as follows:



(3) One of the HCl molecules must contain at least one atom of hydrogen, since fractions of atoms do not exist. (4) Since we have two HCl molecules, we must have at least two atoms of hydrogen which can have come from only the one molecule of hydrogen.

PRACTICE PROBLEMS BASED ON THE PROOF OF THE STRUCTURE OF A MOLECULE OF HYDROGEN

1. We know that 1 vol. of nitrogen unites with 1 vol. of oxygen, forming 2 vol. of nitric oxide. Prove that the molecule of nitrogen contains two atoms.

2. One vol. of hydrogen unites with 1 vol. of bromine vapor, forming 2 vol. of hydrogen bromide gas. Show that the molecule of bromine vapor contains two atoms.

3. One vol. of oxygen unites with 2 vol. of hydrogen, forming 2 vol. of water vapor. Show that the formula for oxygen gas is O_2.

4. Prove the structure of the hydrogen molecule from the fact that 1 vol. of nitrogen unites with 3 vol. of hydrogen, forming 2 vol. of ammonia gas.

The gram-molecular volume of a gas or vapor. You have learned that a chemical formula may represent one molecule of a compound; one molecular weight of a compound; and also one gram-molecular weight, or mole, of a compound. For example, CO_2 may stand for one molecule of carbon dioxide, for the molecular weight of carbon dioxide (44), or for one mole of carbon dioxide (44 grams). If a coefficient appears in front of a formula, it represents a definite number of molecules, molecular weights, or moles. Thus $2CO_2$ stands for two molecules of the gas, two molecular weights (88), or two moles (88 grams). A formula has an additional meaning which is important in many chemical calculations.

In dealing with a gas or vapor, it is often necessary to know the volume that a quantity of it occupies. The unit of measurement of gas volumes is the volume occupied by one mole (abbreviated $\overline{M}$). This is called the *gram-molecular volume* (V). Study has shown that the gram-molecular volume is the same for all gases. *Under standard conditions of temperature and pressure, one $\overline{M}$ of any gas or vapor occupies 22.4 liters.* This may be demonstrated by the experimental process of weighing a given volume of any gas. For example, one liter of hydrogen weighs 0.08987 gram. Therefore 22.4 liters weigh 2.016 grams, which is the gram-molecular weight (mole) of hydrogen.

Since one mole of any gas occupies 22.4 liters, we may use the formula of the gas to represent its gram-molecular volume. For example, CO_2, which represents one mole of carbon dioxide, also represents one gram-molecular volume (V) of carbon dioxide; NH_3 represents one $\overline{M}$ of ammonia and also one V of ammonia. In each case, V = 22.4 liters. If a coefficient appears in front of the formula of a gas, it represents the number of gram-molecular volumes. Thus $2CO_2$ stands for 2V (44.8 liters); $2NH_3$ also stands for 2V. How many liters of gas would be represented by $4CO_2$? by $5NH_3$?

TYPES OF PROBLEMS

TYPE 3B: WEIGHT–VOLUME AND VOLUME–WEIGHT PROBLEMS

In these problems, the weight of one substance is given and the volume of another is to be found. Or the volume of one is given, and the weight of another is to be found. The procedure is the same in both cases. Standard conditions of temperature and pressure (S.T.P.) are assumed.

EXAMPLE: How many liters of nitric oxide can be prepared by action of sufficient dilute nitric acid on 127.2 g. of copper?

Procedure.

1. Write the balanced equation.

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

2. Write the given weight over its formula and *x* l. over the formula whose volume is to be found. Cross out all other formulas.

$$\overset{127.2\ g.}{3Cu} + \cancel{8HNO_3} \rightarrow \cancel{3Cu(NO_3)_2} + \cancel{4H_2O} + \overset{x\ l.}{2NO}$$

3. Under the formula whose weight is given, write its molecular weight. Under the formula whose *volume* is to be found, write its gram-molecular volume (V), *not* its molecular weight.

$$\begin{array}{ccc} 127.2\text{ g.} & & x\text{ l.} \\ 3Cu & \rightarrow & 2NO \\ 3(63.6) = 190.8 & & 2V = 2(22.4) = 44.8 \end{array}$$

4. Write the mathematical equation based on the relationship:

$$\frac{\text{wt. of substance used}}{\text{mol. wt. of substance used}} = \frac{\text{vol. of substance formed}}{\text{V of substance formed}}$$

Solve for x.

$$\frac{127.2}{190.8} = \frac{x\text{ l.}}{44.8}$$

$$190.8x = 127.2(44.8)$$

$$x = 29.9 \text{ liters of NO}$$

The same general procedure is followed in finding the *weight* of one substance when the *volume* of another is given except that x represents the unknown weight rather than the unknown volume. Use an equation based on the same relationship for your final solution.

PRACTICE WORK ON PROBLEMS OF TYPE 3B

1. What volume of H_2 may be obtained by the electrolysis of 90 g. of H_2O?

2. How many liters of NH_3 can be formed by the action of 33 g. of $(NH_4)_2SO_4$ on sufficient $Ca(OH)_2$?

3. How much NaCl is needed to produce 112 l. of HCl gas?

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

4. What weight of H_2O must be decomposed to produce 224 ml. of O_2?

5. A manufacturer requires 10,000 l. of N_2O. What weight of NH_4NO_3 must be decomposed?

TYPE 3C: STRAIGHT VOLUME PROBLEMS

This type of problem involves finding the volume of one gas or vapor when the volume of another is known. As we have learned, the coefficient before the formula of a gas represents the number of gram-molecular volumes of the gas. Since we are dealing only with volumes, weights are disregarded. Only the volumes as represented by the coefficients are considered.

EXAMPLE: How many liters of carbon dioxide are formed during complete combustion of seven liters of benzene, C_6H_6?

Procedure.

1. Write the balanced equation.

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$

2. Write the given volume above its formula. Write x l. above the formula whose volume is to be found. Cross out all other formulas.

$$\begin{array}{c} \text{7 liters} \qquad\qquad x \text{ l.} \\ 2C_6H_6 + \cancel{15O_2} \rightarrow 12CO_2 + \cancel{6H_2O} \end{array}$$

3. Write the number of gram-molecular volumes (shown by the coefficients) under the respective formulas.

$$\begin{array}{c} \text{7 liters} \quad x \text{ l.} \\ 2C_6H_6 \rightarrow 12CO_2 \\ 2 \qquad 12 \end{array}$$

4. Write out the mathematical equation based on the relationship:

$$\frac{\text{vol. of substance used}}{\text{coefficient of substance used}} = \frac{\text{vol. of substance formed}}{\text{coefficient of substance formed}}$$

Solve for x.

$$\frac{7}{2} = \frac{x \text{ l.}}{12}$$
$$2x = 84$$
$$x = 42 \text{ liters of } CO_2$$

PRACTICE WORK ON PROBLEMS OF TYPE 3C

1. 50 l. of H_2 react completely with Cl_2. What volume of HCl gas is formed?

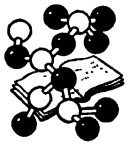
2. What volume of H_2 is necessary to unite with 5 l. of O_2 without leaving any O_2 in excess?

3. What volume of NH_3 can be made from 5000 l. of pure N_2?

4. How many liters of O_2 will be used during the complete combustion of 500 ml. of methane, CH_4?

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

5. What volume of oxygen will convert 50 ml. of NO into nitrogen dioxide, NO_2?



YOU WILL ENJOY READING

Jaffe, Bernard. *Chemical Calculations.* World Book Co., Yonkers, N.Y., 1947. Additional problems of the types discussed in this chapter, together with a more detailed account of methods of determining atomic weights and molecular weights.

Jaffe, Bernard. *Crucibles: The Story of Chemistry,* pp. 157–174. Simon and Schuster, New York, 1948. "The Spirit of a Dead Man Leads a Battle" tells the story of Avogadro.

Perrin, Jean B. *Atoms.* D. Van Nostrand Co., New York, 1923. In this book, Perrin, who won the Nobel prize for his work on the molecule, describes his verification of Avogadro's law.



USEFUL IDEAS DEVELOPED

1. A molecule is the smallest part of either an element or a compound which has the properties of that substance.

2. Gay-Lussac's law states that the relation between the combining volumes of gases and the volumes of their products, if gaseous, may be expressed in small whole numbers.

3. Boyle's law states that the volume of a gas varies inversely as the pressure exerted upon it if the temperature remains constant.

$$V_1/V_2 = P_2/P_1$$

4. Charles' law states that the volume of a gas varies directly as the absolute temperature if the pressure on the gas remains constant.

$$V_1/V_2 = T_1/T_2$$

5. Avogadro's law states that equal volumes of all gases under the same conditions of temperature and pressure are composed of the same number of molecules.

6. Avogadro's law is valuable because (1) it shows that the molecules of certain elementary gases, among them hydrogen, oxygen, nitrogen, and chlorine, consist of two atoms; (2) it makes possible the determination of the molecular weights of gases; (3) it makes possible the determination of the atomic weights of gaseous elements; and (4) it shows the relationships among several apparently conflicting facts concerning the actions of gases.

7. Avogadro's hypothesis was verified by the work of other scientists and today is a chemical law. The actual number of

molecules in the gram-molecular weight of a gas was determined by experiment. This number, called *Avogadro's number,* is the same for all gases. It is 6.02×10^{23}.

8. The gram-molecular volume of a gas is the volume occupied by its gram-molecular weight. Under standard conditions, it is 22.4 liters.



USING WHAT YOU HAVE LEARNED

Group A

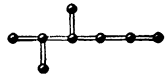
1. In 1860, what was the condition of chemical usage with respect to the terms *atom* and *molecule?*

2. What is the difference between an atom and a molecule?

3. When and by whom was the term *molecule* first clearly defined?

4. What did Cannizzaro do to establish the meaning of *molecule?*

5. (a) State Gay-Lussac's law and (b) give two illustrations of it.



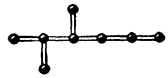
6. The volume of a gas changes from 10 to 5 l. when the pressure on it changes from 1 to 2 atm. What law does this illustrate?

7. The volume of a gas changes from 4 l. to 2 l. when its temperature changes from 500°A. to 250°A. State the law illustrated.

8. State Avogadro's law.

9. Upon what facts did Avogadro base his hypothesis?

10. State two ways in which Avogadro's law is valuable.



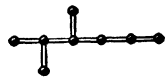
11. What two scientists verified Avogadro's hypothesis?

12. What is a gram-molecular volume of a gas?

13. Outline the method used in working a weight-volume problem.

14. Outline the method used in working a straight-volume problem.

15. If 15 l. of N_2 are needed to unite with O_2 in forming NO, what volume of O_2 will be used?



16. Assume that air contains 20 percent O_2 by volume. What volume of air will be needed in forming 100 ml. of O_3?

17. What volume of air will be needed for the complete combustion of 750 ml. of acetylene, C_2H_2?

18. CO passed over warm $Ca(OH)_2$ reacts as follows:

$$CO + Ca(OH)_2 \rightarrow CaCO_3 + H_2 \uparrow$$

How does the volume of CO compare with that of the H_2?

19. What weight of carbon is in 44.8 l. of CO?

20. What volume of NO_2 will be formed by the complete reaction of 100.5 g. of Hg with concentrated HNO_3?

$$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2H_2O + 2NO_2$$

21. HCl gas was bubbled through a solution of NaOH. As a result, 468 g. of NaCl were formed. What volume of the HCl used actually combined with the base?

Group B

22. From the experimental fact that 3 vol. of O_2 change into 2 vol. of O_3 when an electric discharge is passed through moist O_2, prove that the molecule of ozone contains three atoms.

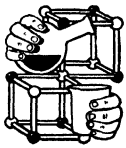
23. Prove nitrogen molecule contains at least two atoms.

24. Which is more economical to use in the preparation of NH_3, $(NH_4)_2SO_4$ at \$8.75 per 100 lb. or NH_4Cl at 12¢ per lb.?

25. (a) Explain the operation of the atomic-hydrogen torch. (b) Account for the extreme heat obtained.

26. What is meant by absolute temperature?

27. Prove by calculation that the *ounce-molecular-volume* of any gas equals 22.4 cu. ft.

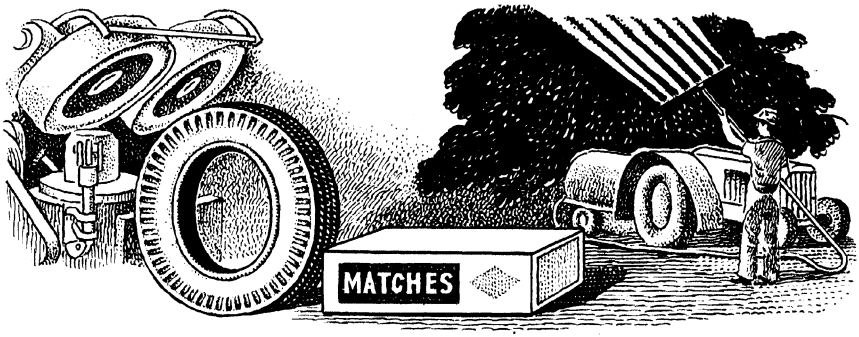


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. In England, Robert Boyle is considered the father of modern chemistry. In France, Lavoisier is called the father of modern chemistry. Can you suggest reasons for this difference of opinion among French and English scientists? Is it justified? Does it illustrate scientific open-mindedness?

2. Suggest possible reasons for the neglect of Avogadro's hypothesis from 1811 to 1860. Can you cite other scientific work which remained unrecognized for a long time?

3. Construct a cardboard or wooden box to represent the gram-molecular volume of any gas at S.T.P. Exhibit it to your class alongside of a quart bottle or carton of milk.



20 SULFUR
AND HYDROGEN SULFIDE

. . . Sulfur has been taken intermittently from Popocatepetl since the time of the ancient Aztecs, who used it for medicinal purposes. Two of Cortez's soldiers, in the sixteenth century, climbed to the crater and obtained sulfur for the purpose of manufacturing gunpowder. Science News Letter

An American pharmacist creates a new industry. The discovery of petroleum in Pennsylvania in 1859 led at once to a wide search for other stores of oil. Only six years later, oil prospectors stumbled upon huge deposits of sulfur, a yellow, brittle, lustrous solid known since ancient times. These deposits were about 500 feet below the surface in Louisiana not far from the Gulf near the Texas line. Here ages ago a vast geyser had spouted, leaving the sulfur within and about its crater. The sulfur was covered with strata of clay, limestone, and, worst of all, gas and quicksand. It was impossible to sink shafts to reach the deposits in order to dig the sulfur out as coal is mined. Many companies were formed to exploit these deposits, but because of the many difficulties, they all failed.

In 1891 Herman Frasch (fräsh) heard about this sulfur. He had come from Germany 25 years before. Leaving high school at 16, he had been apprenticed to a druggist and then had left for the United States, where he opened his own drugstore in Philadelphia. Chemistry fascinated him, and in the back of his drugstore he carried on many researches on petroleum products. Later he sold his store and devoted all his time to chemical engineering. He tackled the problem of extracting sulfur from the Louisiana deposits.

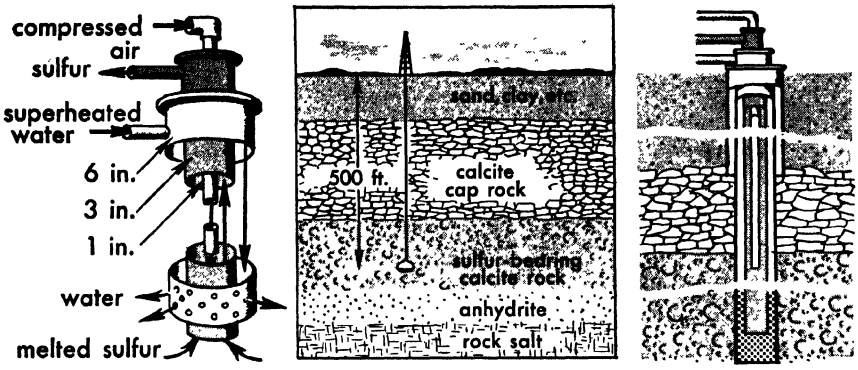


Fig. 64. The Frasch process for extracting sulfur from deposits deep in the earth.

When Frasch described to some of his friends the entirely new process that he had devised, they thought it impossible. One prominent person challenged him in no uncertain terms. He said that he would swallow every ounce of sulfur Frasch extracted by his queer process of pumping a solid out of the earth. But Frasch kept on improving his method and ultimately he succeeded in founding a new American industry based on his process.

The Frasch process of extracting sulfur. Frasch's plan was to sink a well by means of an oil-drilling rig, and lower three concentric pipes (inside a casing) down to the sulfur. Through the outermost 6-inch pipe, superheated water was to be pumped to melt the sulfur. Through the innermost one-inch pipe, compressed air was to be forced down to the sulfur deposit to make the melted sulfur frothy and light. The result was to be a flood of molten, foamy sulfur gushing under pressure from the three-inch pipe between the other two.

Frasch was visibly nervous when he gave the order to start the first pump. More and more slowly went the engine with its increasing load until the man at the throttle sang out at the top of his voice, "She's a-pumping." A liquid appeared at the mouth of the three-inch pipe. Frasch wiped the liquid off a polished piston rod, and gazed upon the first crystals of sulfur extracted by his ingenious process. Then came a steady stream of golden liquid, which, in 15 minutes, filled every one of the 40 barrels available. Still the molten sulfur kept pouring. Embankments were quickly thrown up and lined with boards to hold the sulfur as it solidified.

This is the method of mining sulfur in use today in Texas and Louisiana. These deposits now supply much of the world's needs. In this way, mountains of sulfur, 99½ percent pure, are extracted and stand ready to be dynamited into pieces small enough to be loaded and shipped to many parts of the world.

Sulfur is obtained in Sicily by a different process. Before the time of Frasch, a group of English financiers had been marketing the rich sulfur deposits of the volcanic region of Sicily. Here the sulfur is found mixed with clay and limestone, from which it is separated by melting this ore, allowing the free sulfur to flow away from the impurities. The sulfur is then boiled and is changed to a powder, called *flowers of sulfur,* by chilling the vapors.

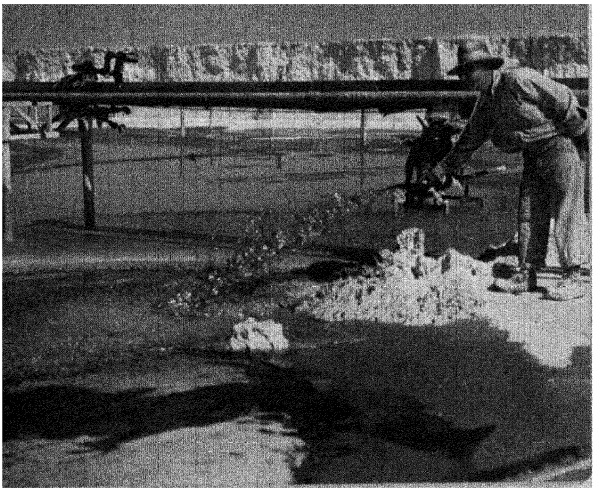
The English monopoly had been supplying more than 90 percent of the world's sulfur. In 1904, when American output reached the point where a single well could supply 400 tons of sulfur daily, the English company went out of business. To prevent the unemployment of hundreds of workers, the Italian government took control. Frasch aided gladly in stabilizing the Sicilian sulfur industry.

Crude free sulfur accounts for about only 40 percent of the world's sulfur production. Iron, zinc, and copper sulfides, natural gas, and industrial gases supply the rest. The United States today leads the world in the production of sulfur. Many countries, including Italy and Mexico, are stimulating their own production of sulfur by subsidies, tariff laws, bounties, and price guarantees.

Physical properties of sulfur. Sulfur is a pale yellow, soft, brittle solid (plastic, or pliable, in the case of amorphous sulfur) with a very faint odor and no marked taste. It is practically insoluble in water, more soluble in carbon tetrachloride, CCl_4, and very soluble in carbon disulfide, CS_2.

Sulfur is a poor conductor of heat. It melts at about 114°C., forming a pale yellow liquid, which on further heating darkens and thickens, becoming almost black at 235°C. At a still higher temperature, it becomes thinner again, and finally changes to a yellow vapor at 445°C. Sulfur is mentioned in the Bible as *brimstone.*

Texas Gulf Sulfur Company



Liquid sulfur flows into the storage vat in which it will solidify. The pipeline leads to the sulfur well.

Allotropic forms of sulfur. Oxygen, as you have learned, occurs in two allotropic forms, O_2 and O_3, but sulfur occurs in two common crystalline forms (*rhombic* and *prismatic*), and one noncrystalline or *amorphous* form. Each has different properties caused by differences in the arrangement of their atoms.

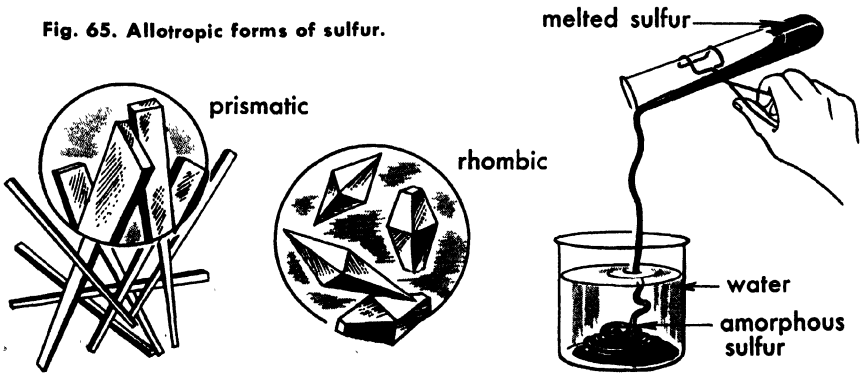
1) **Rhombic sulfur.** Sulfur is found in nature in the form of rhombic crystals, the most stable form under normal conditions. Their molecules consist of rings of eight atoms of sulfur (S_8), and their density is about two. Crystals of this form of sulfur may be prepared by dissolving sulfur in carbon disulfide and allowing the solvent to vaporize slowly. The residue consists of perfect crystals having the shape of two pyramids with their bases joined. *Roll sulfur,* made by cooling sulfur in cylindrical molds, is almost entirely rhombic.

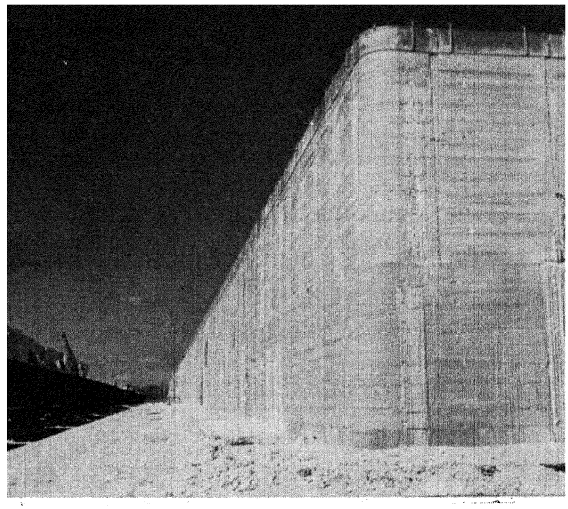
2) **Prismatic sulfur.** When sulfur is heated until it just melts and is then allowed to cool slowly, it forms long needle-shaped crystals whose density is somewhat less than that of rhombic sulfur.

3) **Amorphous sulfur.** When boiling sulfur is suddenly cooled by pouring it into cold water, the rings are broken and are replaced by long chains of sulfur atoms which become entangled and can be stretched like rubber. It is amber in color and, unlike the other two forms, is insoluble in carbon disulfide. Amorphous sulfur changes gradually into rhombic at room temperature. For simplicity, all forms are designated S. *Flowers of sulfur* is a powdered mixture composed of rhombic and some of the plastic. Between 96°C. and 114°C. the most stable form of sulfur is the prismatic.

Chemical properties of sulfur. The atomic weight of sulfur is 32. Its atomic number is 16, and it has, therefore, six electrons in its third, or outermost, ring. This makes it a borrower of electrons. It is a nonmetal, fairly active, and has, under ordinary conditions, a valence of minus two. Therefore, sulfur closely resembles oxygen in its chemical properties.

Fig. 65. Allotropic forms of sulfur.





Exterior of a sulfur storage vat. The solidified sulfur will be blasted into small pieces for shipment in railroad cars.

Texas Gulf Sulfur Company

Like oxygen, sulfur unites with most metals. The compounds of metals and sulfur are called *sulfides*. For example, when sulfur is heated with iron powder, iron sulfide is formed.

$$Fe + S \rightarrow FeS$$

Hot copper burns in sulfur vapor, forming cuprous sulfide.

$$2Cu + S \rightarrow Cu_2S$$

When sulfur is mixed with zinc dust and ignited, the chemical reaction is so vigorous that a great deal of light and heat are liberated and dense clouds of zinc sulfide, which settle out as a powder, are formed.

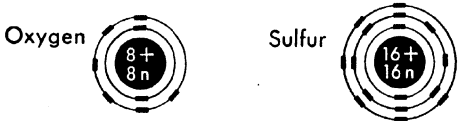
$$Zn + S \rightarrow ZnS$$

Although sulfur is a nonmetal, it is less nonmetallic than oxygen. It therefore combines with oxygen, exhibiting a positive valence of either four or six. Sulfur burns in air with a pale blue flame, forming sulfur dioxide, SO_2. A small amount of sulfur trioxide, SO_3, is formed later by further oxidation of the SO_2.

$$S + O_2 \rightarrow SO_2 \text{ (sulfur dioxide)}$$
$$2SO_2 + O_2 \rightarrow 2SO_3 \text{ (sulfur trioxide)}$$

The electron structure of sulfur and oxygen are shown below.

Fig. 66. The structure of the oxygen atom (left) and the sulfur atom.



Sulfur also shows more metallic properties than chlorine by uniting with the latter, forming sulfur dichloride, SCl_2, a brownish red liquid with a pungent odor used in chlorinating, and also sulfur monochloride, a heavy, amber-colored unstable liquid with an irritating odor, used in *vulcanizing* rubber.

$$2S + Cl_2 \rightarrow S_2Cl_2 \text{ (sulfur monochloride)}$$

When sulfur vapor is passed over carbon heated in an electric furnace, the two elements combine, forming carbon disulfide, CS_2.

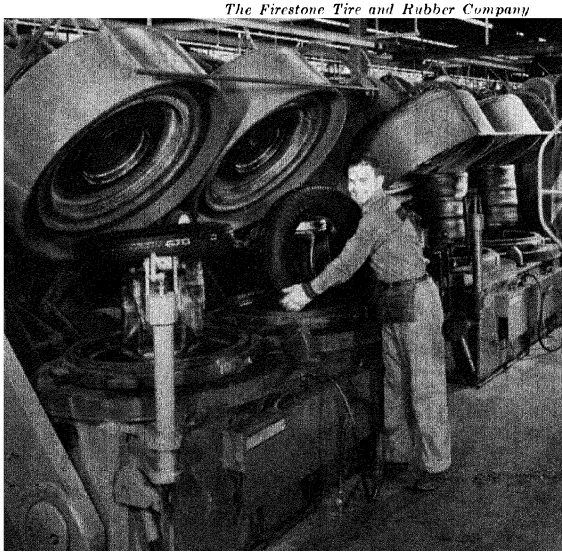
$$C + 2S \rightarrow CS_2$$

Carbon disulfide is a heavy, colorless liquid with a pleasant odor. Generally, however, it has a disagreeable odor caused by impurities. It is very combustible. Its chief use is as a solvent for sulfur, gums, rubber, fats, and waxes. It has been used also as a poison in exterminating ants and other insects, rats, and prairie dogs.

Rubber tires depend on sulfur. The normal annual consumption of sulfur in the United States is more than three million tons. It is one of the fundamental industrial elements. By far the greatest quantities of sulfur are used in the manufacture of sulfuric acid, one of the most widely used of the heavy chemicals. The production and uses of sulfuric acid are discussed in Chapter 21.

Great quantities of sulfur are used in vulcanizing rubber. By this process, soft, sticky, perishable, natural rubber is changed to a harder, less plastic, more durable rubber. Vulcanized rubber is used chiefly in making automobile tires but also in making thousands of other rubber articles.

The Firestone Tire and Rubber Company



In a modern tire factory, a workman removes a finished tire from a steam-heated vulcanizing mold.

When the American, Charles Goodyear, in 1839 while working in his kitchen in Woburn, Massachusetts, accidentally dropped a piece of rubber mixed with sulfur on a hot stove, he discovered the process of *vulcanization* (derived from Vulcan, the Roman god of fire). A new and highly important industry was made possible. To shorten the time required for vulcanizing rubber, a catalyst, or *accelerator,* such as zinc oxide, is added to the mixture of rubber and sulfur.

In making an article of rubber, the washed raw rubber is thoroughly mixed with various chemicals that determine the properties of the finished product. Among these substances are sulfur, carbon black, lead oxide (PbO), zinc oxide, and carbonates of magnesium and calcium. Different combinations of these and other substances in varying quantities may be used in accordance with the properties desired in the finished product. The rubber is then rolled into sheets of the desired thickness or placed in molds of the desired shape. While in the mold, the rubber is heated and vulcanization occurs.

Sulfur is used in controlling fungi and insects. A very effective liquid for destroying fungus growths and fruit tree, shrub, and vine pests is a deep orange-red *lime-sulfur spray* made by boiling sulfur with calcium hydroxide. The spray is both a *fungicide,* a substance that kills fungi and molds, and an *insecticide,* a substance that kills insects. Dusting with very finely powdered sulfur is effective against rose diseases, mildew, and black spot. However, ordinary flowers of sulfur is not fine enough to be of much value as a dusting agent, and even some finely ground commercial dusting powders are too coarse.

Colloidal sulfur and *wettable sulfur,* the first a very highly dispersed sulfur in water and the second sulfur so treated that it disperses on contact with water, are both used in making mild sprays that are particularly useful for the summer spraying of roses and for the control of mildew and true rust diseases of other plants.

Sulfur is used in medicine. Ointments containing sulfur have been used since antiquity to control skin diseases caused by fungi. A common ointment of this kind is made by mixing three parts by weight of sulfur, 15 parts of *white petrolatum,* or Vaseline, one part of *lanolin,* or wool fat, and one part of yellow wax. Such an ointment is effective in killing the very small mites that cause *scabies,* or *itch.* Sulfur ointments may be of value in the control of infectious dandruff.

Other uses of sulfur. Much sulfur goes into the manufacture of calcium bisulfite, $Ca(HSO_3)_2$, which is used in making wood pulp for the manufacture of paper. Sulfur is used also in making synthetic resins, sulfur colors, and gunpowder. Sulfur-lined steel pipes

are used to transport liquids that are very corrosive to the materials of which pipes are normally made. Sulfur cements are used to join bricks in floors and walls that are continually subjected to the corrosive effects of acids or alkalies. Great quantities of sulfur are used in the making of matches.

How matches are made. Early matches were dangerous, hard to use, and hard to carry. Phosphorus matches often caused painful burns and were harmful to the health of the workers who made them.

The first friction match was invented in 1827 by an English pharmacist, John Walker. It contained potassium chlorate ($KClO_3$), an oxidizing agent, and antimony sulfide (Sb_2S_3), a compound with a low kindling temperature. The *locofoco* match was an American adaptation of Walker's friction match. During the presidential campaign of 1840, the Democrats were called *locofocos* because at one of their meetings, they used matchlight when the Whig landlord turned off the gas.

In 1831 white phosphorus was used for the first time in making matches. It was a more efficient fire-producer than antimony sulfide, but played havoc with the health of the match-factory workers, who finally demanded protection. This led in 1906 to an international convention which prohibited the further use of white phosphorus in making matches because of its poisonous nature.

The *strike-anywhere match* in use today also contains both an oxidizing agent and a compound with a low kindling temperature. The head of the paraffin-dipped matchstick contains potassium chlorate and phosphorus sulfide (P_4S_3), a dark solid that is concentrated on the tip of the match. Glue is used to bind the chemicals, and ground glass or other abrasive is sometimes added as a filler.

The tip of a *safety match* is composed of easily combustible antimony sulfide (Sb_2S_3), and potassium chlorate, which provides additional oxygen. The side of the box contains red phosphorus, which

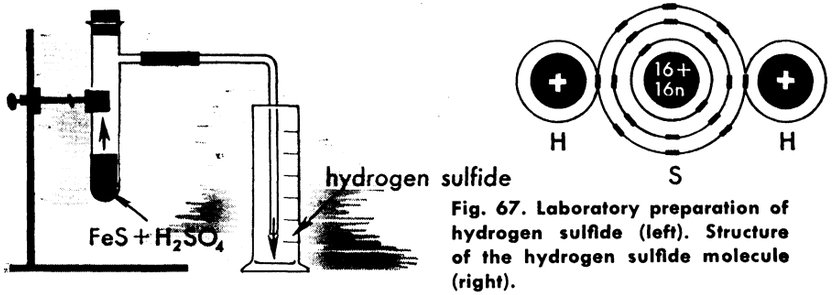


Fig. 67. Laboratory preparation of hydrogen sulfide (left). Structure of the hydrogen sulfide molecule (right).

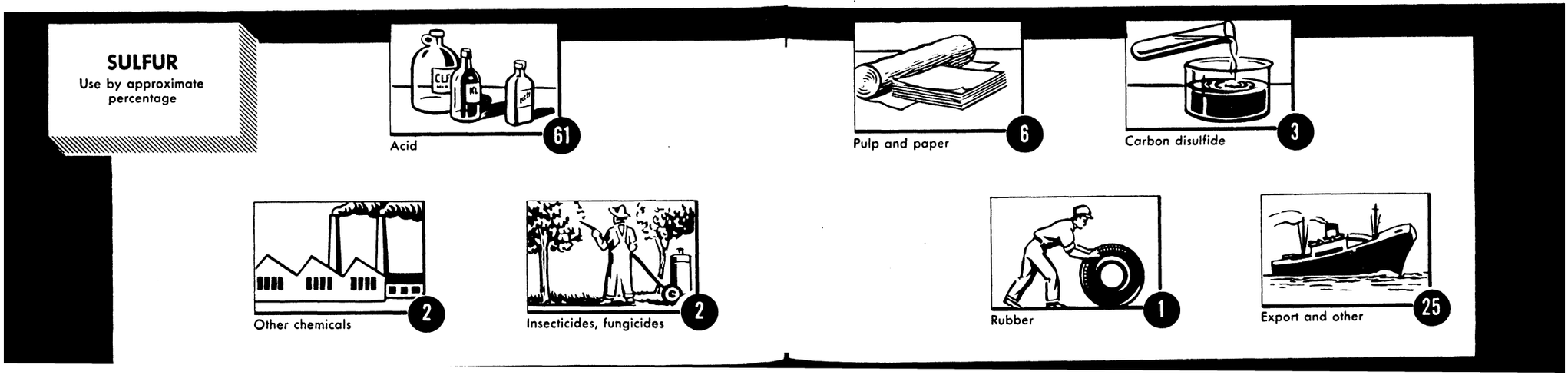
is nonpoisonous. The material on the tip of the match will not ignite easily unless it is rubbed on the treated side of the box.

Disastrous fires are frequently caused by matches that have been blown out but still retain glowing tips. To prevent this dangerous afterglow, matches are dipped in some such solution as sodium sulfate or ammonium phosphate during their manufacture. When blown out, they do not leave glowing tips.

Waterproof matches are treated with a transparent coating with a high-kindling temperature. They will light even after being soaked in water.

The manufacturer of matches uses a continuous-process machine, which takes pine wood, cuts it, dips the sticks in paraffin, coats them with the chemicals needed, dries them, and finally packs them for shipment. More than a million matches can be made by one of these machines each hour.

How sulfur and hydrogen unite. Hydrogen has only one electron. It therefore needs one electron to complete its only ring; but since it shows a strong tendency to lend its one electron, it is said to possess metallic properties. Sulfur, requiring two electrons to complete its outer ring, will combine with two atoms of hydrogen. This union forms the compound, hydrogen sulfide, H_2S, as shown in Fig. 67. In this compound, sulfur exhibits definitely nonmetallic properties. Although it is possible to prepare hydrogen sulfide by direct union of sulfur and hydrogen, it is prepared most easily by other methods.



How hydrogen sulfide is prepared. Hydrogen sulfide is prepared both commercially and in the laboratory by the general method of preparing an acid, that is, by the action of sulfuric acid on a salt (sulfide). The sulfide most generally used is ferrous sulfide, FeS, a black iron ore. When sulfuric acid is poured on ferrous sulfide in a test tube (see Fig. 67), hydrogen sulfide gas is given off immediately without the addition of any external heat.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow$$

Physical properties of hydrogen sulfide gas. Hydrogen sulfide is colorless, slightly heavier than air, and fairly soluble in water (one volume of water dissolves three volumes of hydrogen sulfide). Natural sulfur waters contain hydrogen sulfide in solution and, upon being decomposed, leave a deposit of free sulfur. Easily liquefied, hydrogen sulfide is sold in cylinders for laboratory use. Its most characteristic physical property is its odor, the odor of rotten eggs. In fact, it is hydrogen sulfide that gives such eggs their odor. It is caused by the decomposition of organic sulfur compounds in the yolks.

Hydrogen sulfide forms naturally in marshes, oil wells, mines and coal piles, manure pits, and sewers. In persons who have endured mild exposure to its effects, it produces inflamed throat, headache, a heavy feeling in the stomach, and dizziness. When breathed in large quantities it causes death. Both natural gas and coal gas contain H_2S which is removed before they are used as household fuels.

Chemical properties of hydrogen sulfide gas. When burned in sufficient air, hydrogen sulfide gives off a pale blue flame, and water vapor and sulfur dioxide are formed. This sulfur dioxide gives burning hydrogen sulfide its irritating odor. The equation for the *complete combustion* of hydrogen sulfide is:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \uparrow$$

When hydrogen sulfide is burned in a small amount of air (*incomplete combustion*), water is formed as before, but free sulfur is produced instead of sulfur dioxide. This sulfur separates out as a yellow powder. The fact that it does so probably accounts for the presence of sulfur around volcanoes, which emit hydrogen sulfide gas.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S \uparrow$$

Because of the tendency of hydrogen sulfide to unite with oxygen, it is a fairly good reducing agent. When hydrogen sulfide acts as a reducing agent, the sulfur lends electrons and is oxidized.

In a water solution, hydrogen sulfide dissociates to some extent. Such a solution acts as a weak, unstable acid, sometimes known as *hydrosulfuric acid,* H_2S. On continued boiling, this acid liberates hydrogen sulfide, leaving pure water.

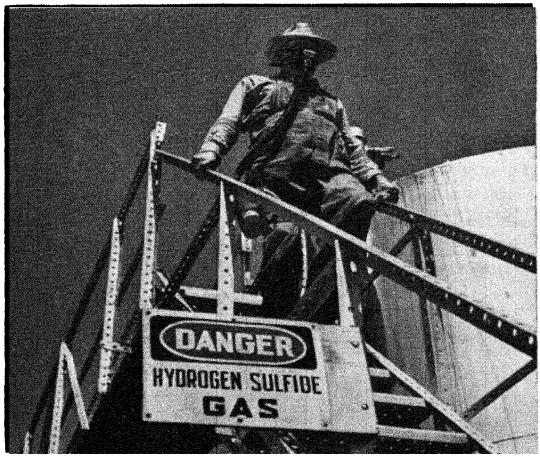
Hydrogen sulfide reacts with certain metals and also with the salts of certain metals, forming sulfides. The tarnishing of silverware is caused by the formation of a brownish-black sulfide of silver, Ag_2S. The blackening of lead paints is caused by the formation of black lead sulfide. *Lithopone,* a white paint base now used widely, consists of a mixture of barium sulfate ($BaSO_4$), and zinc sulfide (ZnS). Lithopone paints do not lose their color by the action of H_2S. Why? *Titanium dioxide,* TiO_2, also is used as a white paint base. It is not blackened by sulfur compounds and has great covering power.

Many important sulfides are found in the earth. The salts of hydrosulfuric acid form an important class of compounds called *sulfides.* Many of them occur in nature and constitute important ores such as *iron pyrites,* FeS_2; *galena,* PbS; *zinc blende,* ZnS; *cinnabar,* HgS; and CuS. Certain colored sulfides are used as mineral pigments in the coloring of paints. Cadmium sulfide, CdS, for example, is a yellow pigment, and zinc sulfide, ZnS, is a white pigment used in paints (see illustration following page 382).

The chief use of hydrogen sulfide. In the analysis of ores and in the separation of groups of certain metals from other groups of metals, hydrogen sulfide gas is indispensable. For this reason, a hydrogen sulfide generator is always present in a laboratory for analytical chemistry. The sulfides of certain metals such as sodium and calcium are soluble in water, while those of other metals such as lead and zinc are insoluble.

By passing hydrogen sulfide into a solution of the soluble salts of such metals, the sulfides of certain metals precipitate out and may be separated by filtration. Thus, certain metals present in an ore or

Standard Oil Company (N.J.)



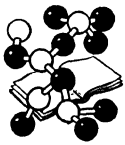
Hydrogen sulfide fumes rising from crude oil may prove fatal to workmen. Hence, protective masks are worn by anyone working near the oil storage tanks.

alloy may be separated with the aid of H_2S. Furthermore, since the colors of the sulfides of many metals differ, chemists can use these differences in color in detecting the presence of these metals. For example, zinc sulfide is white, arsenic sulfide is yellow, antimony sulfide is orange, and copper sulfide is brownish-black.

$$Zn(NO_3)_2 + H_2S \rightarrow ZnS\downarrow + 2HNO_3$$
$$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$$

This difference in color is only one of the very many ingenious methods used by analytical chemists in detecting and isolating elements present in complex mixtures and compounds.

The test for the sulfide ion. If, on the addition of sulfuric acid to a compound, hydrogen sulfide gas is liberated, the substance tested is a sulfide. The hydrogen sulfide liberated is easily detected either by its odor or by its ability to turn a silver coin brownish-black, as a result of the formation of silver sulfide.



YOU WILL ENJOY READING

Fabre, Jean H. *The Wonder Book of Chemistry,* pp. 345–359. Albert & Charles Boni, New York, 1922. Discusses sulfur and includes some simple experiments with this element.

Waggaman, W. H., and Barr, J. A. "Sulfur for Survival." *Chemistry,* October, 1951, pp. 1–10. An illustrated article on sources, extraction, and properties of sulfur.



USING WHAT YOU HAVE LEARNED

Group A

1. When and by whom was the first successful method of obtaining S from the Louisiana deposits invented?

2. What was the great difficulty that had to be overcome before S could be extracted from the Louisiana deposits?

3. How did the Frasch process affect the Sicilian sulfur industry?

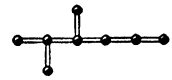
4. (a) Make a labeled diagram of the Frasch process and (b) explain it.

5. What are two ways in which the Louisiana sulfur deposits differ from the Sicilian sulfur deposits?

6. Name the allotropic forms of S and tell how each may be prepared in the laboratory.

7. What two elements other than S occur in allotropic forms?

8. (a) State the chief differences and resemblances of the three allotropic forms of S. (b) How could you prove that all three forms of S are the same element?



9. A piece of plastic S is left overnight in the laboratory. The next morning yellow brittle S is found. Explain.

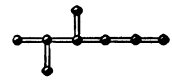
10. (a) How are the two kinds of commercial sulfur, roll sulfur and flowers of sulfur, prepared? (b) What allotropic forms are in each?

11. Make a diagram of an atom of S and use it to find the valence of S, to describe its chemical activity, and to explain why it is a nonmetal.

12. In what three ways does S resemble O_2?

13. Write balanced equations for the: (a) union of sulfur and zinc; (b) complete combustion of hydrogen sulfide; (c) incomplete combustion of hydrogen sulfide; (d) burning of sulfur; (e) union of sulfur and chlorine; (f) complete combustion of carbon disulfide.

14. What are four chief uses of S? List in order of importance.



15. (a) What is meant by the vulcanizing of rubber? (b) What properties does vulcanizing impart to rubber? (c) What American discovered this process?

16. (a) Of what chemicals is the tip of a strike-anywhere match composed? (b) How does a safety match differ from an ordinary match?

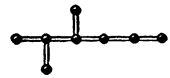
17. Hydrogen sulfide present in natural gas is removed before the natural gas is sent into the pipelines to be used as fuel. Explain.

18. By a labeled diagram describe the laboratory preparation of H_2S.

19. What weight of FeS would be needed to prepare 204 lb. of H_2S?

20. What volume of gaseous H_2S could be prepared from 20 g. of 90 percent pure FeS?

21. A compound of hydrogen and sulfur has a mol. wt. of 34. The percentage of S in the compound is 94.1 percent. Find its formula.



22. What volume of H_2S is required to precipitate all the CuS from a solution containing 80 g. of $CuSO_4$?

23. What volume of SO_2 will be formed by the complete combustion of 896 ml. of gaseous H_2S?

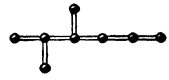
24. Write ionic equations for the following and tell whether each reaction goes to completion (refer to Table 10, page 243):

a) $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$
b) $Pb(NO_3)_2 + H_2S \rightarrow PbS + 2HNO_3$
c) $ZnSO_4 + (NH_4)_2S \rightarrow ZnS + (NH_4)_2SO_4$
d) $Na_2SO_4 + H_2S \rightarrow Na_2S + H_2SO_4$

25. Compare the physical properties of H_2S and N_2O.

26. Describe what happens when gaseous H_2S is bubbled through water.

27. Why is H_2S said to be (a) weak? (b) unstable?



28. Explain the tarnishing of silverware.

29. Why is H_2S solution kept in amber-colored bottles?

30. Using two equations, show the chief use of H_2S.

31. Describe a test for a sulfide.

32. Copy and complete. Do not write in this book. S occurs in our bodies because it is one of the elements found in .... The two chief sulfur-producing states in America are Louisiana and .... A lime-sulfur preparation is used as .... A sulfur compound used in exterminating rats is .... A sulfide that is soluble in water is ....

33. Under a rubber band used to keep pieces of silver cutlery together, a black mark is found. Explain.

Group B

34. How would you tell fool's gold, FeS_2, from genuine gold?

35. In the Frasch process, why is S forced out of the three-inch pipe rather than out of the six-inch pipe?

36. The action of H_2S on a solution of $ZnSO_4$ is reversible. How would you force this reaction to completion?

37. NH_3 leaks may be detected by burning sulfur candles. Explain.

38. (a) Why can we not use HNO_3 in preparing H_2S from FeS? (b) What is formed if H_2S is passed into HNO_3?

39. Why do we write CS_2 and not S_2C?

40. A mixture of sulfur and molasses was given to children as a "spring tonic." What do you think of this practice?

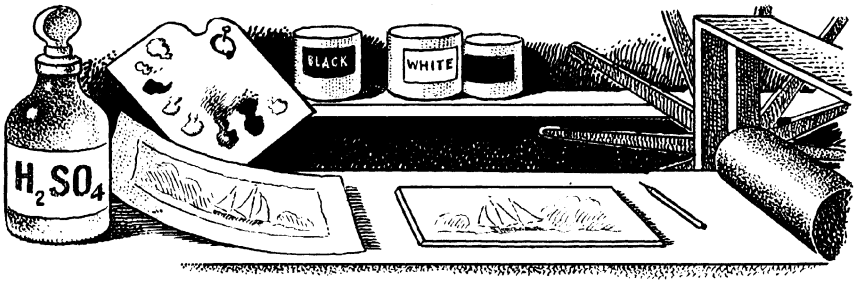


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Discovery of the vulcanization of rubber is generally considered an accident. Had the accident not happened to Goodyear, would the thousands of rubber articles in use today never have come? Explain your answer fully in terms of scientific advance and the needs of society.

2. If you live in a rural section, talk with as many farmers as possible to learn what methods they use to check the losses incurred by insect pests and fungus growths. Report your findings to your class.

3. Filter paper dipped in a solution of $Pb(C_2H_3O_2)_2$ turns black in the presence of H_2S. Hang small strips of it in the basement while the furnace is burning, over the kitchen stove or gas range while dinner is being cooked, and in the living room. Which of the strips turns blackest first? What do you conclude?



21 SULFURIC ACID: THE FUNDAMENTAL ACID

. . . We may fairly judge of the commercial prosperity of a country from the amount of sulfuric acid it consumes. Reflecting upon the important influence which the price of sulfur exercises . . . we can understand why the English Government should have resolved to war with Naples, in order to abolish the sulfur monopoly, which the latter power attempted recently to establish. Justus von Liebig, 1843

Why sulfuric acid is the fundamental chemical today. One of the outstanding differences between our society and the society which preceded it is the tremendous role that machines play. Automobiles, locomotives, steel ships, and airplanes are comparatively new. In the manufacture, operation, and upkeep of these and thousands of other machines, sulfuric acid is directly or indirectly a prime necessity. If the ability to make this acid were lost suddenly, industry would be paralyzed. So fundamental is it to our industrial life that its consumption is a fair index of industrial conditions.

How sulfur dioxide is prepared for use in industry. About 90 percent of the sulfur consumed industrially is first burned in air to produce sulfur dioxide. Heating sulfide ores is another commercial method of preparing SO_2. When an ore, such as iron pyrites, FeS_2, is heated in air, or *roasted,* one of the products formed is sulfur dioxide.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \uparrow$$

Sulfur dioxide occurs in small quantities in the vapors rising from active volcanoes and certain sulfur springs, and in the gases formed during the burning of coal.

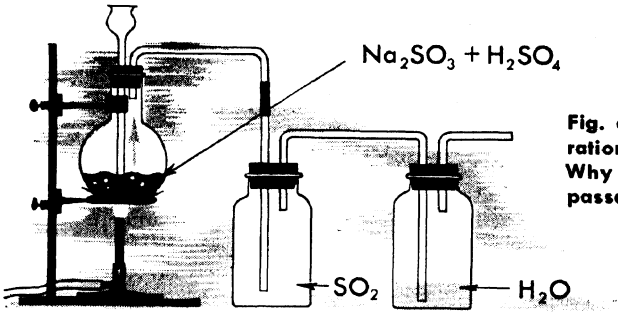


Fig. 68. Laboratory preparation of sulfur dioxide. Why is the excess gas passed through water?

How sulfur dioxide is prepared in the laboratory. When sodium sulfite, Na_2SO_3, or any other sulfite is treated with an acid, sulfur dioxide is liberated. The gas is collected by the displacement of air, as shown in Fig. 68.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

Physical properties of sulfur dioxide. Sulfur dioxide is colorless, has a suffocating odor, is more than twice as heavy as air, and is very soluble in water (one volume of water at room temperature dissolves 40 volumes of the gas). Under a pressure of only three atmospheres (approximately 45 pounds per square inch, or 45 psi) it changes to a colorless liquid, which can be transported in steel cylinders or shipped like gasoline in tank cars.

Chemical properties of sulfur dioxide. Sulfur dioxide does not burn in air, but it may be made to combine with another atom of oxygen, forming sulfur trioxide, SO_3, by passing a mixture of sulfur dioxide and air over a catalyst, such as platinum or vanadium pentoxide.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

This ability of sulfur dioxide to combine with more oxygen makes sulfur dioxide a reducing agent. Sulfur dioxide may also act as an oxidizing agent. When, for example, it is passed through a solution of hydrosulfuric acid, H_2S, it precipitates sulfur. The sulfur (S^{++++}) in the SO_2 takes electrons from the sulfur (S^{--}) of H_2S and changes to free sulfur, S^0.

$$S^{++++}O_2^{--} + 2H_2^{+}S^{--} \rightarrow 2H_2^{+}O^{--} + 3S^0\downarrow$$

Hydrosulfuric acid acts here as the reducing agent. These two actions of sulfur dioxide illustrate the fact that a substance may be either an oxidizing agent or a reducing agent, depending upon the substance to be reduced or oxidized.

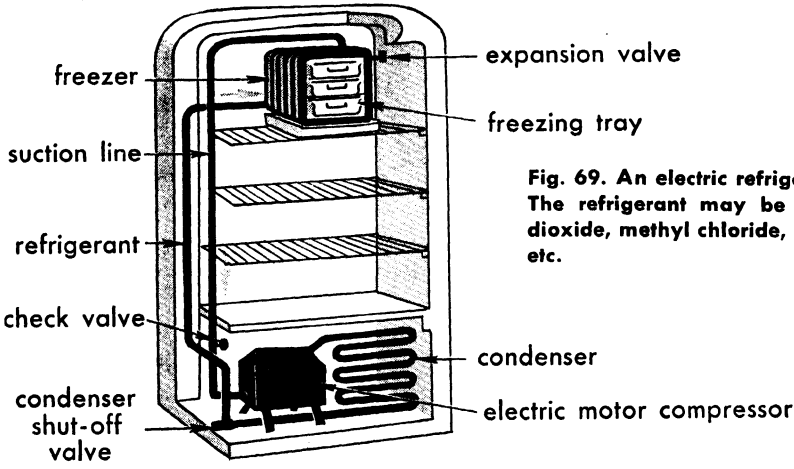


Fig. 69. An electric refrigerator. The refrigerant may be sulfur dioxide, methyl chloride, Freon, etc.

When sulfur dioxide dissolves in water, it combines with some of the water, forming sulfurous acid. Sulfur dioxide, then, is an acid anhydride.

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

Sulfur dioxide has many uses. The most common use of sulfur dioxide is in the manufacture of sulfuric acid. It is used also to some extent instead of ammonia in mechanical refrigeration. Although liquid sulfur dioxide during evaporation absorbs only one-third as much heat as ammonia does, it liquefies under a lower pressure and hence is used in some household refrigerators.

Homer in his *Odyssey* cited the use of burning sulfur in fumigation. Today rooms, houses, or warehouses are sometimes fumigated by burning sulfur candles or by liberating sulfur dioxide gas from cylinders. However, as a fumigant sulfur dioxide has been almost wholly supplanted by more effective substances. It is even extremely doubtful that fumigation by sulfur candles was ever very effective.

How sulfurous acid, H_2SO_3, is prepared in the laboratory. In the laboratory preparation of sulfur dioxide, SO_2 is not the product first formed. Sulfurous acid is the first product of the reaction, but it is impossible to stop the reaction at this point.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SO_3$$

Sulfurous acid is prepared by passing sulfur dioxide gas through cold water.

$$H_2O + SO_2 \rightarrow H_2SO_3$$

Properties of sulfurous acid. Sulfurous acid is a colorless solution with a suffocating odor (sulfur dioxide). It is unstable and decomposes readily into water and sulfur dioxide. By boiling sulfurous acid, all the sulfur dioxide may be driven off. The reaction is reversible, depending upon the temperature.

$$H_2O + SO_2 \rightleftarrows H_2SO_3$$

Sulfurous acid is a very weak acid because it dissociates only slightly, forming few hydrogen ions. When neutralized with a base, it forms salts known as *sulfites.*

$$H_2SO_3 + 2NaOH \rightarrow Na_2SO_3 \text{ (sodium sulfite)} + 2H_2O$$

On exposure to air, sulfurous acid may be oxidized to sulfuric acid to some extent.

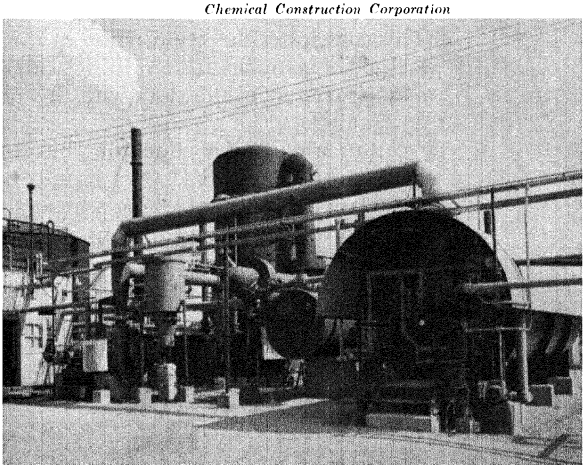
$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$

In a similar way, sulfites may be oxidized to sulfates.

How sulfurous acid, sulfites, and bisulfites are used. The tendency of one molecule of sulfurous acid to unite with one atom of oxygen, forming sulfuric acid, makes it a valuable reducing agent. This property of sulfurous acid enables it to be used in the bleaching of wood pulp, straw, silk, feathers, dried fruits, flour, molasses, and canned corn — all of which would be partially destroyed by other bleaching agents.

Fruits that are to be dyed are frequently bleached with sulfur dioxide (as sulfurous acid). For example, in making maraschino cherries, the cherries are first bleached and then dyed any desired color with edible dye. If sulfurous acid is used either in bleaching or in preserving a food that is sold in interstate commerce, this fact must be clearly stated on the label of the package in which it is sold.

Chemical Construction Corporation



A sulfur combustion furnace for the commercial production of sulfur dioxide. Melted sulfur is pumped into the furnace and burned to form the gas.

Substances of vegetable origin are not easily destroyed by sulfurous acid, and therefore their coloring matter may be reduced to colorless compounds by this weak acid. However, the bleaching action of sulfurous acid is not as lasting as that of chlorine or hydrogen peroxide, because the coloring matter that has been reduced may, on exposure to air, become reoxidized. This explains in part why straw hats, bleached with sulfurous acid, may turn brown.

Calcium bisulfite, $Ca(HSO_3)_2$, containing dissolved SO_2, is used in converting ground wood pulp into *sulfite pulp* by dissolving out the gluelike substances found mixed with the cellulose of the wood pulp (see page 598). Sulfite pulp is used in making paper.

Sodium sulfite mixed with a solid acid, such as oxalic (white crystals), makes up the dry powder used in bleaching straw hats. The action of this mixture of acid and sulfite illustrates the part that ions play in chemical reactions. While the *dry* solid acid and sulfite are in contact, no action occurs. As soon as water is added, however, the substances go into solution, dissociate, and the ions formed react, producing sulfurous acid, which bleaches. Na_2SO_3 is also used as an antichlor (a substance used to remove any excess of chlorine after bleaching) and as an oxygen-removal agent in treating boiler-feed water.

How to test for a sulfite. The characteristic odor of the sulfur dioxide liberated when an acid is added to a sulfite constitutes a test for any sulfite.

$$CaSO_3 + 2HCl \rightarrow CaCl_2 + H_2O + SO_2\uparrow$$

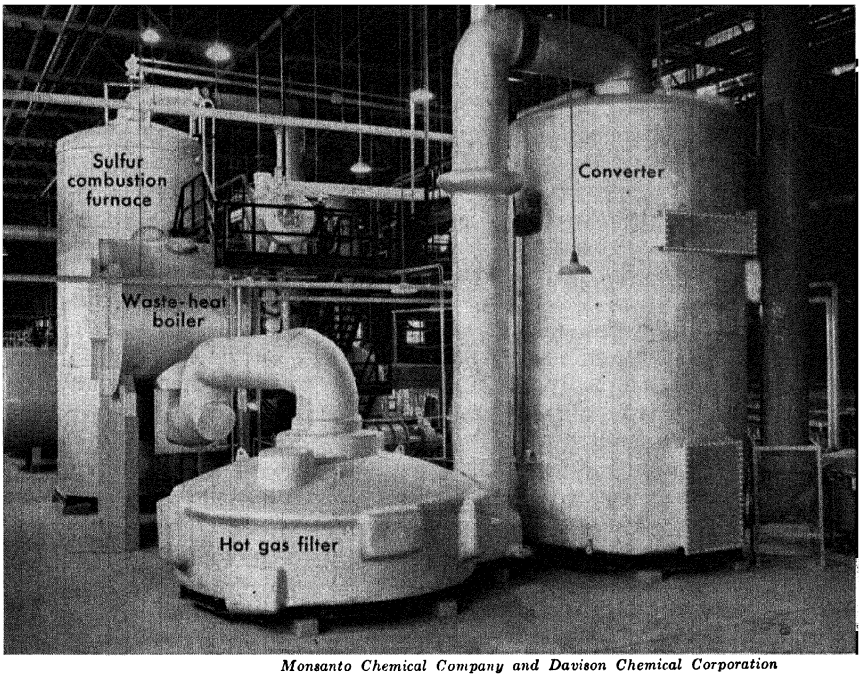
Preparation and properties of sulfur trioxide. When sulfur dioxide is mixed with air and the mixture is passed over a catalyst such as heated platinum, sulfur trioxide is formed.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

This constitutes the key reaction in the most important commercial method of manufacturing sulfuric acid, the *contact process,* so named because contact of the gases with this platinum catalyst plays so important a part.

Sulfur trioxide is a white solid, but it melts at about room temperature and boils at 46°C. The liquid fumes in moist air and reacts vigorously with water making a hissing sound, liberating much heat and forming sulfuric acid. Thus, sulfur trioxide is the anhydride of sulfuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$



Monsanto Chemical Company and Davison Chemical Corporation

A contact process installation. Trace the process in this photograph and that on page 311.

How sulfuric acid is made by the contact process. The manufacture of sulfuric acid by the contact process may be conveniently divided into three stages: (1) burning sulfur to sulfur dioxide in a *combustion furnace,* (2) changing this sulfur dioxide to sulfur trioxide by passing sulfur dioxide and air over a catalyst in a *converter,* (3) changing the sulfur trioxide to sulfuric acid by passing the sulfur trioxide into *absorption towers* through which sulfuric acid is circulated. The chemical reactions that take place are:

$$1)\quad S + O_2 \rightarrow SO_2$$
$$2)\quad 2SO_2 + O_2 \rightarrow 2SO_3$$
$$3)\quad SO_3 + H_2O \boxed{+ H_2SO_4} \rightarrow \boxed{2}H_2SO_4$$

1) *The sulfur combustion furnace.* In the combustion furnace, sulfur is brought into intimate contact with thoroughly dried air. A blower supplies this air at sufficient pressure to force it through the furnace and to force the sulfur dioxide from the furnace through the rest of the system. The heat produced by the combustion of the sulfur is recovered by means of a *waste-heat boiler.* Part of this heat is used in some plants to melt the sulfur that is sprayed into the furnace.

2) *The converter.* The converter is simply a large chamber containing many perforated shelves covered with a catalyst in whose presence the union of warm sulfur dioxide and oxygen takes place, forming sulfur trioxide. Noteworthy developments in the contact process have been the introduction of vanadium pentoxide and platinized silica gel catalysts as substitutes for the more expensive platinum mass. The vanadium catalyst has the further advantage of being insensitive to *poisoning* by impurities, such as arsenic, antimony, selenium, and chlorine, that may be present in the sulfur.

Since, technically, the greatest cost in processes that depend upon a catalyst is keeping the catalyst entirely free from minute traces of poisons, a catalyst less affected by such impurities is preferred. The introduction and use of the vanadium catalyst was soon followed by a platinum catalyst that is immune to arsenic poisoning and may be operated at a lower temperature.

The change of sulfur dioxide to sulfur trioxide, which occurs on the surface of the catalyst, is an exothermic one, that is, heat is given off. Careful temperature control is necessary to insure highest yields. Below 450°C., some SO_2 escapes oxidation to SO_3. Above 450°C., some SO_3 is decomposed to SO_2. At a temperature of 450°C. the reversible reaction

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

goes to the right almost completely. Only about three percent of the total amount of SO_3 theoretically possible is changed back to SO_2.

3) *The absorption towers.* From the converter, the sulfur trioxide passes through a cooler, and then into a series of three or four absorption towers. Through the first two of these towers, filled with quartz pebbles or acid-resisting packing rings, concentrated sulfuric acid is circulated. This concentrated sulfuric acid absorbs the sulfur trioxide, forming sulfuric acid of more than 98-percent concentration. SO_3 vapor is absorbed more easily by concentrated H_2SO_4 than by water. The third tower is a coke-filled filter tower, which absorbs any acid vapor that might otherwise escape into the air.

A contact plant is practically automatic. Control of the process is maintained from one central room containing all the recording and controlling instruments.

How the contact process compares with the lead-chamber process of preparing sulfuric acid. The older commercial process for making sulfuric acid is the lead-chamber process. It was introduced in Birmingham, England, in 1746 by Dr. Roebuck, a physician. Its use

marked the beginning of chemical manufacture on a large scale, for the Industrial Revolution was just then getting under way.

In recent years, the lead-chamber process has given way gradually to the contact process. Because of the large volumes of gases that must react (without a metallic catalyst), large reaction chambers are needed. On account of the action of dilute sulfuric acid on iron, it is necessary to line these large rooms with lead sheets, two inches thick — a second item of expense. Some of the chemical reactions that occur in the chamber process are still not thoroughly understood.

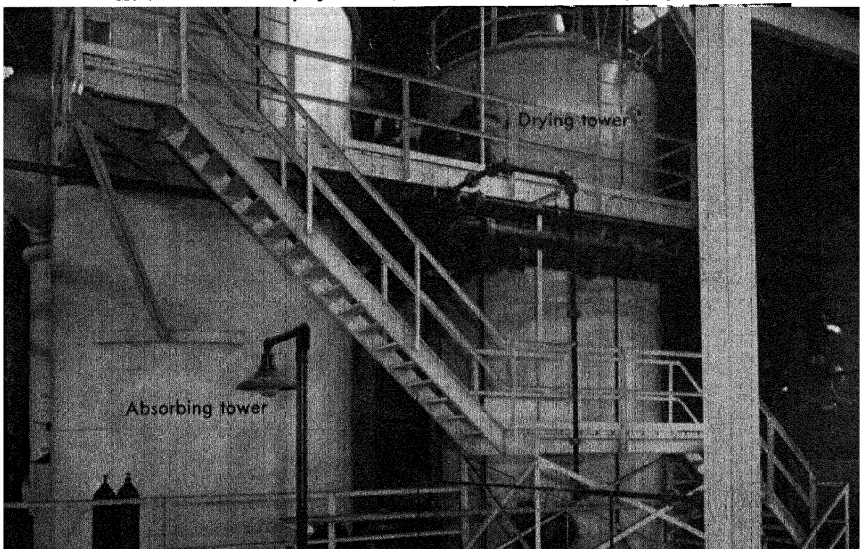
Sulfur dioxide, steam, and the oxygen of the air are converted into dilute sulfuric acid by means of the oxides of nitrogen, which act as catalytic agents. The change of NO into NO_2, which takes place in air, and the subsequent reversal of this reaction are indirect means of getting an extra atom of oxygen to combine with sulfur dioxide. At the end of the process a corrosive, sour drizzle of dilute sulfuric acid falls on the floor of the lead chambers.

Another disadvantage of the lead-chamber process is that only dilute sulfuric acid, often impure and of not more than 78-percent concentration, can be made. If concentrated acid is required, this dilute acid must be concentrated by evaporation with heat.

The chamber process can compete with the contact process only if acid of not greater than 78-percent concentration is required, as in the manufacture of phosphate fertilizers and in the pickling of steel. Sulfuric acid of less than 78-percent concentration must be shipped in glass or in lead-lined steel containers, while acid of

In these towers the final steps of the contact process take place.

Monsanto Chemical Company and Garfield Chemical and Manufacturing Corporation



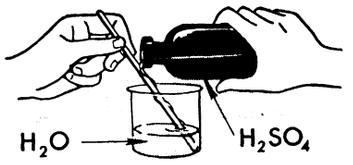


Fig. 70. Diluting concentrated sulfuric acid. Why is such care not necessary when diluting hydrochloric acid?

greater than 78-percent concentration may be shipped in steel drums or tank cars. Why?

Physical properties of sulfuric acid. Sulfuric acid, or *oil of vitriol,* is a water solution of hydrogen sulfate (a liquid). Concentrated sulfuric acid contains 98 percent acid, has a specific gravity of 1.84, and boils at 338°C. It mixes with water in all proportions, liberating much heat. For this reason, great care should be used in diluting concentrated H_2SO_4. The heavier sulfuric acid should be added to cold water *slowly,* and the mixture constantly stirred as shown in Fig. 70. *Always add the acid to the water. Oleum,* or fuming sulfuric acid, contains dissolved sulfur trioxide, and usually its formula is written $H_2SO_4 \cdot SO_3$.

Chemical properties of sulfuric acid. A water solution of sulfuric acid is a very strong acid, because it dissociates to a high degree. The concentrated acid, because it does not dissociate to any appreciable extent, is weaker than the dilute acid.

Because of its strong attraction for water, sulfuric acid is an excellent drying, or *dehydrating,* agent. Its attraction for water is so intense that sulfuric acid will remove the hydrogen and oxygen present in carbohydrates in which these elements occur in the same proportion as in water. Thus, when concentrated sulfuric acid is poured

over sugar, $C_{12}H_{22}O_{11}$, it removes the $H_{22}O_{11}$ as 11 molecules of steam, and a black mass of pure carbon remains.

$$C_{12}H_{22}O_{11} \rightarrow 11H_2O + 12C$$

Likewise, wood, which is composed of cellulose, $C_6H_{10}O_5$, chars when dipped in concentrated sulfuric acid. Cotton, wool, and other substances react similarly. The dehydrating action of sulfuric acid accounts also for the severe burns it may produce on the skin.

At 450°C. and atmospheric pressure, sulfuric acid decomposes completely into water and sulfur trioxide. This chemical reaction is reversible.

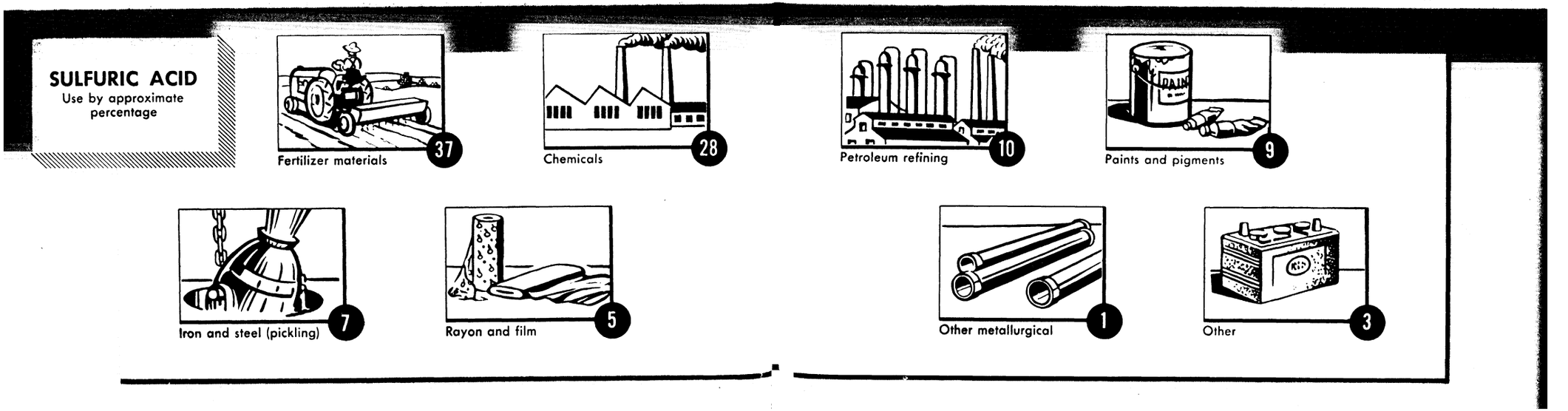
$$H_2SO_4 \rightleftarrows SO_3 + H_2O$$

It has been pointed out that nitric acid is an oxidizing agent because, when added to a metal, it forms water instead of hydrogen, and liberates a gaseous oxide. Warm *concentrated* sulfuric acid, which behaves in a manner similar to nitric acid, is also an excellent oxidizing agent.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2 \uparrow$$

This reaction between concentrated sulfuric acid and copper illustrates another common laboratory method for preparing sulfur dioxide. In contact with certain metals, including zinc, iron, and magnesium, *dilute* sulfuric acid liberates hydrogen as shown in the following equation.

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2 \uparrow$$



Sulfuric acid aids agriculture. In a recent year, the United States produced about 50 percent of the sulfuric acid consumed by the entire world. The domestic consumption amounted to slightly more than 12 million tons. While it is not likely that most farmers believe themselves in any large measure dependent on sulfuric acid, it is a fact that the fertilizers used very widely in agriculture account for almost one-fourth of the sulfuric acid consumed each year.

Phosphorus occurs in nature in a fairly plentiful mineral called *tricalcium phosphate,* or *rock phosphate.* Unfortunately, rock phosphate is insoluble in water and therefore cannot be utilized by plants. However, when treated with H_2SO_4, rock phosphate changes into a soluble compound *monocalcium phosphate* (the active ingredient of superphosphate — see page 487). The phosphorus is then available as plant food.

In cases where the soil is acid, however, pulverized raw rock phosphate is applied directly. The acids of the soil attack the phosphate slowly and make part of it available as plant food.

Sulfuric acid in production of petroleum products. The petroleum industries consume about one-eighth of all the sulfuric acid produced in the United States. Crude petroleum contains a large number of carbon compounds that are dark in color or that become dark from exposure to air. These compounds are removed from crude oil by treatment with sulfuric acid. In this way most of the waxy and gummy materials that clog burners and carburetors are removed.

Other uses of sulfuric acid. Another important use of sulfuric acid is in the cleaning, or pickling, of sheet steel before covering the steel with a layer of zinc in galvanizing, or tin in tin-plating. The iron sulfate that is formed as a byproduct is crystallized and is used in making inks. The common name for crystallized iron sulfate is *copperas,* once known as *green vitriol.*

$$Fe + H_2SO_4 + 7H_2O \rightarrow H_2\uparrow + FeSO_4 \cdot 7H_2O \text{ (copperas)}$$

The manufacture of explosives is dependent upon large quantities of concentrated sulfuric acid. It is used as a dehydrating agent in the process of nitrating the many substances from which explosives are made. Sulfuric acid is used in the production of textiles and rayon and cellulose film. Many acids, including hydrochloric and nitric, are made with the aid of sulfuric acid. Others of the hundreds of processes in which sulfuric acid is used include the making of sulfates, paper, rayon, leather, celluloid, dyes, drugs, and paints. (Many of these processes will be described later.) Sulfuric acid is used also as the electrolyte in lead storage batteries.

Normal, acid, and basic salts. Zinc sulfate, $ZnSO_4$, is formed by the reaction of zinc and sulfuric acid. Here *both* of the hydrogen ions of the acid have been replaced by the metal, and the resulting salt is a *normal salt,* that is, a salt in which all the hydrogen of the acid has been replaced by a metal. In addition to forming normal salts, acids such as H_2SO_4, H_2CO_3, and H_2SO_3, which contain two hydrogen atoms, can also form *acid salts,* and are called *dibasic acids.* Boric acid, H_3BO_3, which contains three replaceable hydrogen atoms, is a *tribasic* acid.

In the preparation of hydrochloric acid by the action of sulfuric acid on sodium chloride, sodium *bisulfate,* $NaHSO_4$ (also called sodium acid sulfate), is obtained as one of the byproducts.

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

Here only *one* of the hydrogen ions has been replaced, and the other remains in the salt, which is called an *acid salt.* Thus it can be seen that either one or both of the hydrogen ions of sulfuric acid may be replaced by a metal.

Acids such as HCl and HNO_3 contain only one hydrogen atom and are called *monobasic acids.* A salt containing one or more hydroxide groups is called a *basic salt.* Such a salt is basic lead carbonate $Pb_3(OH)_2(CO_3)_2$ (see page 449).

Glauber salt and epsom salt. One of the most famous chemists of the seventeenth century was a Bavarian, Johann Glauber. When he was 21 he was attacked by a fever and was advised to drink the water of a certain well. After recovering from his illness he analyzed water from this well, and extracted from it crystals of a salt which he called *sal mirabile,* the wonderful salt. He recommended it as a "splendid medicine for internal and external use." This salt, $Na_2SO_4 \cdot 10H_2O$, known as *glauber salt* has been used as a laxative for more than 300 years. Anhydrous Na_2SO_4, also known as *salt cake,* is used in the manufacture of paper and glass.

Soon after the introduction of glauber salt, an English physician, Nehemiah Grew, who discovered that plants have sex, extracted a salt from some springs in the village of Epsom, near London, England. He wrote a book on the medicinal value of this salt, $MgSO_4 \cdot 7H_2O$, and thus *epsom salt,* a white, soluble, crystalline compound became a rival laxative.

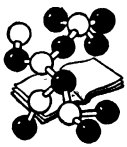
Many proprietary medicines, mineral-water crystals, and mineral waters sold today at ridiculously high prices are laxatives containing one or both of these salts. Such salt mixtures and solutions are sold to be used, often dangerously, as "the modern way to slenderize."

Reducing preparations of this kind should not be taken without the advice of a competent physician.

How to test for a sulfate ion. Most sulfates are soluble in water. However, the sulfates of barium, lead, and strontium are insoluble. When barium chloride is added to a sulfate, a white precipitate, barium sulfate, is formed. This white precipitate is distinguished from other barium salts by the fact that barium sulfate is insoluble in hydrochloric acid.

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + 2NaCl$$

This reaction goes to completion. Why?



YOU WILL ENJOY READING

Aaron, Harold. *Good Health and Bad Medicine.* Consumers Union of United States, Inc., New York, 1940. Carefully prepared and well-written materials on self-medication.

Goldblatt, L. A., Ed. *Collateral Readings in Inorganic Chemistry.* D. Appleton-Century Co., New York, 2nd series, 1942. Article 15 contains an excellent description of a "Contact Sulfuric Acid Plant."

Leicester, H. M., and Klickstein, H. S. *Source Book in Chemistry.* McGraw-Hill Book Company, New York, 1952. Pages 11–16 contain Georg Agricola's description of the manufacture of vitriol, from *De re Metallica.*



USING WHAT YOU HAVE LEARNED

Group A

1. Copy and complete the following statements. Do not write in this book. SO_2 is prepared for industrial use by burning ... or roasting .... It occurs in nature in small amounts near .... The most important use of SO_2 is in the manufacture of .... Its most characteristic physical property is ....

2. (a) What two methods are used in preparing SO_2 in the laboratory? (b) Which method involves reduction? (c) Explain.

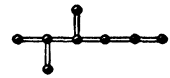
3. (a) Make a labeled diagram showing how SO_2 is prepared from Na_2SO_3. (b) Write the equation for the reaction that occurs.

4. Compare the water solubility of SO_2, NH_3, HCl, and O_2.

5. Write three equations illustrating three chemical properties of SO_2.

6. Describe three uses of SO_2.

7. For what purpose is SO_2 used in the household?



8. (a) Is SO_2 formed first by the action of H_2SO_4 on Na_2SO_3? (b) Explain.

9. (a) Write the reversible reaction between SO_2 and H_2O. (b) How can the reaction be made to go to the right? (c) to the left?

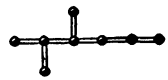
10. (a) Why is H_2SO_3 a weak acid? (b) What is a sulfite?

11. Write an equation showing the formation of Na_2SO_3.

12. (a) By what chemical process does H_2SO_3 bleach? (b) Into what does H_2SO_3 change as it bleaches? (c) Compare the way in which H_2SO_3 bleaches with the way in which Cl_2 bleaches.

13. Write H_2SO_3, H_2O_2, and Cl_2 in a column. Opposite each write the names of the substances that it is best suited to bleach.

14. (a) Why is bleaching with H_2SO_3 less permanent than bleaching with other chemicals? (b) Illustrate.



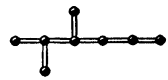
15. Distinguish between a sulfite, a sulfate, and a sulfide.

16. How much S would be needed to prepare 500 tons of 98 percent H_2SO_4?

17. Cu is added to concentrated H_2SO_4 and 448 ml. of SO_2 are liberated. How much H_2SO_4 is decomposed?

18. Calculate the percentage of S in each of its two oxides.

19. What are three properties of SO_3?



20. Write the equation for the burning (roasting) of FeS_2.

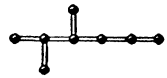
21. What are the stages in the contact process of making H_2SO_4?

22. Write equations that show the three chief chemical changes that take place in the preparation of H_2SO_4 by the contact process.

23. (a) Why must the catalyst used in the contact process be chosen with special care? (b) What advantage has V_2O_5 over the old plantinum catalyst used in the manufacture of H_2SO_4?

24. Describe briefly the chemical change that is the basis of the chamber process for making H_2SO_4.

25. (a) What are the disadvantages of manufacturing H_2SO_4 by the chamber process? (b) This process competes favorably with the contact process in producing H_2SO_4 for what industry? (c) Why?



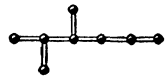
26. What are the physical properties of oil of vitriol?

27. In mixing concentrated H_2SO_4 and H_2O, why should the acid always be added to the H_2O rather than the H_2O to the acid?

28. Devise an experiment to show the dehydrating action of H_2SO_4.

29. By its action on Cu, show that concentrated H_2SO_4 is an oxidizing agent.

30. (a) Make a list of the uses of H_2SO_4. (b) From the viewpoint of the amount consumed, what is its chief use? (c) Explain fully, using an equation to show the reaction involved.



31. Why does the refining of petroleum require immense quantities of H_2SO_4?

32. Name three experiments in which you used H_2SO_4 in making laboratory preparations.

33. What is sulfite pulp?

34. What is the difference between a normal, a basic, and an acid salt?

35. (a) Name three sulfates and (b) state an important use of each.

Group B

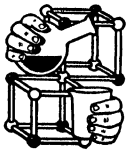
36. Why is SO_3 not added directly to water in making H_2SO_4 in the last stage of the contact process?

37. Make a diagram of the apparatus you would use in preparing SO_2 in the laboratory by the action of H_2SO_4 on Cu.

38. Explain: (1) Black rings often form on wooden shelves that hold bottles of H_2SO_4. (2) A full bottle of concentrated H_2SO_4 overflows when exposed to air. (3) An open bottle of concentrated H_2SO_4 is sometimes placed in a desiccator. (4) Frightful burns result from getting concentrated H_2SO_4 on the hands.

39. Compare the three strong acids with respect to their action on Cu and Zn. Consider both dilute and concentrated acids.

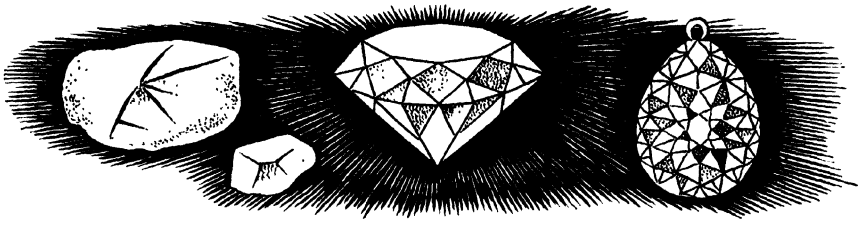
40. A load of scrap iron weighing 2715 pounds and containing 95.5% iron is added to a large vat of dilute sulfuric acid. What is the maximum amount of ferrous sulfate that can be obtained?



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. If you happen to have epsom salt in your medicine chest, bring it to school, read the label to your class and make a test for a sulfate with some barium chloride solution your teacher will supply.

2. Write a two- or three-page report to justify the statement that H_2SO_4 is "king of chemicals," and the "basis of the machine age." Prepare a debate or a class discussion based on these statements.



22 ALLOTROPIC CARBON: KEY SOURCE OF ENERGY

> . . . *It (the light from my lamp) was hurled out of the sun 200,000,000 years ago, and was captured by the leaves of the Carboniferous tree-fern forests, fell with the falling plant, was buried, fossilized, dug up and resurrected. It is the same light. And, in my little fig tree as in the ancient ferns, it is the same unchanging green stuff from age to age.* Donald Culross Peattie in *Flowering Earth,* 1939.

The fascinating chemistry of carbon. Carbon is the eleventh most abundant element of the earth by weight. In the form of coal and graphite, it helps to drive as well as lubricate the wheels of our machine age. As petroleum, it propels our locomotives, ships, automobiles, and airplanes. In the form of diamond and "Carborundum" (synthesized directly from free carbon), carbon is used in making tools that drill our hardest rocks and grind and polish our machines, tools, and household utensils.

In combined carbon we find one of the most fascinating stories in the whole romance of chemistry. Each year carbon's 650,000 known compounds are being increased in number by thousands of compounds synthesized in our industrial and university laboratories. Synthetic chemistry reaches its greatest development in *organic chemistry,* the chemistry of the compounds of carbon.

Woehler (vû-lēr), in 1828, synthesized urea, the first organic compound made outside the living body. By this synthesis the old idea that organic compounds could be formed only in living matter was destroyed, and a new era in chemistry was ushered in, witnessing "the great tragedy of science, the slaying of a beautiful hypothesis by an ugly fact."

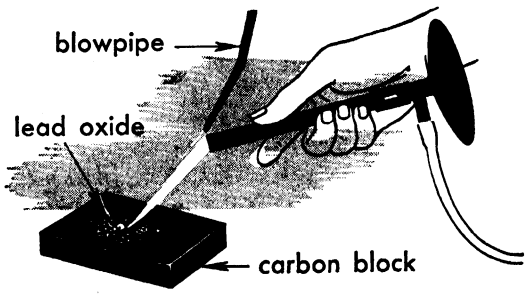
One hundred and twenty-five years after Woehler's achievement, sugar ($C_{12}H_{22}O_{11}$) was synthesized from its elements. What a century and a quarter of research between Woehler's urea and synthetic cane sugar! Berthollet went to the red ant and learned the secret of preparing formic acid, the liquid responsible for the sting of this insect. William Perkin, washing bottles in a London laboratory, mixed at random the contents of two bottles and discovered a method of synthesizing mauve — the first of a long series of organic dyes that rival the colors of nature. And this is only the beginning. The mind fairly reels at the accomplishments and possibilities of this branch of chemistry. More of this entrancing story is told in later chapters.

What is the valence of carbon? Carbon has an atomic weight of 12. The nucleus of the carbon atom contains six protons; hence, the outer ring contains only four electrons. Therefore, the carbon atom must either lose four electrons or gain four electrons to complete its outer ring. The valence of carbon then is either plus four or minus four, depending upon the substance with which it reacts. That is, it may act as either a metal or a nonmetal. Carbon almost always forms firm covalent bonds involving four pairs of shared electrons.

The properties of carbon. Carbon occurs in three allotropic forms: two of them, *diamond* and *graphite,* are crystalline; the third is *amorphous,* or noncrystalline, in form. All forms of carbon combine with oxygen, forming either carbon monoxide, CO, or carbon dioxide, CO_2. The different forms of carbon vary widely in the ease with which they may be oxidized. Coal burns easily particularly when powdered. On the other hand, diamond combines with oxygen only at extremely high temperatures.

$$C + O_2 \rightarrow CO_2 \text{ (carbon dioxide)}$$
$$2C + O_2 \rightarrow 2CO \text{ (carbon monoxide)}$$

Its attraction for oxygen makes carbon a good reducing agent. The reducing action of carbon may be shown by heating a mixture of



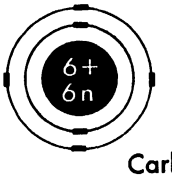


Fig. 71. Blowpipe analysis of an ore (left) using the reducing power of charcoal. (right) The carbon atom.

carbon and lead oxide on a charcoal block, using a blowpipe. A little ball of pure lustrous lead is formed and CO_2 is given off.

$$2C + Pb_3O_4 \rightarrow 3Pb + 2CO_2 \uparrow$$

Millions of tons of coke (carbon) are used industrially every year in reducing iron oxide to commercial forms of iron.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \uparrow$$

This reaction shows carbon acting as a metal, a lender of electrons. Carbon may also behave as a nonmetal, a borrower of electrons. At the very high temperatures reached in an electric furnace, carbon unites with metals such as calcium and wolfram and with less *electronegative* elements such as silicon, forming carbides.

$$\underset{\text{calcium oxide}}{CaO} + 3C \rightarrow \underset{\text{calcium carbide}}{CaC_2} + CO \uparrow$$

$$\underset{\text{silicon dioxide}}{SiO_2} + 3C \rightarrow \underset{\text{silicon carbide}}{SiC} + 2CO \uparrow$$

Carbon unites directly with hydrogen also at the high temperatures of an electric arc, forming acetylene gas, C_2H_2.

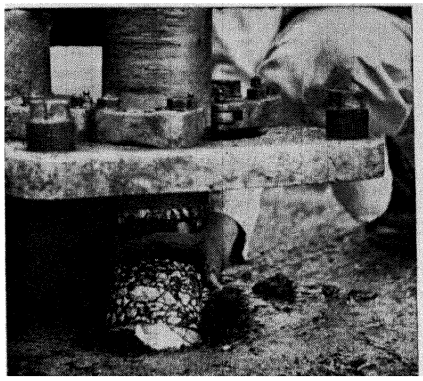
$$2C + H_2 \rightarrow C_2H_2 \uparrow$$

All forms of carbon are insoluble in water, acids, and bases. Amorphous carbon, however, is soluble in some molten metals including iron.

Physically, the allotropic forms of carbon resemble one another in some respects. They are all odorless, tasteless, and insoluble in water. On heating, they do not melt but vaporize.

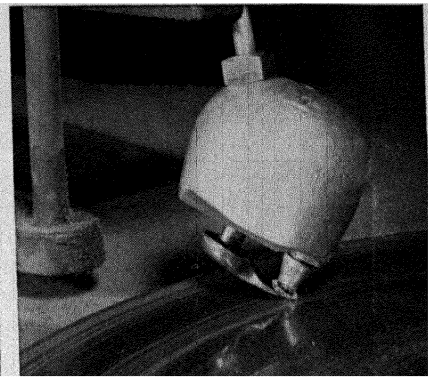
The hardest substance known. In the eighteenth century, diamond was shown by Lavoisier to be almost pure carbon. This French chemist burned a diamond in the presence of a distinguished audience by concentrating the sun's heat on it with a lens. He showed that the gas which was formed was pure carbon dioxide. This startling discovery strengthened Lavoisier's theory of burning. Why?

Diamond, chief among precious stones, is found mainly in South Africa, Brazil, and Borneo. It occurs in various sizes and states of purity, buried deep in the ground frequently in the pipes of extinct volcanoes, or in the loose sands along certain streams. The brilliance of diamond, caused by its power of refracting light, is brought out by removing any surface impurities or imperfections and by cutting facets on its surface. Small amounts of metallic oxides in diamonds



Shell Oil Company

This asphalt core, neatly cut from a roadbed by a diamond drill, will be taken to a laboratory for study.



Baumgold Bros., Inc.

Before use in jewelry, a diamond is polished against a rotating iron disc coated with olive oil and diamond dust.

give them various colors, the rarest of which are red, green, and blue. The density of diamond is 3.5.

Diamond is weighed in *carats,* a unit of weight based on the weight of the bean of the carob tree. One carat is equal to one-fifth of a gram. The largest diamond ever mined was the flawless *Cullinan* found in South Africa in 1905. It weighed 3026 carats, or 21.35 ounces, and was about the size of a man's fist.

From the first little diamond found in a pebble picked up by a child in 1867, the diamond industry of South Africa has grown to world leadership. In a recent year, more than three million carats of diamonds were mined. About half of this amount is used in jewelry.

Though brittle, diamond is the hardest substance known, and for this reason is used extensively in making tools for drilling rock, grinding, sawing, engraving, and polishing. Impure black diamonds, called *carbonado* and *bort,* are used in drills. Diamonds are also used as bearings in watches and delicate instruments, and in wire-drawing dies made by drilling tapered holes through diamond crystals.

Can diamonds be made synthetically? Scientists believe that diamonds were formed under great heat and pressure by the crystallization of carbon dissolved in molten iron or other substances. To test this theory of the formation of diamonds, Henri Moissan (mwȧ'-säN'), in 1893, subjected some pure carbon to extremely high temperatures and pressures. He dissolved carbon in molten iron, and quickly plunged the molten mass into cold water. The sudden contraction of the iron exerted tremendous pressure on the dissolved

carbon, causing it to crystallize. The iron was dissolved with acids, and, aided by a microscope, Moissan reported seeing synthetic diamonds formed of tiny cubical crystals. Other attempts have been made to synthesize diamonds, but thus far these attempts have not proved a threat to the diamond industry.

Black, soft, and greasy. A second allotropic form of carbon, graphite, is lustrous, black, soft, and oily to the touch. The great difference in hardness between the allotropic forms of carbon is caused by the different arrangement of the atoms. The atoms of the diamond molecule are very closely interlaced and bound firmly together. Graphite, on the other hand, is made up of piles of flat layers of atoms firmly bound to one another, but far apart and only feebly hanging on to the next layer. For this reason graphite is soft and slippery. The flat planes slide over one another like cards in a pack. A few electrons between the planes are loosely held, making graphite an excellent conductor, whereas diamond is a nonconductor.

Natural graphite, which is found chiefly in Ceylon, Siberia, and Canada, contains many impurities. It is believed to have been formed, like diamond, under high temperature and pressure.

Electric furnaces and uses of synthetic graphite. In 1896 Edward Acheson, of Pennsylvania, patented a process for making *synthetic graphite,* today a widely used article of commerce. It is superior to natural graphite, because it is free from grit and contains almost no impurities. Acheson was at different times a blast-furnace helper, oil gager, railroad ticket agent, store clerk, miner, bookkeeper, and engineer. He also worked for Edison and was sent abroad to the International Exposition in Paris to exhibit the Edison electric lamp which he had helped to improve with a graphite filament. His method of making synthetic graphite consists of subjecting anthracite coal or molded carbon to the high temperature of an electric furnace, keeping air out by covering the coal with sand.

An electric furnace, as you know, transforms electric energy into heat energy. The resistance to an electric current offered by loose carbon, in the center of the *resistance* type of electric furnace used in making graphite, produces high temperatures. Other electric furnaces utilize the heat produced by the passage of electricity through

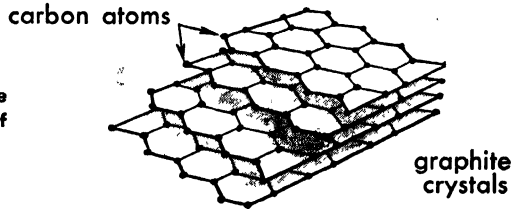
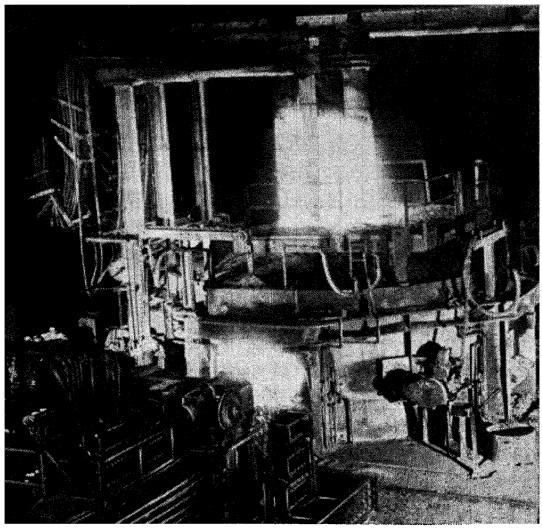


Fig. 72. Diagram of a graphite particle showing the layers of atoms.



Alloy steels are produced in this electric furnace. The electrodes of the furnace are made from graphite.

Electro Metallurgical Company

high-resistance wire, such as an alloy of nickel and chromium. Another type of electric furnace is the *arc* type. Here the passage of electricity across an air gap produces a high temperature as a result of the resistance of the air. Arc-type electric furnaces are used in the synthesis of nitric oxide, NO, during the preparation of nitric acid by nitrogen-fixation.

Like other forms of carbon, graphite does not melt and has an extremely high point of vaporization. For this reason it is used in making graphite crucibles in which steel and other alloys of high melting point are prepared. Because of its smoothness, oiliness, and high temperature of fusion, graphite is mixed with oils used in lubricating heavy, swiftly moving parts of machinery, in which even heavy oil would evaporate or burn off.

Graphite electrodes are used in electric furnaces, arc lamps, and in general, for conducting electricity at very high temperatures. Powdered graphite is used in dry cells, and in certain *oil-retaining bearings* produced by *powder metallurgy* (see page 467).

Graphite is used also in lead pencils. The "lead" in a pencil is graphite mixed with clay to vary the hardness of the lead. Graphite is also a constituent of stove polishes. Most synthetic graphite is produced at Niagara Falls, where hydroelectric power is available at low cost.

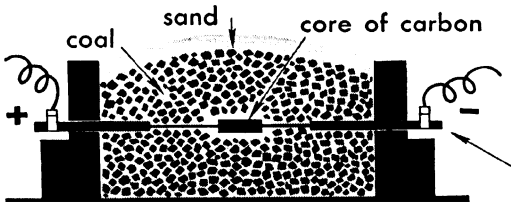


Fig. 73. Cross section of an electric furnace used in the commercial production of synthetic graphite.

"Formless," yet of many forms. The noncrystalline allotropic form of carbon is amorphous carbon. The purest form of amorphous carbon can be prepared easily by heating pure table sugar. The hydrogen and oxygen are driven off as water; pure amorphous carbon is left.

$$C_{12}H_{22}O_{11} \rightarrow 11H_2O + 12C$$

Among the most common forms of amorphous carbon are (a) *lampblack* and *carbon black,* (b) *gas carbon,* (c) *coke,* (d) *charcoal,* and (e) *animal charcoal,* or *boneblack.*

Valuable soot. Lampblack was known to the Chinese and Egyptians who used it in making ink. It is amorphous carbon dust formed by the incomplete burning of compounds rich in carbon. It is manufactured commercially by burning heavy liquid *hydrocarbons* (compounds of hydrogen and carbon) in an insufficient supply of oxygen. The escaping particles of carbon dust, or *soot,* from the small flames are collected on a revolving metal plate that is kept at a low temperature by flowing water. The smokiness of a kerosene lamp burning with an insufficient air supply or with the oil supplied too rapidly illustrates the way in which lampblack is formed.

Carbon black is made in the same way as lampblack except that natural gas is used instead of liquid hydrocarbons. It is finer than lampblack, which it is gradually replacing. Carbon black is such an important item of commerce that in a recent year its production accounted for more than ten percent of all the natural gas produced in the United States. Most of the carbon black manufactured in this country is added to rubber tires to improve their resistance to tear and abrasion. It is also used as a basic raw material in making printer's ink, typewriter ribbons, carbon paper, phonograph records, and black paints.

Almost graphite. Gas carbon is amorphous carbon that collects on the walls of retorts during the manufacture of illuminating gas from coal. In structure, gas carbon is semicrystalline and resembles graphite. It is used in the rods of arc lamps and other electrodes.

Coke from the destructive distillation of coal. Heating a complex carbon compound in an oven from which air is excluded, and condensing the vapors formed is called *destructive distillation.* When soft coal is so treated the most important solid product is coke, a steel-gray, hard, brittle substance used chiefly as a reducing agent in the extraction of iron, and as a fuel. The coal is heated to 2000°F. for 16 hours, and then the white-hot coke is pushed out from the oven and quickly quenched in cold water.

In the *byproduct* coke oven many valuable chemicals are recovered. As the gases pass through oil-absorption tanks, a light oil separates, from which benzene, toluene, xylene, and naphthalene are distilled. From the coal tar which is formed anthracene, phenol, and pitch are also separated by fractional distillation. Ammonia gas and coal gas are also obtained (see pages 362–363 for a detailed account of this process). Less than ten percent of our coke is still made in *beehive* ovens from which none of these byproducts are recovered.

Charcoal-broiled. If wood is subjected to destructive distillation, charcoal is one of the products. Charcoal retains the fibrous structure of wood.

Powdered charcoal is frequently put together under tremendous pressure, forming compact, pillow-shaped blocks called *charcoal briquets.* These burn with no smoke and leave very little ash. They are used in camping or picnicking, on pleasure boats, and in foundries.

Charcoal-broiled meats, especially steaks and chops, are particularly delicious. Meats broiled over charcoal do not pick up odors or flavors from the burning fuel.

Activated charcoal. This is a specially-prepared charcoal used for removing or *adsorbing* gases. *Adsorption* is caused by the collection of thin layers of molecules of gases and other impurities on the surfaces of the porous charcoal. It is not a chemical union but a physical attraction. Ill-smelling colored liquids, passed through such charcoal, are cleared of impurities responsible for the odor and color. Adsorption is used also in recovering many industrial solvents and waste substances, in air purification, and to concentrate a desired substance such as the drug streptomycin from its mold culture.

Activated charcoal is used in gas masks to adsorb poison gases met in industry. "Nuchar" is the trademark for an activated carbon of vegetable origin containing about 90 percent pure carbon.

A black decolorizer. The chief solid left after the destructive distillation of clean cattle bones is a black powder called *boneblack.* This boneblack, or *animal charcoal,* is a mixture containing only about ten percent amorphous carbon and 80 percent calcium phosphate, the chief compound found in bones. It, too, has great adsorptive powers and is used mainly in the refining of crude sugar, from which it removes impurities that cause objectionable colors and odors. It is used also as a black pigment in paints.

How coal was formed. Coal is found in all continents, including Antarctica, but the largest coal-producing areas are in North America and Asia. Scientists now believe that many millions of years ago,

during the Carboniferous period, great portions of the earth were covered with a dense vegetation more luxuriant than that found today even in tropical jungles. As the level of the earth sank during one of the many upheavals that occurred, vast portions of these jungles were flooded by the ocean and became swamps. Later these swamps were completely submerged and then gradually covered with mud, sand, or clay deposited as sediment by streams and rivers.

Partial decomposition of the wood and other vegetable matter, aided by bacteria and fungi, changed the woody material first into *peat.* Minnesota, Florida, and several other states contain large peat deposits. Near Chester, Wisconsin, is a peat deposit that covers 32,000 acres. Its average depth is six feet and it contains about 40,000 tons of air-dried peat. Peat bogs also occur in Ireland and elsewhere. When dried and pressed, peat may be used as a fuel. It burns with a great deal of smoke and produces little heat.

Scientists believe that the next step in the formation of coal was the changing of the peat into brown or black *lignite,* which still retains the structure of the plants from which it was formed. Sometimes branches or twigs are found in lignite in the form in which they grew. Lignite is found in some of the states west of the Mississippi, and, where no other form of coal is available, is used as a household fuel. In North Dakota, for example, lignite is being mined at the present time and utilized in making gas and briquet fuels, and for the production of electric power.

Further decomposition and pressure, away from air, drove out more oxygen and hydrogen from the lignite, leaving hydrocarbons and some free carbon and forming *bituminous,* or *soft, coal.* Further heat and greater pressures changed the soft coal to jet black, lustrous *hard coal,* or *anthracite.*

Strong evidence supports this theory of coal formation. The fossils embedded in coal deposits include forms of both animal and vegetable life. Some of the animals appear to have been marine. Among the plants, mosses and ferns occur most commonly.

The chief kinds of coal. The chief kinds of coal used in this country are soft, or bituminous, coal, and hard coal, or anthracite. Most of the anthracite mined in the United States comes from Pennsylvania, yet this state, together with West Virginia, produces more than half the bituminous coal mined in this country. For every ton of anthracite mined, 11 tons of bituminous coal are dug. Anthracite contains practically no *free* carbon and produces less volatile material than bituminous coal (see Table 11). It is cleaner to handle and burns with a short, pale blue flame.

The use of anthracite is confined largely to the northeastern states, because these states have the advantage of being near the deposits and thus have short and low-cost transportation from the mines. In other parts of the country anthracite is relatively unfamiliar.

The problem of smog. Smog, a mixture of *smoke* and *fog*, is formed largely by the incomplete combustion of coal, fuel oil, gas and rubbish. The products of this incomplete combustion are oxidized by the ozone in the air to create the smog. Smog may be aggravated by natural particles in the air, such as dust or pollen, or even by local weather conditions.

People who live in cities where smog is a problem spend far more for soaps and other cleansers than might be necessary if better *smoke control* were practiced. It has been shown in several cities that smog may be eliminated. However, success in reducing smoke depends upon the cooperation of every consumer of fuel from the largest industry to the individual homeowner.

Smoke control is particularly necessary in cities in which bituminous coal is a major fuel. Bituminous coal, when burned in an inadequate supply of oxygen, produces a very smoky flame. If the coal is properly fired (see page 355), smoke may be greatly reduced.

British thermal units. A chief factor in determining the price of coal is its fuel value. This value is measured either in calories or in *British thermal units,* Btu. One Btu is the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit. One Btu is equivalent to 252 calories. Burning one pound of average anthracite liberates about 12,700 Btu; burning the same weight of bituminous coal liberates about 13,100 Btu. The percentage of ash and free sulfur is another factor important in determining price. In general, anthracite contains a smaller percentage of these materials than does bituminous coal.

A scene in Pittsburgh, Pa., before (left) and after a smog-control program was instituted.

Allegheny Conference on Community Development

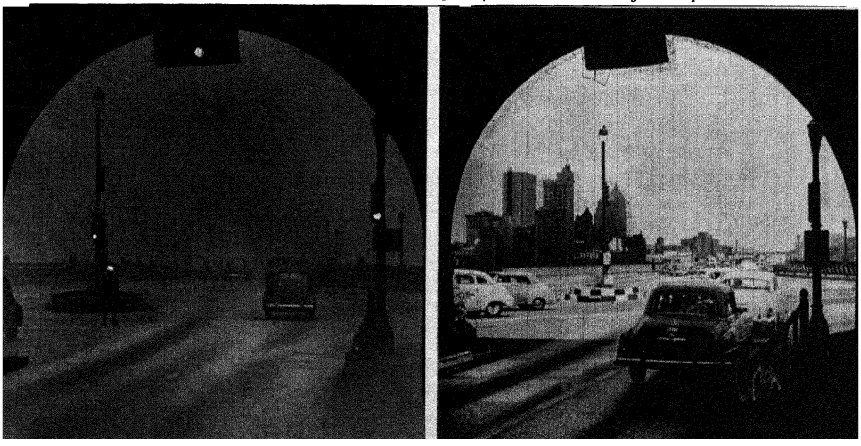
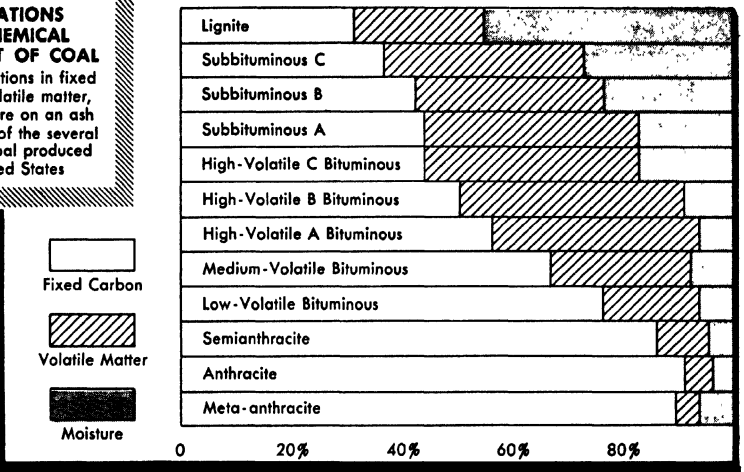


TABLE 11.
VARIATIONS IN CHEMICAL CONTENT OF COAL
Variations in fixed carbon, volatile matter, and moisture on an ash free basis of the several ranks of coal produced in the United States



Coal, a major source of power. Coal has been used as fuel for centuries. Marco Polo, 700 years ago, reported the Chinese burning "black stone dug out of mountains where it runs in veins." But it was not widely used until the sixteenth century. By 1661 "a hellish and dismall cloud of Sea-Coale hung perpetually over London," where coal was used to make iron, glass, and other products. During the Industrial Revolution it became a vital source of energy.

Our civilization uses energy at a staggering rate. In 1900, the total supply of energy from mineral fuels and water power in the United States was 7.4 quadrillion Btu; by 1950, the total had reached 36.2 quadrillion Btu — an increase of almost 400 percent! Each year our growing population and industries need added amounts of energy. It is expected that before the end of the century the annual production of energy will be more than double the present rate.

Today, petroleum, coal, natural gas, and hydroelectric dams are our major sources of energy. In a recent year, petroleum supplied 40 percent of our nation's total energy requirement; coal supplied 34 percent; natural gas, 22 percent; and water power, 4 percent. In the years ahead, the use of nuclear energy will, in all probability, change these figures radically.

Coal has many uses. Production of anthracite coal is now about 40 million tons per year. About three-fourths of this output goes to the retail market to be used as fuel for commercial and institutional buildings, as well as for heating homes. The remainder of the yearly tonnage is used by a variety of industrial consumers.

Annual production of bituminous coal is now about 450 million tons per year. The major use of this coal is in generating electricity.

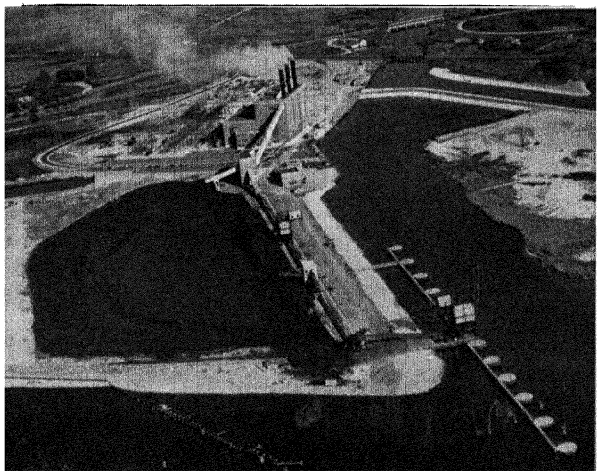
About one-half of our nation's total electric power is produced by coal-fired steam plants. In all, the electric utilities consume considerably more than 100 million tons of coal each year, or about 25 percent of all bituminous coal marketed. The production of electric power is expanding rapidly and it is expected that there will be an increase in the amount of coal used for this purpose.

The steel industry is the second most important customer for bituminous coal, consuming about 20 percent of all coal marketed. Most of this enormous quantity of coal is converted into coke by roasting in coke ovens. Coke is used to some extent as a fuel, but its chief use by far is as a reducing agent in the production of steel. Coke robs the iron ore, an oxide of iron, of its oxygen and leaves pig iron which is later converted to steel. The chemicals recovered in the coking process (see page 327) are the source of many plastics, dyes, drugs, medicines, and industrial chemicals. Today, coal chemicals are also produced directly from the "raw" coal without any attempt at burning it or changing it to coke. This use of coal as yet constitutes a very small market, but it may become increasingly important in the future. Coal is also destructively distilled in the manufacture of coal gas.

All other types of manufacturing consume another 15 to 20 percent of the bituminous coal marketed annually. A similar amount goes to the retail market for use as a fuel in public buildings, commercial establishments, and homes. In addition to coal in its conventional lump form, the retail market each year uses over a million tons of coal in the form of *fuel briquets*. Fuel briquets are pressed cubes, cylinders, or ovoids of very fine bituminous coal (slack) or lignite held together by a burnable binder.

The railroads, once the coal industry's best customer, now use considerably less than ten percent of the total annual tonnage as the

Consumers Power Company



The importance of coal in generating electricity is illustrated by this coal storage pile at a modern power station. This plant burns about 675,000 tons of coal each year.

coal-burning "iron horse" has been displaced by the more efficient diesel-electric locomotive.

Buying coal for your home. The most important consideration is the amount of heat the coal will produce. Your coal dealer usually knows the Btu value of the coal. Such information may also be obtained from the United States Bureau of Mines, from your state bureau of mines, or from the company that mined the coal.

If you know the number of Btu in a pound of coal, the product of this number multiplied by 2000 is the number of Btu per ton. The quotient of the number of Btu per ton divided by the cost per ton in dollars is the number of Btu per dollar. As far as heat value alone is concerned, the coal with the greatest number of Btu per dollar is the best buy. Expressed as a formula, this method of comparing coals may be written:

$$\frac{\text{Btu per lb.} \times 2000}{\text{Cost per ton in dollars}} = \text{Btu per dollar}$$

However, as anyone who has ever carried out "ashes" knows, the ash content of coal is an important consideration also. One coal with a slightly higher Btu-per-dollar value than a second coal actually may not be as desirable as the second coal, if its ash content is appreciably higher. Moisture content and dust content are two other factors that must be considered. Coal dealers may control the dustiness of coal either by sprinkling the coal with water or by spraying the coal with special oils. From the point of view of the consumer, which of these methods is preferable? Why?

In buying coal, it is advisable to buy the size and grade recommended by the manufacturer of the equipment in which you intend to burn it. Buying the appropriate size and grade of coal will enable you to get more Btu out of the coal you buy. Most coal-burning equipment is designed to operate most efficiently with coal of certain size and grade.

Because of seasonal demands, coal is usually lower in cost during summer than in winter. Since coal does not deteriorate appreciably in dry storage, for example, in a coal bin, it is good policy to buy next winter's supply in the summertime.

Changing energy relationships. The sources of energy upon which our civilization depends are, as we know, coal, petroleum, natural gas, and water power. Nuclear energy holds great promise, but its use as a major source of energy is still in the future.

Petroleum and natural gas constitute but a tiny part of our nation's total fuel deposits. Taken together, they make up less than

two percent of the known reserves of all fuels. Of the remaining 98 percent, oil shale forms eight percent and coal forms 90 percent. More than 92 percent of the total coal reserve is bituminous and lignite; the remainder is anthracite. Although the experts disagree on the exact number of years involved, it is generally accepted that, at our present rate of use, our reserves of high-quality petroleum and natural gas may be consumed in less than half a century, while our coal reserves are adequate for several hundred years. Oil shale is an unexploited resource and we do not yet know the extent of its usefulness.

Because of coal's abundance, it seems likely that it will see increased use in the future as oil and gas reserves shrink. Because our society is completely dependent upon a plentiful and continuous supply of energy, proper use and conservation of our fuel reserves is a problem which deserves the thoughtful attention of every citizen.

The energy of running water, while limited in amount, is nevertheless almost limitless in duration. For, in harnessing such energy, nothing is actually used up that will not occur again. The water cycle takes care of this problem for us. However, water power suffers from a serious drawback in that it is not constant. That is, during certain seasons of the year, more water is available than at others. Even dams and huge reservoirs have not yet succeeded in solving this problem completely, but they have made tremendous strides in doing so, and more and more water power is being harnessed as the years go by. However, even if developed to the fullest extent, our water resources could not provide more than a small fraction of our total annual energy requirements.

The utilization of hydroelectric power had to wait for science to develop methods of sending electric energy over long distances, and also for the building of immense dams and hydroelectric plants. Recently, the capacity of existing hydroelectric power plants in the United States totaled 25 million horsepower, while the undeveloped water power was estimated at 117 million horsepower. Engineers believe that, long before we can no longer depend upon coal, petroleum, natural gas, and the harnessed power of running water, nuclear energy will do much of the world's work.

Motor fuels from coal. Chemists, faced with an imminent world-shortage of petroleum, turned to the development of methods of synthesizing essential liquid fuels. One of the most widely used developments has been the changing of low-grade coal into gasoline and other petroleum products. The most successful results were obtained by the German chemists, Friedrich Bergius (bĕr'gĭ-o͝os), Franz

Fischer, and Hans Tropsch. In 1931, Bergius was awarded the Nobel prize in chemistry.

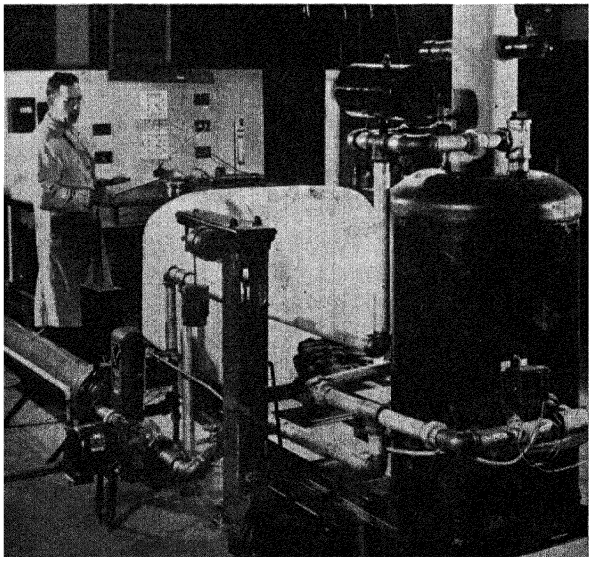
Bergius found that coal contained half as much hydrogen as petroleum. By doubling the amount of hydrogen chemically combined in coal, he hoped that he could obtain a product that would resemble gasoline. He developed a process now called the Bergius process, in which a thick paste of powdered coal mixed with heavy oil is introduced into steel drums and heated to a temperature of about 400°C. under about 200 atmospheres pressure. Hydrogen is forced into the mixture, which also contains a catalyst. When the hydrogenation is complete, a mixture of gasoline and heavier fuel oils is obtained. The carbon of the coal combines chemically with hydrogen, forming certain kinds of hydrocarbons, and the successful liquefaction of coal is achieved.

Assuming the composition of average gasoline to be represented by the formula C_7H_{16}, we may represent the hydrogenation of coal by the equation:

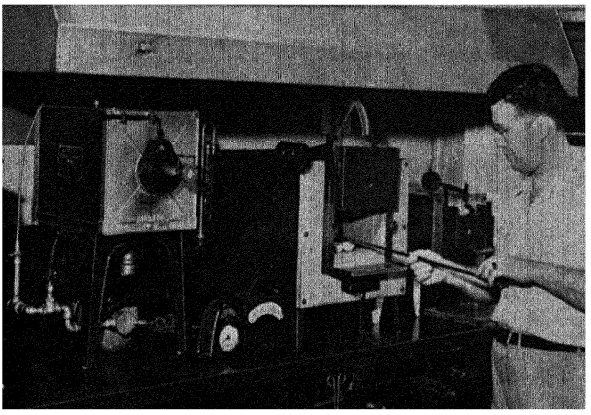
$$7C + 8H_2 \rightarrow C_7H_{16}$$

During World War II, the Germans demonstrated that synthetic gasoline from coal can be used for the same purposes as petroleum-derived gasoline. In the United States, following the war, both the federal government and private industry conducted research on the production of gasoline from coal and from natural gas. It was found that synthetic gasoline is more expensive to produce than gasoline from petroleum, but would be commercially practical in the event of shortages of the latter.

National Coal Association



Apparatus in a coal-industry research laboratory for testing stoker coal and thus establishing standards for determining the best use for the various grades.



The testing laboratory of a coal preparation plant. The crucibles contain powdered coal which is burned in the electric furnace. By analysis of the ash, the composition of the coal is determined.

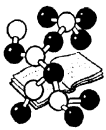
National Coal Association

Both the Bergius and Fischer-Tropsch processes were tested. The Fischer-Tropsch process depends either upon the reaction of steam and coal, or oxygen and natural gas, to form *synthesis gas.*

$$C + H_2O \rightarrow \underbrace{CO + H_2}_{\text{synthesis gas}} \quad \text{or} \quad 2CH_4 + O_2 \rightarrow \underbrace{2CO + 4H_2}_{\text{synthesis gas}}$$

This mixture of gases is then converted with the aid of a catalyst into gasoline.

$$\underbrace{7CO + 15H_2}_{\text{synthesis gas}} \xrightarrow[\text{catalyst}]{\text{iron}} \underbrace{C_7H_{16}}_{\substack{\text{synthetic} \\ \text{gasoline}}} + 7H_2O$$



YOU WILL ENJOY READING

Bragg, William. *Concerning the Nature of Things.* Dover Publications, New York, 1954. Lecture IV on crystals covers the various allotropic forms of carbon. A classic.

Storch, H. H.; Lowry, H. H.; Kiebler, M. W., Jr.; Howard, H. C.; Thiessen, Gilbert; and Charmbury, H. B. "Hydrogenation of Coal." *Industrial and Engineering Chemistry,* April, 1944, pp. 291–298. A round-table discussion of problems in this process.



USEFUL IDEAS DEVELOPED

1. Destructive distillation is the heating of a complex organic compound in a chamber from which air is excluded and condensing the vapors formed.

2. Fuel value of coal is measured in calories or British thermal units, Btu. One Btu is the amount of heat required to raise 1 lb. of water 1°F. A calory is the amount of heat required to raise 1 g. of water 1°C. One Btu is equivalent to 252 calories.

3. Organic chemistry is the chemistry of carbon compounds. At present more than 650,000 compounds of carbon are known. Synthetic chemistry reaches its greatest development in this branch of chemistry and has already produced dyes, drugs, and solvents many of which are better than natural substances.

4. Today, man's chief sources of energy are coal, petroleum and natural gas, and water power. In the years just ahead, nuclear energy is likely to assume greater importance.



USING WHAT YOU HAVE LEARNED

Group A

1. C may act either as a metal or as a nonmetal. (a) Why? (b) Why is C not active at ordinary temperatures?

2. (a) What are the three allotropic forms of C? (b) Name the allotropic forms of two other elements.

3. (a) What chemical property is common to all allotropic forms of C? (b) What product depends on this property?

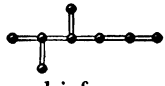
4. What accounts for the extreme hardness of diamond?

5. How did the action of extreme heat on diamond aid Lavoisier in securing acceptance of his theory of burning?

6. (a) What are two possible products of the oxidation of C? (b) Write equations to illustrate.

7. (a) What are the three chief uses of diamond? (b) Upon what properties do these depend?

8. What evidence supports the accepted theory of diamond formation?

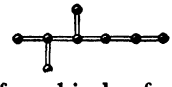


9. (a) What are the chief uses of graphite? (b) Upon what properties do these depend?

10. Describe briefly the commercial preparation of graphite.

11. (a) What is an electric furnace? (b) Name three kinds.

12. Make a diagram of one kind of electric furnace and explain how it produces high temperatures.



13. Make a table of four kinds of amorphous C, giving the

method of manufacture, composition, and chief uses of each.

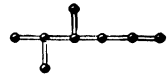
14. (a) What is destructive distillation? (b) Describe the making of coke, and (c) name six byproducts of the process.

15. Activated charcoal is used in gas masks. Why?

16. Below are two lists of items. Match each item in the list on the left with the correct item from the list on the right.

1) watch bearings	a) activated charcoal
2) Moissan	b) graphite
3) peat	c) printer's ink
4) Bergius	d) diamond crystal
5) lampblack	e) coke
6) manufacture of iron	f) artificial diamonds
7) lead pencils	g) bacteria
8) adsorption	h) hydrogenation

17. What weight of coke containing 80 percent C is needed to reduce 5 lb. of CuO?



18. Assume the formula of gasoline to be C_7H_{16}. If 500 ml. of water vapor are formed during the combustion of a certain quantity of gasoline, what volume of CO_2 will be formed?

19. What volume of CO_2 will be formed during the combustion of 2000 lb. of coal containing 80 percent C? (Note: the *ounce*-molecular volume of any gas is 22.4 cu. ft.)

20. According to available evidence, how were coal deposits formed?

21. Compare anthracite and bituminous coal for use in household heating.

22. What factors should be considered in buying coal?

23. How may the heat value of one coal be compared with the heat value of another?

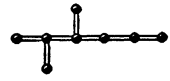
24. Complete and balance the following equations:

a) $C + H_2 \rightarrow$ c) $CaO + C \rightarrow$

b) $Fe_2O_3 + C \rightarrow$ d) $SiO_2 + C \rightarrow$

25. What is meant by saying that a certain sample of coal liberates 14,000 Btu?

26. What is the major use of anthracite coal? What two industries are the major consumers of bituminous coal?



27. Explain the Bergius process for the hydrogenation of

coal. Why did he experiment to achieve this result?

28. With the aid of equations explain the synthesis of gasoline by the Fischer-Tropsch process.

29. (a) What are three physical properties possessed by all allotropic forms of C? (b) In what physical property do they differ radically?

30. Explain why the term *lead pencil* is a misnomer.

31. Give two reasons why graphite is used in making stove polishes.

Group B

32. 2 g. of coal raised the temperature of 2000 ml. of water 6°C. Determine the fuel value of this coal in calories.

33. Name four reducing agents and give an example of the reducing power of each.

34. How is an imitation diamond distinguished from the genuine?

35. Wooden posts are sometimes charred before being placed in the ground. Explain.

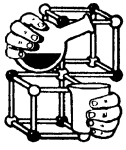
36. Charcoal tablets are sometimes used in the treatment of certain stomach disorders. Explain.

37. What produces chemical changes in an electric furnace: the heat or the electric current? Explain.

38. How does a large percentage of ash or S in coal affect its quality as a fuel?

39. (a) Why is Woehler sometimes called the father of organic chemistry? (b) What is the difference between organic and inorganic compounds?

40. How would you identify three black powders in a mixture of graphite, manganese dioxide, and copper oxide?

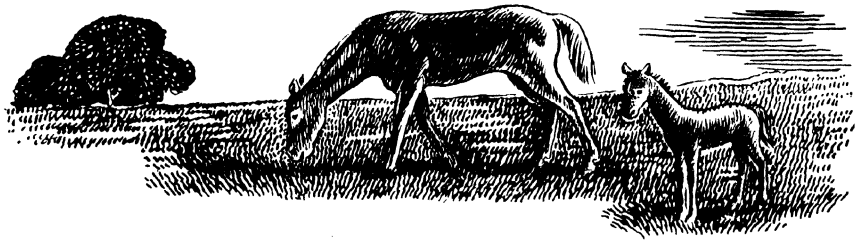


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Place a small amount of sugar on a hot stove or hot plate and report what happens, indicating as many changes as you observe.

2. Make a small working model of an electric furnace used in the production of graphite.

3. Large users of coal purchase coal according to definite specifications as to the percentage of C, volatile material, ash and sulfur content, and fuel value. Does your father buy coal according to definite specifications? Why do most domestic consumers not bother about specifications in buying coal? Is this a sensible state of affairs? Explain.



23 CARBON DIOXIDE: GAS OF LIFE AND DECAY

. . . In 1757 Joseph Black discovered that carbonic acid gas could not be breathed by animals, and had a poisonous effect on them. Sparrows introduced into an atmosphere of the gas died in 10 or 11 seconds, but if their nostrils were stopped with lard, their death took place only at the end of 3 or 4 minutes. Robert Routledge in *A Popular History of Science,* 1881

A Scottish physician discovers carbon dioxide. Joseph Black, a physician, was very much interested in a lively discussion between two professors of medicine. One professor believed that limewater made from limestone was a more effective medicine than limewater made from oyster shells. Black, to settle this controversy in true scientific manner, undertook a thorough study of several carbonates. In 1754, while heating one of these carbonates (magnesium carbonate), he obtained pure carbon dioxide gas for the first time. This was 20 years before the isolation of pure oxygen. Black called carbon dioxide "fixed air."

$$MgCO_3 \rightarrow MgO + CO_2 \uparrow$$

The atmosphere is a vast storehouse of this gas. Immense quantities also occur dissolved in surface and ground water. Large quantities escape from volcanoes and crevices in the earth; it is also ejected in tremendous volumes from wells that produce petroleum or natural gas. In fact, enough carbon dioxide could be obtained from oil wells in the United States alone to supply the world. Carbon dioxide is formed when carbon or its compounds are burned. Because all common fuels contain carbon either free or in compounds,

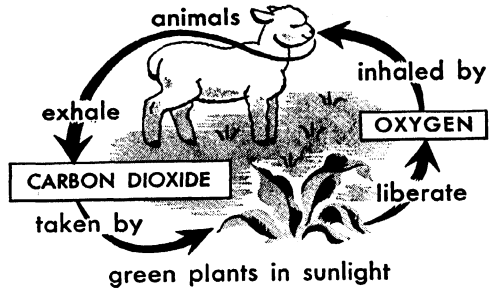


Fig. 74. The carbon dioxide-oxygen cycle.

carbon dioxide is produced whenever such fuels are burned. Finally, tremendous volumes of carbon dioxide are locked up chemically in the great masses of metallic carbonates and bicarbonates found in the earth's crust.

Why carbon dioxide is necessary for life. Life, as we know it today, would be impossible without this percentage of carbon dioxide gas in the air, small though it is (0.04 percent). For without it, plants even with the aid of sunlight could not manufacture starch. As a result, our food supply would diminish and finally vanish altogether. Since coal was formed in prehistoric days by the destructive distillation of plants, even this great source of power would never have been formed if carbon dioxide had not been present in air.

On the other hand, a much larger concentration of carbon dioxide in the atmosphere would be fatal, for it would dilute the oxygen and choke the breath of life out of living things. The delicately balanced ratio of oxygen to carbon dioxide in the air may be better appreciated after a study of the *carbon dioxide-oxygen cycle.*

The carbon dioxide-oxygen cycle. Carbon dioxide is constantly being added to the air by the breathing of animals. It is made in the body tissues by the oxidation of carbon compounds in these tissues. Some of the oxygen inhaled in air is changed to carbon dioxide, which passes out of the body through the lungs. Every breath of air exhaled contains 100 times as much carbon dioxide as was inhaled. At the same time, the amount of oxygen decreases from about 21 percent in the air inhaled to about 16 percent in the air exhaled.

Every ton of coal and liquid fuel burned sends about four tons of carbon dioxide into the air, diminishing, at the same time, the oxygen content of the air. During the decay and fermentation of organic material, immense volumes of carbon dioxide are given off into the air.

You might suspect that, after hundreds of thousands of years, these three processes — breathing, burning, and decay — would have filled the air with enough carbon dioxide to destroy life. But compensating devices offset this increase in carbon dioxide.

All the waters of the earth are continually dissolving carbon dioxide, thus removing it from air. In the formation of carbonates and bicarbonates in nature, great quantities of free carbon dioxide of the air are used up in the chemical weathering of rocks. Most important of all, during daylight hours all green plants are absorbing carbon dioxide, converting it into a form of sugar (fruit sugar) and into starch, and returning free oxygen to the air. The process that is responsible for this change, *photosynthesis,* has been described by some writers as the most important chemical process in the world, for if it should cease man and other animals would have no food.

In higher plants, photosynthesis takes place only in parts that contain *chlorophyll,* a green coloring matter that acts as a catalyst. The final equation for the formation of starch is:

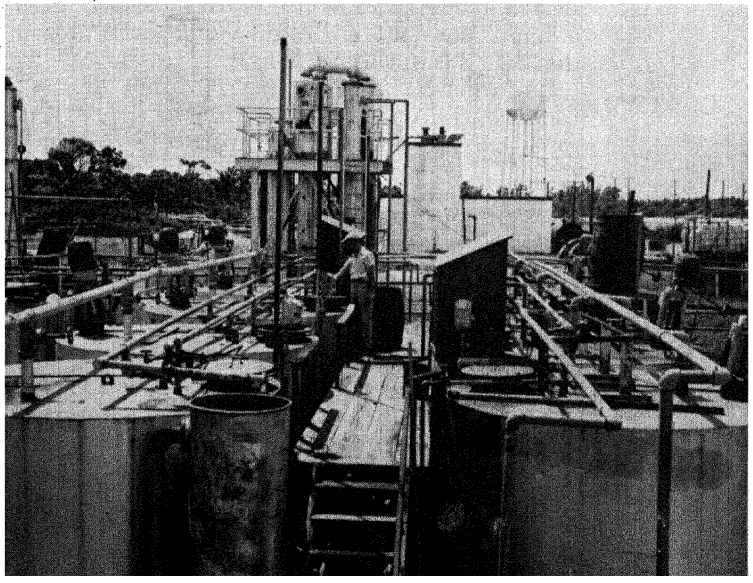
$$6CO_2 + 5H_2O \rightarrow 6O_2 + C_6H_{10}O_5 \text{ (starch)}$$

In Chapter 36 photosynthesis in relation to food-building is discussed, but at present we are concerned particularly with its effect upon the composition of air and the way in which it helps to maintain the balanced ratio of carbon dioxide to oxygen. This balance, as it relates to plant and animal life, is indicated by Fig. 74.

How carbon dioxide is prepared. When an acid is added to a carbonate or bicarbonate, carbon dioxide is liberated. In the laboratory, calcium carbonate, in the form of chips of marble or limestone, is treated with hydrochloric acid, and the CO_2 is collected by water

In these tanks, chlorophyll, the catalytic agent in photosynthesis, is extracted from alfalfa leaves.

American Chlorophyll Division Strong, Cobb and Company, Inc.



displacement, as shown in Fig. 75 below. This gas may also be collected by air displacement, for CO_2 is heavier than air.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

Most of the carbon dioxide used commercially is obtained as a byproduct from coke furnaces, gas wells, and fermentation processes. The heating of limestone to make quicklime

$$CaCO_3 \rightarrow CaO + CO_2$$

also furnishes carbon dioxide for industrial use. Carbon dioxide for industrial use is separated thoroughly from all impurities before being liquefied and stored in steel cylinders under pressure. It is known commercially as *carbonic acid gas.*

Physical properties of carbon dioxide. Carbon dioxide is a colorless, odorless gas; it is $1\frac{1}{2}$ times as heavy as air, and is soluble in water volume for volume (at room temperature and pressure). At higher pressures and lower temperatures, it dissolves in water in much greater volumes.

At ordinary temperatures, a pressure of 52 atmospheres is sufficient to condense carbon dioxide to a colorless liquid. When the pressure over this colorless liquid is decreased, it evaporates rapidly. During this process, evaporation of part of the liquid withdraws heat so rapidly from the remaining liquid that a great amount of the liquid carbon dioxide is changed to solid carbon dioxide, called *carbon dioxide snow* or *dry ice.*

Chemical properties of carbon dioxide. Carbon dioxide does not burn. It will support the combustion of only very active substances, such as sodium. Because it is heavier than air, it can be poured like a liquid. When a bottle of the gas is poured over a lighted candle, the flame is extinguished. Why?

The chief chemical property of carbon dioxide is its ability to combine with water, forming carbonic acid. When carbon dioxide gas is bubbled through water, part of it combines chemically and

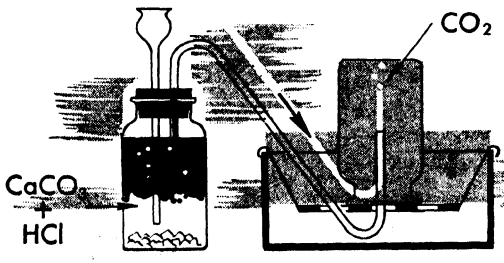


Fig. 75. Laboratory preparation of carbon dioxide. What other gas may be collected in this manner?

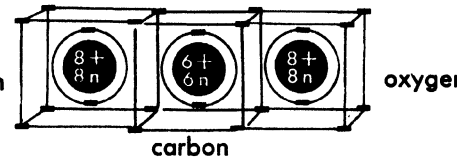


Fig. 76. A cubical diagram of the carbon dioxide molecule.

forms carbonic acid; the rest merely dissolves in the water. Carbon dioxide is, therefore, the anhydride of carbonic acid.

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

Electron structure of carbon dioxide. Carbon dioxide is a nonpolar, covalent compound whose structure may be represented as shown in Fig. 76. Notice that each oxygen atom shares two pairs of electrons with the carbon atom. The carbon atom shares four pairs of electrons with the two oxygen atoms. Since the valence of an element in a nonpolar compound is equal to the number of shared pairs of electrons, the valence of oxygen is two and the valence of carbon is four.

Carbonic acid. Carbonic acid closely resembles sulfurous acid. It is unstable, decomposing, when warmed, into water and its anhydride, CO_2. Thus the reaction for the formation of carbonic acid is reversible.

$$H_2CO_3 \rightleftarrows H_2O + CO_2$$

Because of the highly unstable nature of carbonic acid, it has never been isolated in the pure state.

Like sulfurous acid, carbonic acid is a weak acid, dissociating only slightly, forming few hydrogen ions. Carbonated waters containing dissolved carbon dioxide are so weakly acid that they may be consumed in large quantities without ill effect. Although carbonic acid turns blue litmus paper pink, its sour taste is scarcely noticeable.

Some of the many uses of carbon dioxide. The chief uses of carbon dioxide are: (1) in the manufacture of effervescent beverages, (2) as dry ice for refrigeration, (3) in the leavening of bread, (4) in extinguishing fires, (5) in the manufacture of washing and baking soda, and (6) in the modern synthesis of urea, $(NH_2)_2CO$, a white crystalline substance used in the impregnation of wood, in the treatment of wounds (under the name *carbamide*), and in making a valuable fertilizer, "Uramon":

$$2NH_3 + CO_2 \rightarrow H_2O + (NH_2)_2CO$$

The normal human adult eliminates about 30 grams of urea as a waste product daily in liquid excretions.

Rubber life rafts and life belts are inflated by means of carbon dioxide. The carbon dioxide so used is stored under pressure in small steel bulbs not unlike the carbon dioxide cartridges used on siphons in making charged water.

Another use of carbon dioxide is in making *carbogen,* a mixture of 95 percent oxygen and five percent carbon dioxide, administered to victims of gas poisoning and pneumonia to induce more rapid respiration. Carbon dioxide in the blood appears to stimulate the respiratory nerve centers that control breathing. The heavy breathing of a runner, for example, is caused by the large quantity of carbon dioxide produced in his body during violent exercise. Adding more carbon dioxide to the air inhaled, therefore, causes the more rapid breathing needed by a patient under treatment.

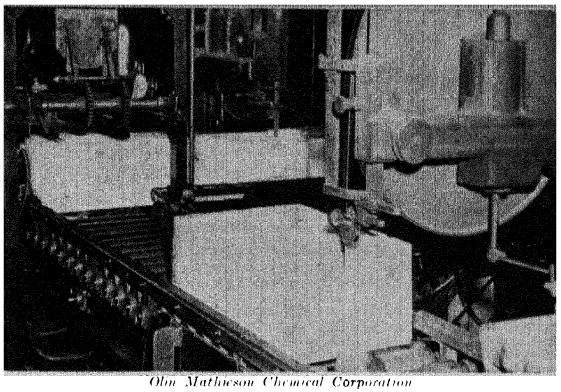
How carbon dioxide is used in effervescent beverages. Priestley discovered the pleasant taste of water containing dissolved carbon dioxide. Before the Royal Society of England he prepared "a glass of exceedingly pleasant sparkling water which could hardly be distinguished from Seltzer water," and received the Society's gold medal for his discovery. This was the first great and unforgettable triumph of this amateur chemist.

Years later, when he was forced to come to America, Priestley interested Dr. Physick, of Philadelphia, in this beverage. In 1807, Dr. Physick had a chemist prepare carbonated water with a little fruit juice for his patients. This was the beginning of the soft drink industry in America, which uses annually more than 200 million pounds of carbon dioxide.

Soda water, so named because sodium carbonate was then used in preparing the carbon dioxide, is now prepared by forcing carbon dioxide gas into cold water at high pressures. When the pressure is released, the excess carbon dioxide gas is liberated, causing the bubbling, or *effervescing.* Carbon dioxide is supplied to soda fountains in liquid form in steel cylinders.

Dry ice. White, solid carbon dioxide has come into wide use for the refrigeration of foods especially perishable products in transit. It has three advantages over ice: (1) the temperature of dry ice, — 78°C., is much lower than that of ice; (2) dry ice does not melt into a liquid, but changes directly into a gas; and (3) in changing from a solid to a gas, dry ice absorbs three times as much heat as ice does when it melts.

Some dry ice is used in the cooling and hardening of rivets made of aluminum alloys, and in *shrink-fitting.* This is a process by which a metal fitting of correct size is expanded by heating until it can



Olin Mathieson Chemical Corporation

Blocks of carbon dioxide dry ice, direct from the hydraulic presses, are cut into cubes before being wrapped for shipment.

be placed over or around the base to which it is to be attached. The fitting is then shrunk by cooling until it adheres to the base with great pressure. Dry ice is also used in the low-temperature drying of many different kinds of biological materials, in the preservation and shipment of blood plasma, and in the quick-freezing of many different kinds of foods.

Baking powders liberate carbon dioxide for leavening. Bread that is not porous is hard, unpalatable, and somewhat indigestible. Leavening bread makes it porous, light, and more easily digested. Although bread may be leavened by beating air into the dough, the method more generally used is to liberate large volumes of carbon dioxide gas in the dough by chemical action. Carbon dioxide is an ideal gas for leavening because it is colorless, odorless, nonpoisonous, and easily and inexpensively prepared.

It is generally produced by *baking powders*, which are mixtures of two white powders, one of which is sodium bicarbonate, or baking soda, and the other a substance such as monocalcium phosphate, $Ca(H_2PO_4)_2$, cream of tartar, $KHC_4H_4O_6$, or sodium aluminum sulfate, $NaAl(SO_4)_2$. While dry, the two powders do not react, since most inorganic reactions take place between ions. However, when water is added, the powders dissolve, dissociate, and an ionic reaction takes place with the liberation of carbon dioxide gas, causing the reaction to go to completion. One of these reactions may be represented as follows:

Baking soda	**+ cream of tartar**	**→**	**Rochelle salt**
$NaHCO_3$	$+ KHC_4O_6$	$\rightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow$	
Sodium bicarbonate	**+ potassium acid tartrate**	**→**	**potassium sodium tartrate**

Baking powders differ mainly in their speed of action. They also contain about 15 percent starch or flour as a filler to keep the salts dry and thus prevent them from reacting before being added to the dough.

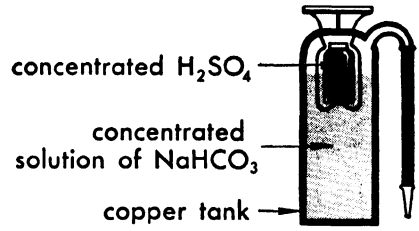


Fig. 77. Cross section of a portable carbon dioxide fire extinguisher.

Some housewives prefer to use their own ingredients in leavening. For example, in making sour-milk biscuits, which many people prefer to baking-powder biscuits, the housewife uses baking soda and sour milk, which contains lactic acid.

Carbon dioxide for leavening is produced also by yeast, one of the oldest of leavening agents. Yeast consists of living plant cells, which produce *zymase*. Zymase, which is a mixture of several enzymes, acts catalytically on the sugar present in the dough and breaks it down into alcohol and carbon dioxide (see page 548). What advantage has yeast over commercial baking powders?

How carbon dioxide is used in firefighting. Carbon dioxide gas is an ideal firefighter. It does not support combustion, is heavier than air, and can be quickly and cheaply liberated in large volumes.

One kind of common portable fire extinguisher consists of a copper tank partly filled with a concentrated solution of sodium bicarbonate. Resting on a shelf inside the top of the tank is a bottle of concentrated sulfuric acid covered with a loose lead stopper. When the tank is inverted, the sulfuric acid pours out of the bottle, and reacts with the sodium bicarbonate, liberating carbon dioxide gas, which carries out of the nozzle with it a fine spray of water and some sodium sulfate. The equation is:

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2 \uparrow$$

To put out stubborn fires, such as oil conflagrations which water cannot extinguish, "Foamite-Firefoam" mixture is used. In this, an aluminum sulfate solution takes the place of the sulfuric acid in the ordinary type of fire extinguisher. This aluminum salt combines with water by a process called *hydrolysis*, forming gelatinous aluminum hydroxide. The carbon dioxide liberated is held fast in large, tough bubbles by the aluminum hydroxide as well as by a sticky extract of licorice. Thus, the mixture spreads over the fire a layer of large bubbles of carbon dioxide. These smother the fire by keeping out the oxygen of the air. The equation is:

$$Al_2(SO_4)_3 + 6NaHCO_3 \rightarrow 2Al(OH)_3 + 6CO_2 + 3Na_2SO_4$$

Fighting fire with liquid carbon dioxide. Another form of fire-fighting apparatus used very widely depends on liquid carbon dioxide under pressure in steel containers. The liquid carbon dioxide may be in portable cylinders or in built-in systems (such as in airplane engines). When the valve is opened, the liquid carbon dioxide vaporizes and rushes very rapidly out of the tube. This sudden evaporation of part of the carbon dioxide cools the remaining liquid to a white solid, and this carbon dioxide snow, played over the fire, quickly puts it out. The fact that carbon dioxide is able to penetrate obstructions without damaging equipment makes it one of the most rapid and efficient of firefighting substances.

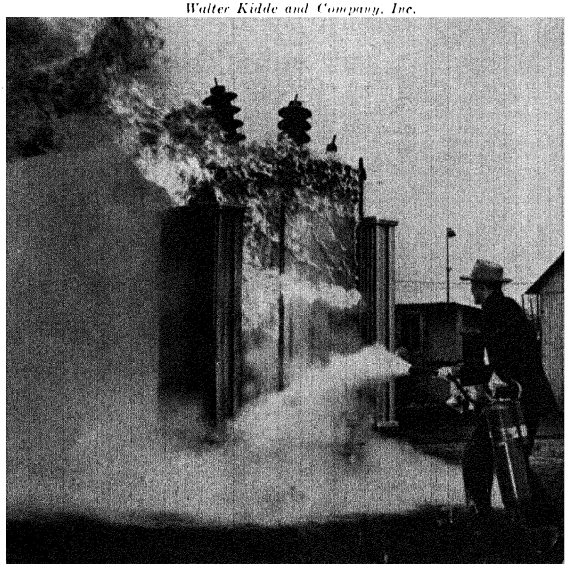
Many ships, including the *Queen Mary,* are equipped to use carbon dioxide for fighting fires in the various storage compartments throughout the ship. In a recent year, more than 500 million pounds of liquid carbon dioxide and carbon dioxide gas were produced in this country.

Salts of carbonic acid. Because carbonic acid contains two replaceable hydrogen atoms, it is a dibasic acid. As you know, one or both of these atoms may be replaced by a metal. Hence carbonic acid forms two series of salts, carbonates and bicarbonates. Thus carbonic acid reacts with sodium hydroxide, forming sodium carbonate or sodium bicarbonate, depending upon the conditions.

$$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 \text{ (sodium carbonate)} + 2H_2O$$
$$H_2CO_3 + NaOH \rightarrow NaHCO_3 \text{ (sodium bicarbonate)} + H_2O$$

With the exception of sodium carbonate, potassium carbonate, and ammonium carbonate, all carbonates are insoluble in water. When a

Walter Kidde and Company, Inc.



Demonstrating the effectiveness of a carbon dioxide extinguisher against a fire in electrical equipment.

carbonate is heated, carbon dioxide is liberated and the oxide of the metal remains.

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

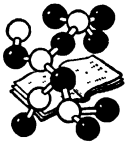
The carbonates of sodium and calcium are discussed in Chapters 30 and 31.

How to test for a carbonate or bicarbonate. An acid liberates carbon dioxide gas from either a carbonate or a bicarbonate. If this gas is then passed into limewater, $Ca(OH)_2$, a white precipitate, calcium carbonate, $CaCO_3$, forms.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

On bubbling more carbon dioxide gas through the mixture, the white precipitate disappears as a result of the solubility of calcium bicarbonate which is formed.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \text{ (calcium bicarbonate)}$$



YOU WILL ENJOY READING

Armstrong, George B. "Dry Ice." *Chemistry,* Feb. 1951, pp. 24–31. An excellent, illustrated article on the history, properties, manufacture of and uses of solid carbon dioxide.

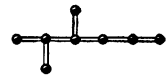
U.S. Department of Agriculture, 1945. *Safe Use and Storage of Gasoline and Kerosene.* Farmers' Bulletin No. 1678. Supt. of Documents, Washington, D.C. 10¢. Some excellent advice on putting out gasoline and kerosene fires.



USING WHAT YOU HAVE LEARNED

Group A

1. What are the chief sources of CO_2?
2. How and by whom was CO_2 discovered?
3. In what way does life depend upon CO_2?
4. Copy and complete the following statements. Do not write in this book. CO_2 is being added to the air constantly by . . ., . . ., and . . . . CO_2 is removed from the air by . . ., . . ., and . . . .
5. Make a diagram representing the carbon dioxide-oxygen cycle.
6. By what three commercial methods is CO_2 produced?



7. Write the equation for one commercial method of producing CO_2.

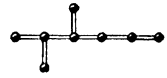
8. Make a labeled diagram for the laboratory preparation of CO_2.

9. (a) Write the chemical equation for the laboratory preparation of CO_2. (b) Why does this reaction go to completion?

10. (a) Can carbon dioxide be collected by air displacement? (b) Explain.

11. What are the physical properties of CO_2?

12. What are three chemical properties of CO_2?



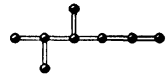
13. (a) Write the reversible reaction of carbon dioxide and water. (b) How could you make large quantities of CO_2 combine with H_2O? (c) The behavior of CO_2 with water places it in what class of compounds?

14. What other acid closely resembles H_2CO_3?

15. (a) What are six uses of CO_2? (b) Opposite each use state the property or properties on which that use depends.

16. Describe briefly the beginning of the soft-drink industry in America.

17. (a) How is dry ice made? (b) Dry ice has what advantages over ice?



18. What is the general composition of baking powder?

19. What is the function of each ingredient in one type of baking powder?

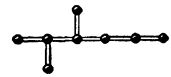
20. Write a balanced equation representing the liberation of carbon dioxide from one type of baking powder.

21. (a) Describe the chemical action of some other type of leavening agent. (b) What advantage has it over commercial baking powders?

22. What are four reasons that CO_2 is an ideal leavening agent?

23. A manufacturer makes enough baking powder to produce 15 tons of CO_2. What weight of $NaHCO_3$ does he use?

24. A sample of baking powder liberated 200 ml. of CO_2. Considering that the reaction went to completion, what weight of $NaHCO_3$ was used if the baking powder was of the cream-of-tartar type?



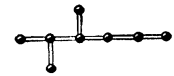
25. What volume of air would be needed to burn completely enough coke to make 10,000 cu. ft. of CO_2?

26. Why do baking powder reactions go to completion?

27. Describe with diagram and equation the principle of one type of portable fire extinguisher.

28. (a) H_2O is not a good agent for putting out a fire of burning oil. Why? (b) Why is CO_2 from the ordinary type of fire extinguisher ineffective? (c) What principle is used in the "Foamite-Firefoam" method?

29. (a) H_2CO_3 has two series of salts. What are they? (b) Write two equations to illustrate.



30. What is the action of heat on carbonates?

31. (a) Describe a complete test for a carbonate. (b) Write the equation for this chemical test.

32. When sour milk is used in cooking, $NaHCO_3$ is used instead of, or in addition to, baking powder. Explain.

33. How can CO_2 be removed from a sample of air?

34. Can pure CO_2 alone be used in fighting fire? Explain.

Group B

35. (a) Why does CO_2 collect in wells and caves? (b) What is its source?

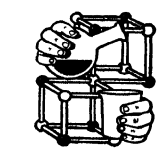
36. Does the effervescence of a solution when an acid is added prove the liberation of CO_2? Explain.

37. 250 ml. of a gas weigh 0.49 g. This gas contains 27.3 percent carbon and 72.7 percent oxygen. Find the formula of this compound.

38. Most chemical reactions take place between ions. However, $CaCO_3$ is insoluble in water. Explain the liberation of CO_2 when HCl is added to solid $CaCO_3$.

39. Explain why a knowledge of chemical arithmetic is essential in preparing baking powders.

40. SO_2 is a reducing agent but CO_2 is not. Explain.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make a study of the cost per ounce of a half-dozen widely advertised baking powders. Nearly all baking powders liberate

the same amount of CO_2 for equal weights of baking powder. Is the wide range of prices for such baking powders warranted? Give reasons for your answers. Why do such wide ranges in prices exist?

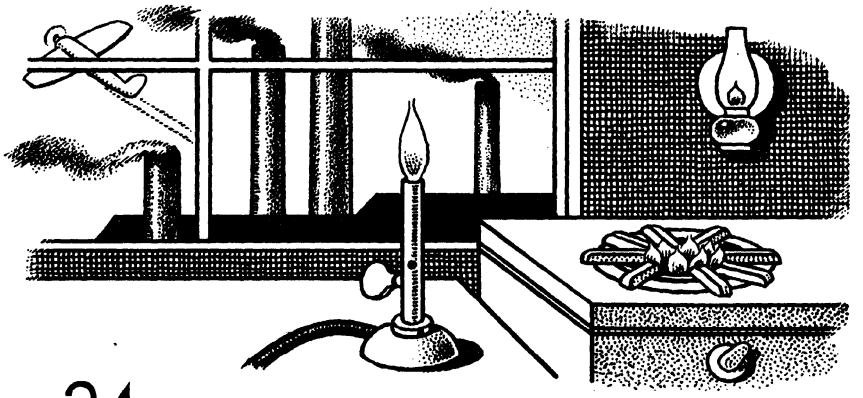
2. Question your mother, or other members of your family, and friends about their preferences in leavening agents. List the data you obtain and give your own reactions to such preferences.

3. Visit a soft-drink bottling plant in your neighborhood, and report on the method used in charging the soft drinks with CO_2.

4. After consulting your teacher of biology on sources of information, prepare a two- or three-page report on microorganisms, other than yeast, that are used by man in the preparation of his food supply. Arrange a class discussion on this topic.

5. Construct a glass model of an acid-sodium bicarbonate type of portable fire extinguisher. Demonstrate its action before the class.

*



24 CARBON MONOXIDE: OTHER GASEOUS FUELS

. . . The introduction of gas lighting (1810) met with much opposition, as one can understand, on the part of the tallow chandlers and sellers of whale oil — at that time used as an illuminant; but after a time the new method of lighting was welcomed. Alexander Findlay, 1930

Priestley discovers an oxide of carbon that burns. Almost half a century after the discovery of carbon dioxide, another quite different oxide of carbon was found, carbon monoxide, CO. Not until the last year of the eighteenth century was carbon monoxide known to be a new compound of carbon.

Priestley again was the first to recognize clearly a new gaseous compound in the flickering blue flame which played over his furnace fire. This valuable discovery was made in America, where this dissenting English minister had fled to escape political and religious tyranny.

How carbon monoxide is formed. Priestley's observation indicated that when coal or other carbonaceous fuel is burned in a limited supply of air, carbon monoxide, rather than carbon dioxide, is formed.

$$2C + O_2 \rightarrow 2CO$$

Carbon monoxide is formed also in a house furnace by the reduction of carbon dioxide gas as it passes over glowing coal, which, as you know, is an excellent reducing agent.

$$CO_2 + C \rightarrow 2CO$$

Normally, carbon monoxide burns at the surface of a coal fire, giving off heat and changing to carbon dioxide, but if the supply of air is insufficient, or if the flame is chilled, some of the carbon monoxide may escape without burning.

How carbon monoxide is prepared in the laboratory. *Formic acid* is a colorless liquid with a characteristic odor, that is, a distinct odor that can be used to identify it. Its formula is HCOOH (only the last H is a replaceable hydrogen atom). When warm concentrated sulfuric acid, a powerful dehydrating agent, is added to formic acid, it extracts the HOH of the acid, leaving pure CO.

$$\mathbf{HCOOH \rightarrow HOH + CO \uparrow}$$

Physical properties of carbon monoxide. Carbon monoxide is a colorless, tasteless, almost odorless gas, slightly lighter than air, and slightly soluble in water. Its odor is very difficult to detect. It can be liquefied, but only under high pressures and low temperatures.

Chemical properties of carbon monoxide. Carbon monoxide burns in air with a pale blue flame, forming carbon dioxide, which, because it is unable to unite with any more oxygen, cannot burn.

$$\mathbf{2CO + O_2 \rightarrow 2CO_2}$$

Because of carbon monoxide's great attraction for oxygen, it is an excellent reducing agent, and therefore it is used in the extraction of iron from its oxide. The carbon monoxide is formed by the reaction of coke (carbon) and CO_2 in the upper part of a blast furnace.

$$\mathbf{Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 \uparrow}$$

Carbon monoxide combines with certain metals, forming a series of compounds called *carbonyls*. For example, when nickel is heated in the presence of carbon monoxide to a temperature of about 40°C., nickel carbonyl, a poisonous liquid, is formed.

$$\mathbf{Ni + 4CO \rightarrow Ni(CO)_4}\ \textbf{(nickel carbonyl)}$$

Upon further heating, carbonyls liberate CO and give up their metals. Nickel carbonyl is used in the extraction of nickel from its ores.

Carbon monoxide in the presence of suitable catalysts also combines directly with hydrogen, forming wood alcohol (see page 548), and with chlorine, forming *phosgene*.

$$\mathbf{CO + 2H_2 \rightarrow CH_3OH}\ \textbf{(wood alcohol)}$$
$$\mathbf{CO + Cl_2 \rightarrow COCl_2}\ \textbf{(phosgene)}$$

Some uses of carbon monoxide. Carbon monoxide is an excellent fuel, burning with intense heat and leaving no solid residue. It is most often used in conjunction with other gases as a mixed fuel, as in *water gas,* for example, which is a mixture of carbon monoxide and hydrogen.

Carbon monoxide is used widely in the *metallurgy* (extracting a substance from its ores) of iron and nickel.

Deadly carbon monoxide, a cumulative poison. Carbon monoxide is the most widespread poison connected with human life and activity. It acts painlessly. Furthermore, it gives no warning of danger, because it is almost odorless, and its victim slowly passes into a state of unconsciousness. Its physiological action is caused by the strong affinity of carbon monoxide for hemoglobin, an attraction that is 300 times greater than the attraction of oxygen for hemoglobin.

Hemoglobin is present in the red blood corpuscles and its function is to unite chemically with oxygen and carry it to all parts of the body by the circulation of the blood. By forming a stable compound with the hemoglobin in blood, carbon monoxide prevents oxygen from reaching millions of cells in the body. The victim is thus killed by *suffocation* — a lack of oxygen.

The formation of carbon-monoxide-hemoglobin takes place gradually, and this substance remains in the blood. When the percentage of this stable compound has reached 40 percent, the victim collapses; when it reaches 80 percent, death occurs. Such a poison, which collects slowly in the body and over a long period of time until it reaches a dangerous concentration, is said to be a *cumulative poison.*

The treatment for carbon monoxide poisoning consists of inducing respiration by the Schäfer prone-pressure or the more recently adopted Holgar-Nielsen "back-pressure, arm-lift" method in the open air, while carbogen is administered. No alcohol should be given. As you know, the carbon dioxide makes the patient breathe more deeply. The injection into the blood stream of *methylene blue,* a dye, as an antidote for carbon monoxide poisoning has been reported to be effective in certain cases.

Where the danger of carbon monoxide poisoning lurks. The exhaust gas of automobiles, in which carbon monoxide exists in varying percentages up to about 12 percent, is one of the most common sources of carbon monoxide. Hundreds of persons are killed by this gas every year, usually in some such ways as these.

1) A motorist drives his car into his garage. It is cold, and he shuts the doors of his garage to keep warm. He keeps the motor running while he gets under the machine to make some repairs. Before he is

aware of it, carbon monoxide from the exhaust pipe of the automobile causes unconsciousness. Death soon follows.

2) On a very cold morning a driver may start the engine before opening the garage door, or he may sit in a closed car with the engine running while waiting for a friend. Carbon monoxide gas from the exhaust finds its way into the confined space and takes its toll.

The carbon monoxide comes from the incomplete combustion of the gasoline. Although gasoline is a mixture of hydrocarbons, we may represent its composition by the formula C_7H_{16}. During incomplete combustion, the following reaction is one that may take place:

$$C_7H_{16} + 8O_2 \rightarrow 6CO + 8H_2O + CO_2$$

The most serious industrial cases of carbon monoxide poisoning occur from exposure to gases, such as producer and blast furnace gases used in many manufacturing plants (see pages 359 and 407).

Most poisonings from carbon monoxide outside of industrial and auto cases are caused by the escape of gas from kitchen ranges and stoves, gas refrigerators and other gas appliances because of leaks and the accidental extinguishing of the burning gases. A furnace, improperly adjusted, may give off quantities of this gas and become a menace to life. As shown below, every coal stove and furnace should have an adequate circulation of air, otherwise carbon monoxide may be formed and finally reach dangerous concentrations.

Firing for complete combustion. In firing a coal-burning furnace, the object is to obtain as much heat from the coal as possible. This can be done only when combustion of the coal is complete, or nearly so, with a minimum of intermediate products, including carbon monoxide and free carbon, or soot, remaining unburned. Incomplete combustion is dangerous because of the dangers from the carbon monoxide produced. It is also wastefully inefficient and robs

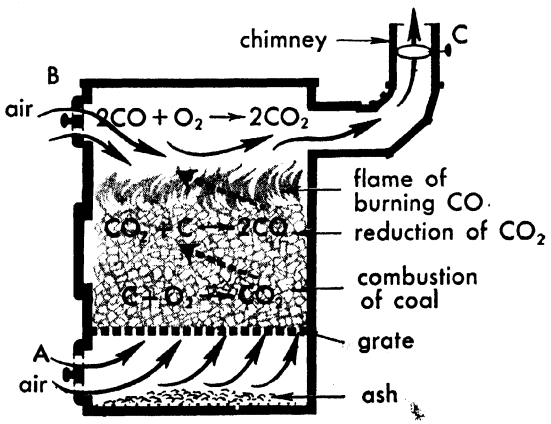


Fig. 78. Stove in operation. When damper *A* is open, but dampers *B* and *C* are not, incomplete combustion results. When *B* and *C* only are open, the fire burns slowly.

the consumer of many Btu per dollar of fuel. In addition, the great quantities of smoke and soot produced are a menace to health and greatly increase expenditures for laundry and dry cleaning.

Complete combustion of coal depends upon adequate quantities of air and upon proper firing methods, that is, proper placement of coal in the firebox. In adding coal to a burning fire, push the glowing coals from the front of the firebox to the rear, and place the additional coal in the space from which the coals were pushed. In this way, the fire is not smothered and great clouds of smoke do not result. The glowing coals at the rear of the firebox heat the added coal, combustible vapors are formed and oxidized relatively completely in the region separating the new coal from the glowing coals.

If the new coal is spread completely over the glowing coals the fire is partially smothered. Combustible vapors are formed, to be sure, but for a long period, the temperature above the added fuel is lower than the kindling temperature of the vapors, and very small amounts of heat are produced.

Proper regulation of the air supply is a most important factor in securing complete, or nearly complete, combustion. If the supply of air is insufficient, incomplete combustion results, and carbon monoxide and free carbon, or soot, are produced in large quantities. If too much air is available, combustion is relatively complete but very rapid, and results in uneven heating. If far too much air is available, much of the heat produced is carried out the chimney without transferring its heat to the water, steam, or air in the heating system.

Finding the damper settings that result in relatively complete combustion is not difficult, but it does require some patience and much observation, for under varying outside conditions, damper settings vary also. If you can adjust the dampers so that the flame produced in the firebox has a minimum of yellow flame, the conditions necessary for nearly complete combustion probably are present.

Coal fires should not be poked or shaken as often as most persons poke and shake them. Shaking of ashes should occur only when the accumulation of ashes becomes so deep that the air supply may be impeded. Ashes insulate the metal grates of the firebox from the intense heat of the fire, and if they are all removed, the grates may be damaged as a result of receiving more heat than they were designed to receive. Poking a fire frequently spreads the burning coals throughout the firebox and results in too rapid combustion.

The simple principles just discussed will, if followed, do much to increase the heat that consumers get from the coal they buy; smoke nuisances will be reduced, and fuel bills will be cut materially.

How carbon monoxide can be removed from air. For a long time no simple method of removing noxious carbon monoxide from air was known. Activated charcoal, which adsorbs various gases, such as ammonia, acetone, benzene, and chlorine, will not remove carbon monoxide from air.

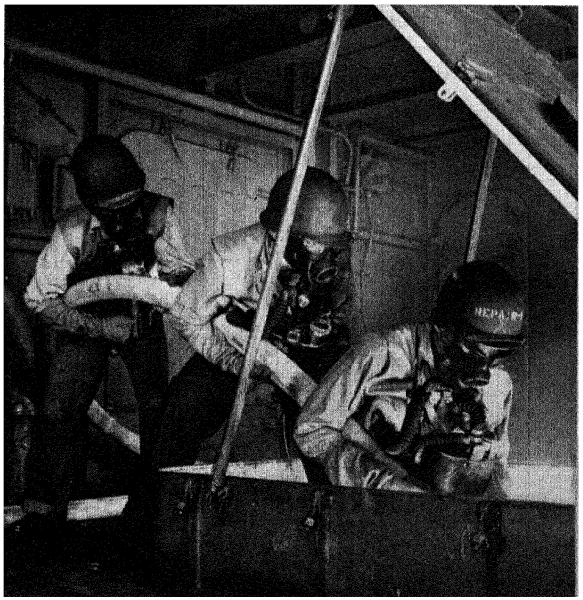
A catalyst called "Hopcalite," which consists of a mixture of metallic oxides, causes carbon monoxide to change to carbon dioxide at ordinary temperatures and pressures. In the presence of "Hopcalite," 1 molecule of carbon monoxide combines with another atom of oxygen from the air. A rescue-breathing apparatus containing a "Hopcalite" canister is now used by persons who find it necessary to enter regions where concentration of carbon monoxide is high.

How can carbon monoxide be detected? Simple color-detector tubes have been devised for determining minute amounts of carbon monoxide in air. One such preparation called *hoolamite* contains specially prepared iodine pentoxide, I_2O_5, which oxidizes carbon monoxide to CO_2.

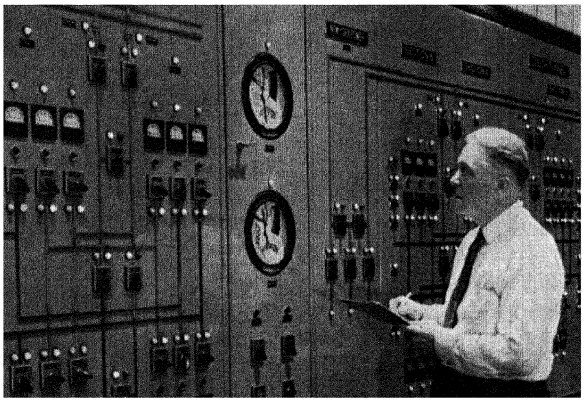
$$5CO + I_2O_5 \rightarrow 5CO_2 + I_2$$

The iodine fumes liberated cause a change in color that is directly proportional to the amount of carbon monoxide present. This amount can be determined by comparison with a standard color scale. The color fades, and the tubes may be used again. Before this method was developed, canaries were often used as detectors because these birds are very sensitive to minute amounts of this poison and show its effects before man does.

Official U.S. Navy photograph



Navy firefighters ready for action. Their rescue-breathing apparatus will protect them from carbon monoxide and other dangerous fumes.



These recording devices keep a constant check on the condition of the air in the Lincoln Tunnel. The 8000-foot vehicular tunnel connects the New York and New Jersey banks of the Hudson River.

The Port of New York Authority

In some tunnels, such as the Holland and Lincoln Tunnels at New York City, machines have been installed which record on a time chart the amount of carbon monoxide present in the air. A warning bell is caused to ring when the carbon monoxide reaches a concentration of four parts in 10,000. At this point, also, dampers and fans begin to operate automatically to change the air.

What are the more important gaseous fuels? The fuel gases burned each year in this country are worth more than two billion dollars. The total volume of gas produced is about eight trillion cubic feet. Besides pure carbon monoxide, which is seldom used alone, the most important gaseous fuels are *water* (or *synthesis*) *gas, producer gas, coal gas, natural gas, acetylene gas,* and hydrogen. Hydrogen has already been discussed; a brief discussion of the others follows.

A gas from steam and carbon. Water gas is manufactured by passing water in the form of steam over glowing coke or hard coal. The coke is first burned in a draft of air until it is red-hot. The air is then shut off and the steam turned on. The temperature of the coke falls gradually because the reaction is endothermic, and when it reaches about 1000°C., the steam is cut off and the air supply renewed. During the process the carbon, which is an ideal reducing agent, combines with the oxygen of the water, leaving hydrogen.

$$H_2O + C \rightarrow \underbrace{CO + H_2}_{\text{water gas}}$$

At a temperature of about 1000°C., the most gas is produced. Above this temperature, the carbon monoxide formed may react with the steam and change to carbon dioxide.

$$H_2O + CO \rightarrow CO_2 + H_2$$

Water gas is thus a mixture of carbon monoxide and hydrogen. It is used, either alone or mixed with coal gas, for domestic heating purposes. Since both carbon monoxide and hydrogen burn with almost colorless flames, a mixture of the two cannot be used for illuminating purposes unless it is made luminous by injecting into it gaseous hydrocarbons from petroleum, which, on burning, give a yellow flame. This process of adding hydrocarbon vapors to water gas is called *enriching* the gas. When water gas burns, it forms water vapor and carbon dioxide.

$$\underbrace{CO + H_2}_{\text{water gas}} + O_2 \rightarrow H_2O + CO_2 \uparrow$$

When used in the synthesis of gasoline and other chemicals it is called *synthesis gas.*

The gasification of coal. In areas where natural gas is not available as a fuel for factories and homes, *producer gas* is most generally used. It is produced by burning low-grade coal in a furnace with a limited supply of air. The chief product formed during the incomplete combustion of the coal is carbon monoxide. The gas issuing from this furnace is mixed with large quantities of nitrogen, which is too inactive to unite with the coal. Producer gas, then, is chiefly a mixture of about 60 percent nitrogen and 30 percent carbon monoxide. It contains also about ten percent hydrogen.

$$2C + \text{air } (O_2 + N_2) \rightarrow 2CO + N_2$$

Producer gas is a much poorer fuel than water gas because it contains such a large amount of nitrogen, an incombustible gas. Its manufacture constitutes the most efficient means of converting low-grade coal into power.

A gas similar in composition to producer gas was first proposed by Mendeleyeff and later produced in 1933 in the Soviet Union by burning coal underground. Instead of mining the coal in the usual way, a coal seam was sealed off, set on fire, and the gases produced were brought to the surface through pipes. Later, pure oxygen was mixed with the blast of air sent into the mine, and the gas that came out of the mine was richer in composition than producer gas.

This gasification of coal underground (gas mining), held feasible by the U.S. Bureau of Mines after several years of experimentation, may turn out to be a revolutionary development. By this method we may be able to recover valuable coal in mines abandoned because of the low-grade nature of the coal or because of the thinness of the coal

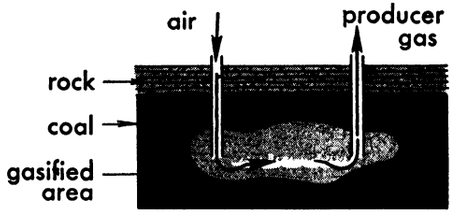


Fig. 79. Underground gasification of coal.

vein. In addition, this method makes coal working safer and healthier, a consideration which is always desirable. Another advantage is pipeline distribution of this fuel.

Natural gas, the Cinderella fuel. More than 80 percent of the gaseous fuel consumed each year in the United States is natural gas. In various sections of the world, especially where coal and petroleum deposits are found, natural gas issues from the earth when porous rocks saturated with it are tapped. The gas may flow out under pressure, or pumping may be required.

Many gas wells do not yield oil, but an oil well almost always produces both gas and oil. The gas from wells that do not yield oil is usually very rich in methane, CH_4, some wells yielding as high as 95 percent methane.

In the early days of the petroleum industry, little or no use was found for natural gas, and most of the wells were ignited and allowed to burn for years. When the waste of natural resources involved in such practices was realized, controls were established and the burning of natural gas greatly diminished.

Methane, also called *marsh gas,* is a colorless, practically odorless, insoluble gas which burns with an almost colorless flame, forming CO_2 and water vapor.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

It has a calorific value about twice that of manufactured gas which it has largely replaced. It is about half as heavy as air. Natural gas is purified, some high quality casing-head gasoline being obtained in

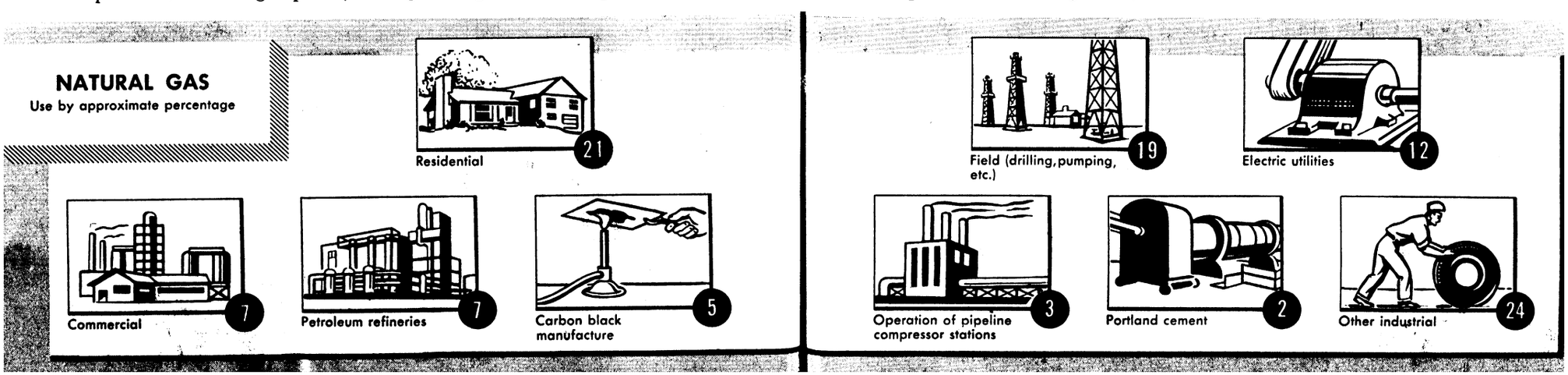
this process. H_2S is also removed before it is sent into pipelines. It is also stripped of its heavier hydrocarbons such as butane and propane before being piped many hundreds of miles to supply factories, farms, and homes with light, heat, and power. For example, there is an 1840-mile pipeline (the Big Inch) from Texas to New York.

Probably the origin of our great supply of natural gas is the same as that of petroleum, which most scientists believe to be the result of the incomplete decomposition of vegetable or animal matter, either with or without bacterial action. The formation of petroleum does not require millions of years as was formerly believed. This is demonstrated by the formation at the present time of petroleum in off-shore marine sediments. Some scientists believe, however, that natural gas originates from the interaction of metallic carbides and water, just as acetylene is formed by the reaction between calcium carbide and water.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow \text{ (acetylene)}$$

A gas from a gray solid. The gaseous fuel called *acetylene,* C_2H_2, is colorless and odorless when pure, very slightly soluble in water, and somewhat toxic. Acetylene has a tendency to explode when liquefied. The gas is therefore not liquefied, but is forced at low pressure into a solvent called *acetone,* a colorless liquid obtained from the destructive distillation of wood, and mixed with some inert porous material, such as wood charcoal or asbestos fiber. It is sold in portable steel cylinders and is used widely in oxyacetylene torches. When the valve of one of these cylinders is opened, the pressure is reduced, and some of the gas escapes from solution.

For emergency use, and in lighthouses and isolated districts where electric lighting and illuminating gas are not available, special acetylene generators have been constructed. These special generators allow water to come in contact with calcium carbide at regulated rates of speed, so that the gas may be liberated as needed.



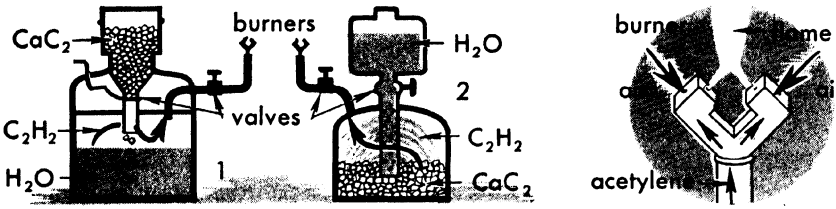


Fig. 80. (left) Carbide-to-water acetylene generator for large installations. (center) Water-to-carbide generator. (right) The acetylene burner.

The burner used with acetylene gas must be specially constructed to permit the access of a large amount of air to the burning gas. Because acetylene is rich in carbon, it would otherwise burn incompletely and produce a smoky flame.

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O \text{ (complete combustion)}$$
$$2C_2H_2 + O_2 \rightarrow 4C + 2H_2O \text{ (incomplete combustion)}$$

Alcohol, acetone, vinegar, chloroform, plastics, and synthetic fibers, rubber, and gasoline have been built up chemically from acetylene gas (see Chapters 34 and 35).

A gas from the destructive distillation of coal. About the time that Priestley was studying carbon monoxide, coal gas was introduced as an illuminant. William Murdock, a Scottish workman employed by James Watt, developer of the steam engine, carried out experiments that led to lighting part of the Boulton and Watt factory in Birmingham, England, with gas in 1798. A few years later, gaslighting was introduced in the United States. Much opposition was raised against it, but the advance of science could not be stopped for long. Manufacturers of candles and whale oil, fought against illuminating gas, even as other manufacturers have since struggled unsuccessfully against other innovations.

Coal gas is obtained from coal by destructive distillation. Fig. 81 shows the method of manufacture and purification in a *byproduct coke oven*. Coal is heated in a closed oven. The vapors formed are first passed into the hydraulic main, where some of the vapors of

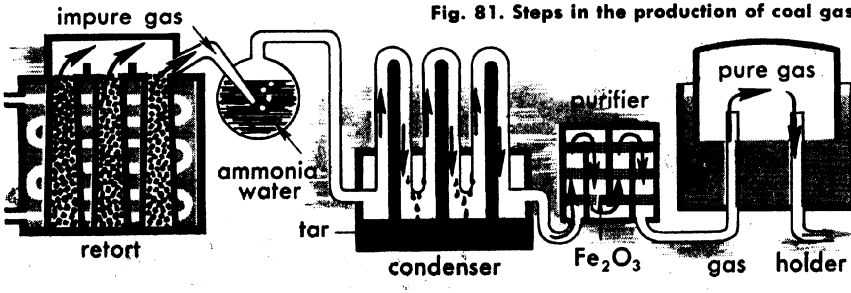


Fig. 81. Steps in the production of coal gas.

coal tar and ammonia are condensed. The remaining vapors then enter the condensers, where the rest of the ammonia is absorbed and the coal tar condensed. The purifier, containing iron oxide or lime, removes hydrogen sulfide and other sulfur compounds. The purified coal gas then enters the gas holder. Coal gas contains about ten percent carbon monoxide, 40 percent hydrogen, and 40 percent methane. It contains also about ten percent nitrogen.

The destructive distillation of one ton of coal yields approximately 10,000 cubic feet of coal gas, 20 gallons of ammonia water, and 120 pounds of coal tar. About 1400 pounds of coke remain in the retort. A tarry matter called *pitch* is left also, which is used as a binder in road construction.

What is an explosive mixture? All the gases discussed in this chapter burn quietly in air. However, when they are mixed with air in the right proportions to secure nearly complete combination and then ignited, very rapid oxidation takes place, suddenly producing extremely *large volumes of gases.* The high temperature of the reaction helps to account for the large volume of gases formed, since gases expand as their temperature is raised. High temperatures also result in high pressures. If the explosive mixture is confined, as, for example, in a mine or factory, great destruction takes place.

Gases and vapors differ from one another in the range of composition of their explosive mixtures. Thus coal gas will explode when anywhere from six percent to 29 percent of it is mixed with air. Air containing less than six percent or more than 29 percent of coal gas will not explode.

The character of the explosive mixture is of prime importance in the working of internal-combustion engines. For example, the degree of smoothness and of power in the running of an automobile engine depends upon getting the right mixture of air and gaseous fuel admitted to the cylinders and ignited at the proper instant by an electric spark. The closer the proportions of the mixture to those necessary for securing complete combustion, the greater the power produced and the less the waste of fuel.

Because of the importance attached to securing this proper mixture, the carburetor, in which the mixing is done, is often called the *heart* of the internal-combustion engine. This needs adjustment from time to time to insure highest efficiency (see Fig. 82).

Gasoline vapor mixed with air may form a very explosive mixture. Many serious accidents have resulted from the careless use of gasoline in dry cleaning at home. Such cleaning operations should be done in the open and away from any source of ignition. In using

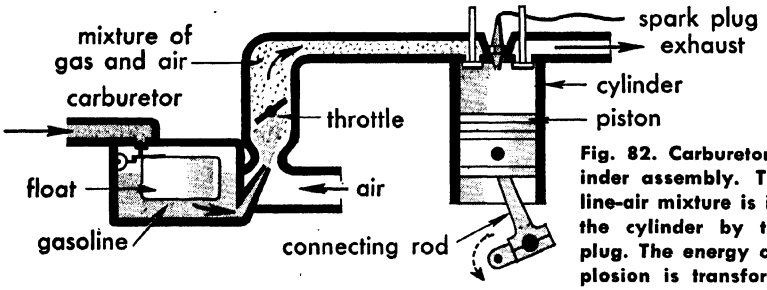


Fig. 82. Carburetor and cylinder assembly. The gasoline-air mixture is ignited in the cylinder by the spark plug. The energy of the explosion is transformed into motion by the piston.

gasoline for dry cleaning, vigorous or continued rubbing of the fabric should be avoided lest the friction ignite the gasoline.

Safety measures against mine explosions. For centuries the ignition of explosive mixtures, especially in coal mines, has caused serious loss of life. In 1556, Agricola (*ă*-grĭk'ō-lă) published a book on mining, one section of which dealt with "the ailments and accidents of miners and the methods by which they can guard against these." But life was cheap in those days and little was done to protect miners against explosions. At the end of the eighteenth century, there came an emphasis on the rights of man and with it a new humanitarianism. An interest in occupational accidents and diseases was aroused. Gases in mines and mine ventilation were studied.

Davy, who discovered sodium and potassium, and made other important contributions to chemistry, was among those interested in the plight of the miners in England. He devised a simple *safety lamp* to prevent mine explosions. It is based upon two principles: (1) An explosive mixture does not undergo chemical change until its kindling temperature is reached. (2) Metal surfaces spread heat rapidly.

In the Davy lamp, the flame is surrounded by a wire gauze, which distributes the heat produced by the flame over a wide area, and thus prevents the explosive mixture outside the lamp from reaching its kindling temperature. A lighted match brought over a wire gauze, as shown in the illustration below, will set fire to the gas above the gauze, but the gas below will not catch fire. Why? This is an illustration of the principle of the Davy safety lamp.

In commercial mining, the Davy lamp has been replaced by a battery-operated electric lamp.

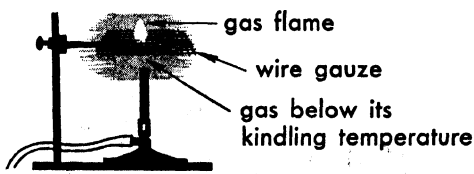
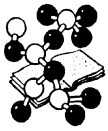


Fig. 83. Demonstration of the principle of the Davy lamp. Why does the gas below the wire gauze not catch fire?



In an underground coal mine, the air is tested for the presence of methane immediately after coal is blasted from the seam. The flame of the safety lamp turns blue when the gas is present.

National Coal Association



YOU WILL ENJOY READING

Faraday, Michael. *The Chemical History of a Candle.* "Kings' Treasuries of Literature" Series, E. P. Dutton & Co., New York, 1920. This book consists of six lectures delivered by Faraday before young boys and girls at the Royal Institution of London in 1860–1861. Lecture I covers flames – sources and structure. The book is a classic, and though about 100 years old may still be read with pleasure and profit.

Manchester, Harland. *New World of Machines,* pp. 174–189. Random House, New York, 1945. "Power for Tomorrow" is a fine chapter in this carefully written book.

Oettingen, W. F. von. *Carbon Monoxide: Its Hazards and the Mechanism of Its Action.* Public Health Bull. No. 290, 1944. Supt. of Documents, Washington, D.C. 35¢.



USING WHAT YOU HAVE LEARNED

Group A

1. Where and by whom was pure CO first studied?

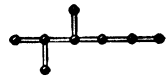
2. (a) How is CO formed in a furnace? (b) Write an equation to illustrate. (c) Write the equation for the oxidation of CO.

3. (a) How is CO usually prepared for laboratory use? (b) What is the function of the H_2SO_4 used?

4. Compare the physical properties of N_2 and CO.

5. (a) What are two chemical properties of CO in addition to its combustibility? (b) Write equations to illustrate each.

6. Write balanced equations for the following. Name the products. (a) Action of chlorine and carbon monoxide, (b) action of hydrogen and carbon monoxide, (c) action of carbon monoxide on heated nickel, and (d) formation of phosgene.



7. Discuss four uses of CO.

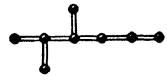
8. (a) Explain how CO acts on the hemoglobin of the blood of a person breathing it. (b) What first-aid treatment should be given a person who has been overcome by CO? (c) What is the function of the small amount of CO_2 administered?

9. Poisoning by CO often occurs in closed garages. (a) Why? (b) What precautions should be taken to prevent this danger?

10. (a) What gases are generally adsorbed by the C used in gas masks? (b) What substance is used in CO detectors?

11. (a) What are two important factors in firing with coal for complete combustion? (b) What is the most efficient method of firing? (c) Why?

12. In firing with coal, what are the results of (a) inadequate air supply? (b) too much air? (c) far too much air?



13. How can you tell when the conditions necessary for complete, or nearly complete, combustion are likely to be present?

14. (a) What do large quantities of black smoke issuing from a chimney indicate? (b) Why?

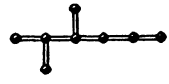
15. (a) Is black smoke undesirable? (b) Why?

16. (a) What are two pure gaseous fuels? (b) What are three that are mixtures of gases? (c) Which of (b) contain large quantities of CO?

17. (a) Write an equation for the manufacture of water gas. (b) What is "synthesis gas"?

18. What volume of steam is used in making 1500 cu. ft. of water gas?

19. What weight of coal, containing 85 percent C, is used in making 2000 cu. ft. of water gas? (One ounce-molecular weight of a gaseous substance occupies 22.4 cu. ft.)



20. Water gas contains 60 percent CO and 40 percent H_2. What volume of air is necessary for the complete combustion of 200 cu. ft. of this gas?

21. (a) What is meant by enriching water gas? (b) Why is it done?

22. Producer gas contains about 60 percent noncombustible N_2, yet it is used in great quantities as a fuel for gas engines. (a) How does this N_2 affect its fuel value? (b) What process uses producer gas? Why?

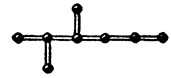
23. Explain the gasification of coal underground.

24. (a) On the basis of present evidence, what do we think was the source of natural gas? (b) How does its present consumption rank with that of other gaseous fuels? (c) What is its chief constituent?

25. (a) What are the properties of methane? (b) What other name has it? (c) Why?

26. Make a table showing the source, composition, and chief use of four gaseous fuels.

27. Describe briefly the stages in the manufacture of purified coal gas.



28. (a) What is destructive distillation? (b) Name the chief products of destructive distillation of bituminous coal?

29. (a) How is C_2H_2 made? (b) What are its principal properties? (c) Why must a C_2H_2 burner be so constructed that it allows the access of large quantities of air?

30. How many cubic feet of air are used in burning completely 2500 cu. ft. of C_2H_2?

31. How would you identify CO_2, H_2, CO, N_2, and NO?

32. (a) What happens when an explosive mixture is ignited? (b) Why are explosive mixtures dangerous? (c) What is the most important factor to consider in the mixing of gases for explosive effect?

33. (a) How is the explosive mixture in an automobile regulated? (b) Why?

34. Describe a situation at home in which a dangerous explosive mixture of gases might be formed.

35. What might happen if the ventilating system in an underwater tunnel such as the Lincoln Tunnel in New York City suddenly got out of order?

Group B

36. Why does CO burn, whereas CO_2 does not burn?

37. In making water gas, what would happen if the temperature used were too high?

38. Why has the byproduct furnace replaced the beehive coke oven?

39. Why is a blue flame seen when fresh coal is added to burning fuel?

40. A gas sample from a sealed fire area in a mine shows CO, four percent; O_2, ten percent; CH_4, seven percent; and N_2, 79 percent. Is the fire blazing, or is a methane explosion possible? Explain.

41. Suppose a sample of gasoline is half hexane, C_6H_{14}, and half heptane, C_7H_{16}. How many cubic feet of air are necessary for the complete combustion of 20 cu. ft. of this gasoline vapor?



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. If you live near an oil or natural-gas field, visit the gas wells and write a report on the gas waste, if any. Do you think Federal control of such waste desirable? Explain.

2. Davy refused to take out a patent on his miner's lamp, saying, "No, my good friend, I never thought of such a thing; my sole object was to serve the cause of humanity, and if I have succeeded I am amply rewarded in the gratifying reflection of having done so." Write a report expressing your views on this incident. Cite similar instances.

3. Study the recently introduced Holgar-Nielsen "back-pressure, arm-lift" method and compare it with the Schäfer prone-pressure method.

4. Using a test tube, a one-hole rubber stopper, a short delivery tube and some dry sawdust or wooden splint, show that a combustible gas can be obtained from the wood similar to coal gas from coal. Consult your laboratory workbook.



25 METALS
AND THEIR CHEMICAL ACTIVITY

. . . Potassium and sodium are the names by which I have ventured to call the two new substances . . . They agree with the metals in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination. Their low specific gravity does not appear a sufficient reason for making them a new class.

Sir Humphry Davy, 1807

Elements may be classified as metals or nonmetals. Thus far we have discussed a number of elements including oxygen, nitrogen, chlorine, bromine, iodine, fluorine, sulfur, and phosphorus. Each of these elements has more than one-half the number of electrons in its outer electron ring that are necessary to complete this ring. Hence, each is a borrower of electrons, has a negative valence, and has an oxide (or oxides) that is an anhydride of an acid. Each of these elements is called a *nonmetal.*

But the properties of these elements are not characteristic of all the elements. Certain elements have less than half the number of electrons in their outer electron rings necessary to complete these rings. Hence, each of these elements is a lender of electrons, has a positive valence, and possesses an oxide (or oxides) that is an anhydride of a base. Each of these elements is called a *metal.* Of the 100 chemical elements, 78 are metals.

A comparison of sulfur and magnesium will help to make clear the differences between a metal and a nonmetal.

This classification of elements into metals and nonmetals is very old, but it still continues to be of service. We must remember, however, that certain elements behave either as a metal or as a nonmetal.

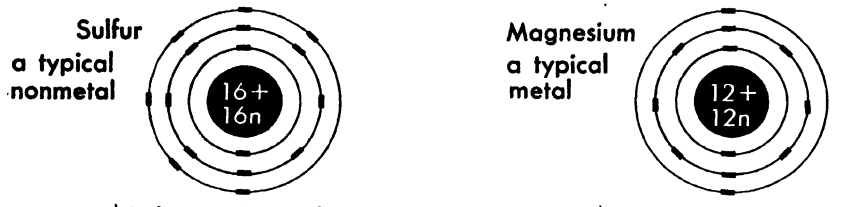


Fig. 84. Structure of the atoms of a typical metal and nonmetal.

How metals occur in nature. Metals occur either *free* (uncombined), or *chemically combined* in compounds. Gold, silver, copper, and platinum are examples of metals that occur in the free state. The oxide of iron, the fluoride of aluminum, the chloride of sodium, the bromide of magnesium, the sulfate of barium, the carbonate of lead, and the phosphate of calcium are examples of compounds of metals that are found in the combined state. All these compounds are *minerals, inorganic substances of definite composition found on the earth.* A mineral such as mercuric sulfide, HgS, or rock salt, NaCl, from which an element, usually a metal, may be profitably extracted is an *ore.*

How metals are extracted from ores. In mining operations, a mineral is first separated mechanically from the rock, or *gangue* (găng), with which it is mixed by a process known as *ore-dressing.* The particular process used depends upon the differences in properties between the ore and the gangue. Low-grade ores must be concentrated to reduce the cost of extracting the metal. Various methods of ore-dressing, such as hand or gravity separation, leaching, magnetic, and *flotation,* are described in the discussion of specific ores.

The process of extracting a metal from its ore is called *metallurgy.* In general, the metallurgy of any metal depends upon the nature and purity of the ore, the properties of the metal to be extracted, and the cost of the processes. The four most widely used metallurgical processes are: (1) *electrolysis;* (2) *reduction* by means of carbon; (3) *roasting,* that is, heating the ore to change it to its oxide by *oxidation* (usually roasting is followed by reduction with carbon); (4) *aluminothermy,* that is, reduction with aluminum powder.

The most widely used metal obtained by electrolysis is aluminum. Iron is the chief metal obtained by reduction, and copper and zinc are the most common metals obtained by roasting followed by reduction. Chromium and manganese are made by aluminothermy. These four metallurgical processes are discussed in connection with aluminum, iron, copper, zinc, and chromium.

Characteristic physical properties of a metal. Metals have many physical properties in common. A brief study of these characteristic properties helps us to realize why the classification of elements into metals and nonmetals has aided the development of chemistry.

1) *A metal is lustrous.* That is, a metal has a definite shine. The luster of gold, silver, nickel, and copper is well known.

2) *A metal is malleable.* That is, a metal can be hammered into thin sheets such as gold leaf and tin foil. The most malleable metal is gold, which has been beaten into sheets so thin that 300,000 of them placed one above the other make a pile only one inch thick. Carbon, a nonmetal, breaks when hammered; it is brittle.

3) *A metal is ductile.* That is, a metal can be drawn into wire. Platinum, for example, can be drawn into such a fine wire that it cannot be seen by the unaided eye. The degree of ductility of metals varies greatly. Sulfur, a nonmetal, cannot be drawn into wire.

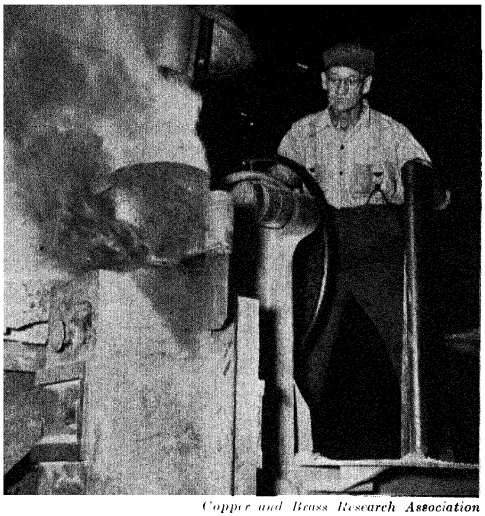
4) *A metal is a good conductor of heat.* Place one end of a copper wire a foot long in a flame and notice how quickly your fingers holding the other end of the wire become warm.

5) *A metal is a good conductor of electricity.* Although silver is the best conductor of electricity, copper is used most generally because of its much lower cost. On the basis of evidence now available, scientists think that good conductors of electricity, including metals in general and copper and silver in particular, are composed of atoms whose outer rings have only a few electrons loosely held. These

(left) A prospector in Utah examines a sample of uranium ore. (right) Testing the ore with acid for the presence of copper and limestone.

Photographs, Standard Oil Company (N.J.)





Copper and Brass Research Association

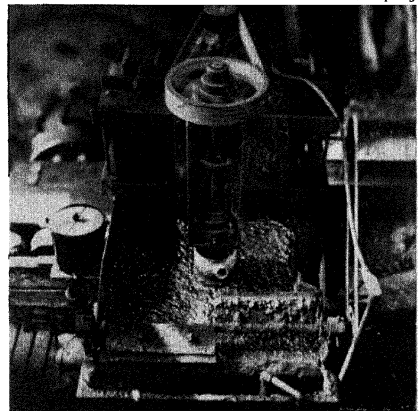
Pouring molten copper from an electric furnace into a mold. The "melt" consists of both virgin metal and high-grade scrap.

electrons can, therefore, move along to the next atom, and so on, producing a flow of electricity. Nonmetals, such as sulfur, have in their outer rings a large number of electrons, not so free to move. Hence nonmetals are poor conductors of electricity.

6) *Other properties of a metal.* All metals, with the exception of mercury, are solids at ordinary temperatures. They range in melting points from mercury (−39°C.) to wolfram (3380°C.). Metals differ widely in *tensile strength,* that is, the ease with which they can be pulled in two. Some steel has a tensile strength of 500,000 lbs. per sq. in. cross section.

They range in density from lithium (a little more than half as heavy as water), whose density is 0.53, to osmium, whose density is 22.5. Most metals are gray in color, the two most common exceptions being copper (red) and gold (yellow). They range in hardness from lithium, which is as soft as wax, to others which are very hard. All metals are crystalline.

Carbide and Carbon Chemicals Company



A flotation cell in which the ores of non-ferrous metals are concentrated. Unwanted impurities settle to the bottom of the cell and the ore is skimmed off with the froth.

Characteristic chemical properties of a metal. Metals also possess many chemical properties in common.

1) *Certain metals unite with oxygen,* forming oxides that are *basic anhydrides.* The burning of magnesium, for example, produces magnesium oxide, which is the anhydride of magnesium hydroxide.

$$2Mg + O_2 \rightarrow 2MgO; \quad MgO + H_2O \rightarrow Mg(OH)_2$$

2) *Certain metals unite with water,* forming either bases or oxides, and liberating hydrogen. Thus steam passed over hot iron forms iron oxide and hydrogen, whereas calcium reacts with water, forming calcium hydroxide and hydrogen.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$$
$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$$

3) *Certain metals decompose acids,* liberating hydrogen or other gas.

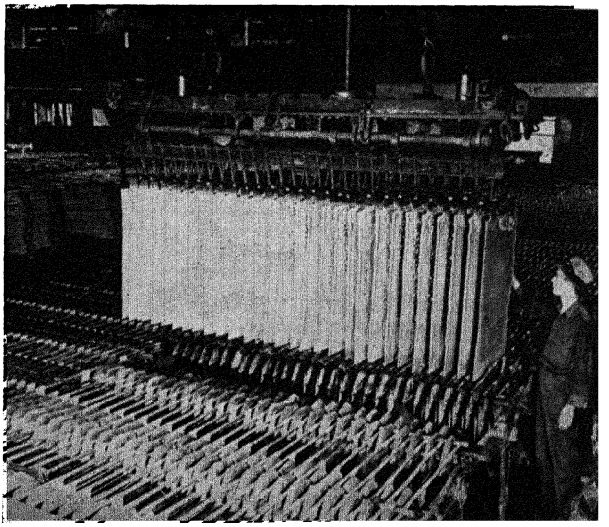
$$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$$
$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$
$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow$$

4) *Metals combine with nonmetals,* forming salts. For example, they unite with chlorine, sulfur, and bromine, forming chlorides, sulfides, and bromides, respectively.

5) *Certain metals unite with bases,* liberating hydrogen. Thus, both aluminum and zinc react with sodium hydroxide, liberating hydrogen.

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 \text{ (sodium aluminate)} + 3H_2\uparrow$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 \text{ (sodium zincate)} + H_2\uparrow$$

Copper and Brass Research Association



These plates of impure copper are about to be suspended in a tank containing copper sulfate and sulfuric acid. The copper will be refined by an electrolytic process described in Chapter 28.

Metals may be listed in the order of their replacement power. It is generally known that gold does not tarnish in air and is not acted upon by any one acid. It is equally well known that iron, on exposure to air, is oxidized readily. We could, if it served any useful purpose, arrange all the metals in the order of their ability to resist oxidation.

A more useful arrangement is based upon the ability of one metal to replace another from a solution of a salt of the latter. For example, when an iron nail is placed in a solution of copper sulfate, the iron becomes coated with a layer of pure copper, and iron sulfate is formed.

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

Similarly, copper placed in a solution of silver nitrate becomes coated with pure silver and will, itself, go into solution as copper nitrate. The reverse reactions will not take place under normal conditions. That is, a copper nail placed in an iron sulfate solution will not deposit iron.

If we try these experiments, using a number of different metals and their salts, we can arrange the common metals in a definite *replacement series.* This replacement series of the common metals is also called the *electrochemical series,* and the *electromotive series.*

How the electron theory explains the replacement series. Metals differ in their tendency to lose electrons and become ions. When free iron (Fe^0) replaces copper from a copper sulfate solution, the following electron reaction occurs:

$$\overbrace{Fe^0}^{\text{loses 2 electrons}} + \underbrace{Cu^{++}(SO_4)^{--}}_{\text{gains 2 electrons}} \rightarrow Fe^{++}(SO_4)^{--} + Cu^0$$

Electrically neutral iron loses two electrons and becomes ionic Fe^{++}, which is positively charged. Ionic copper from the copper sulfate solution gains two electrons, becomes electrically neutral, and precipitates out as free copper atoms. The sulfate ions remain unchanged.

TABLE 12. REPLACEMENT SERIES OF THE COMMON METALS

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

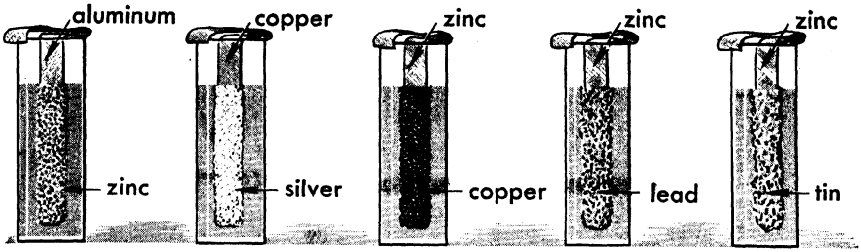


Fig. 85. A strip of metal, placed in a solution of a salt of a metal below it in the replacement series, replaces the less active metal, which precipitates onto the strip.

The only change that takes place, then, is a transfer of two electrons from free iron to ionic copper. Thus it seems that iron has a greater tendency than copper to lose electrons. That is, iron is more metallic than copper, and hence appears higher up in the replacement series. If we place iron in a solution of calcium chloride, no reaction takes place because the tendency of iron to lose electrons is less than that of calcium.

$$Fe^0 + Ca^{++} + 2Cl^- \rightarrow \text{no reaction}$$

The elements high up in the replacement series are so typically metallic and have such a great tendency to lose electrons, that even light causes them to throw off electrons. This fact is made use of in the *photoelectric cell.* Such a cell is frequently lined with a thin film of potassium, rubidium, or cesium, the most active metal known. When light strikes this film, it throws off electrons, which travel to a positively charged plate in the center of the cell. A very feeble electric current is produced. This feeble current, whose strength depends upon the intensity of the light that strikes the cell, may be amplified and thus made to control larger supplies of energy. This amplified current may close a switch, called a *relay,* which will start a motor and open a door, or count people going through a passage.

The photoelectric cell is a vital part of sound-motion-picture and television equipment, and it is used also in the transmission of pictures by wire. Photoelectric cells are used in controlling the "blow" of Bessemer converters in making steel.

Selenium, an element belonging to the sulfur family, was used in certain "electric eyes." Selenium is a good electric insulator in the dark, but in light it conducts an electric current to some extent. Later it was replaced by copper covered by a thin film of Cu_2O.

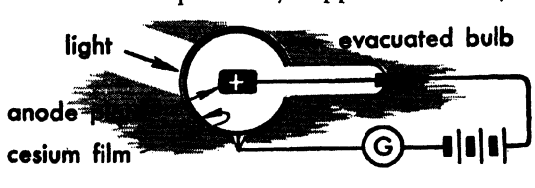
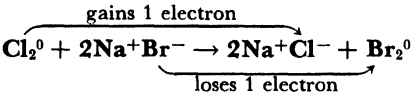


Fig. 86. Construction of a photoelectric cell.

The replacement series of the nonmetals. In studying the halogens, we learned that they, too, could be arranged according to their ability to replace one another from solutions of their salts. Thus, when chlorine is added to a solution of sodium bromide, bromine is liberated and sodium chloride is formed. According to the electron theory, this reaction is explained as follows:

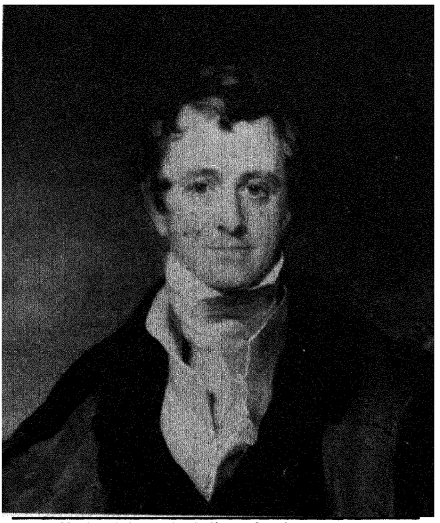


Chlorine is more typically a nonmetal than is bromine. Therefore, it has a greater tendency to gain electrons. Free chlorine, which is neutral, takes one electron from the bromine ion and changes to Cl^-, that is, it goes into solution. The bromine ion, on the other hand, after losing one electron, becomes electrically neutral, changes to the atomic form, joins with another atom of bromine, and is liberated as a free bromine molecule. Other nonmetals also may be grouped in a series according to their replacement powers.

The replacement series of the metals is a useful tool. Understanding the replacement series of the metals is of great value in studying these elements. Those above iron in the series are so very active that they are never found free, while those below iron occur both in the free state and chemically combined. As we go down the series, the tendency of the metal to lose electrons diminishes, and hence the tendency to oxidize and to react with water or acids diminishes also. Thus gold and platinum, which are at the bottom of the list, do not oxidize in air even when hot, and are not attacked by water or even by any one acid. Therefore, knowing the position of a metal in this series, you can predict fairly well its chemical properties.

Why hydrogen is included in the replacement series of the metals. Hydrogen, which from its physical properties could never be considered a metal, belongs in the replacement series because its ion is usually positively charged and behaves chemically as a metal. All metals above hydrogen in the replacement series liberate hydrogen from acids. Those metals below hydrogen require oxidizing acids to dissolve them and liberate gases other than hydrogen from these oxidizing acids. For example, when copper reacts with nitric acid, nitrogen dioxide is given off.

Humphry Davy isolates potassium and sodium. At the head of the replacement list of the metals are the *alkali metals,* lithium,



National Portrait Gallery, London

Sir Humphry Davy (1778–1829), the son of a poor wood carver, was born at Penzance, Cornwall. The poet, Samuel Coleridge, declared that if Davy "had not been the first chemist, he would have been the first poet of his age."

potassium, and sodium. Two of these elements had been known for a long time as part of the alkaline compounds, potash and soda, before they were isolated in a pure state. The alkali metals were originally found in the ashes of certain plants. The name was taken from the Arabic *al,* meaning *the,* and *quili,* meaning *ashes.*

Because of the extreme activity of these metals, many unsuccessful attempts had been made to isolate them. After the discovery, in 1800, of the galvanic current and the invention of the electric battery which soon followed, scientists used this new force in an effort to isolate sodium and potassium.

Humphry Davy, an eminent English chemist, rose from humble beginnings to knighthood. He was the first to prove chlorine an element and, incidentally, he was versatile enough to spend his leisure hours writing fairly good poetry. In 1807 he sent the energy of 150 electric cells through molten potassium hydroxide. At the negative platinum electrode, Davy saw globules of a silvery substance form, and then spontaneously catch fire. "His joy knew no bounds, he began to dance, and it was some time before he could control himself to continue his experiments."

London received Davy's isolation of potassium as another wonder of the world, and he was lionized. Some people paid 100 dollars to attend his lectures on chemistry. Soon afterward, Davy obtained free sodium in the same way, and lithium from fused LiCl.

How sodium is prepared for industrial use. The most recent method of obtaining sodium in large amounts differs somewhat from the method originally used by Davy. An electric current is sent through melted sodium chloride in a cell, such as is shown in Fig.

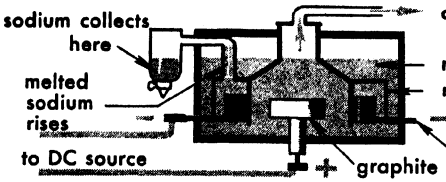


Fig. 87. Downs cell for the preparation of sodium. The cell was invented in 1924 by J. C. Downs, an American chemist.

87. Sodium ions travel to the iron or copper cathode, gain electrons, become sodium atoms, and collect as a mass of metallic sodium, which is drawn off from time to time. Chlorine ions travel to the graphite anode, lose electrons, and become gaseous chlorine, which leaves the apparatus as shown. This entire process is continuous. Potassium and lithium may be prepared in this same way using melted potassium chloride and lithium chloride.

Physical properties of potassium and sodium. Sodium is a soft, silvery metal that melts just below the boiling point of water. Potassium, which is also soft and silvery white, melts at an even lower temperature. They are both lighter than water. Strangely enough, these two solids when mixed form a liquid alloy at ordinary temperatures.

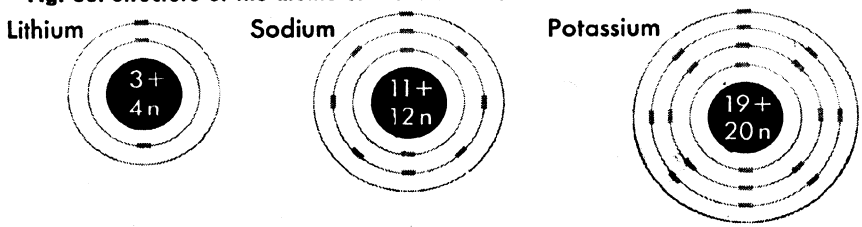
Some chemical properties of sodium and potassium. The electron pictures of lithium, sodium, and potassium are shown in Fig. 88.

From these pictures we can tell that the valence of each of these elements is one. Each reacts with nonmetals, forming salts, and, on exposure to the oxygen of the air, each is quickly tarnished with a coating of its oxide.

Since sodium has only one electron to lend, and oxygen must borrow two electrons to complete its outer ring, two sodium atoms combine with one atom of oxygen, and the oxide of sodium is, therefore, Na_2O. Sodium peroxide, Na_2O_2, (Na — O — O — Na), is formed when sodium is heated in air free from carbon dioxide. Because of its extreme activity, sodium cannot be kept exposed to air or under water. It is usually stored under kerosene, because kerosene contains no oxygen. At high temperatures both sodium and lithium combine with hydrogen to form hydrides which react with water liberating hydrogen.

$$LiH + H_2O \rightarrow LiOH + H_2\uparrow$$

Fig. 88. Structure of the atoms of the alkali metals.



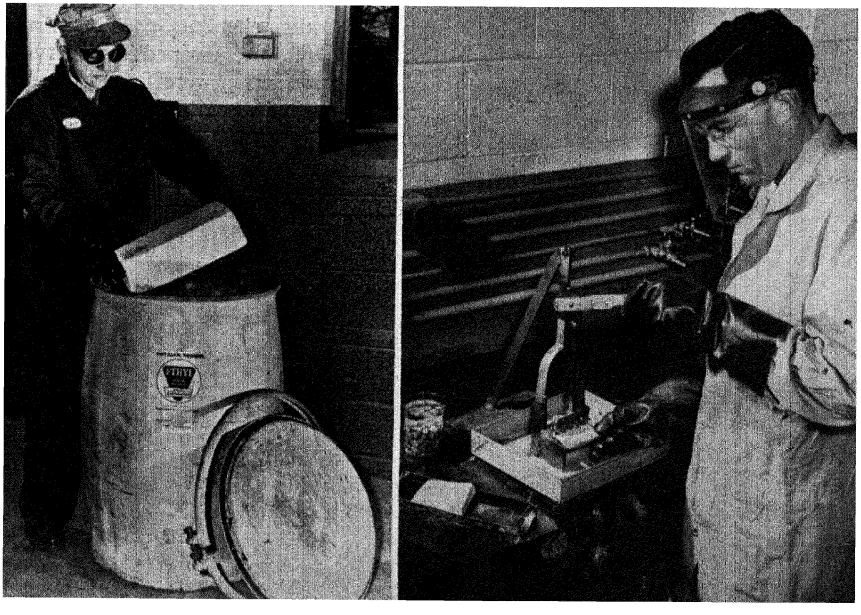
What has been said about the chemical activity of sodium applies also to other alkali metals, namely, potassium, lithium, cesium, and rubidium.

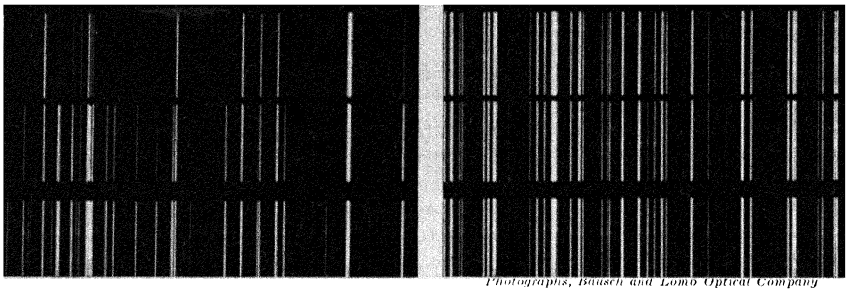
How the alkali metals are used. In a recent year 150,000 tons of sodium metal were used in the manufacture of several compounds, such as sodium peroxide, sodium cyanide, sodamide ($NaNH_2$) used in making indigo, sodium hydride (NaH) used as a reducing agent in removing surface oxides from steel, and several detergents. A sodium-lead alloy is used in the manufacture of tetraethyl lead. Liquid sodium, because it is an excellent heat conductor, is employed as a coolant in some nuclear reactors. Sodium is also used in the hot cathode sodium vapor lamp, which gives twice as much light as the common filament electric lamp using the same amount of current. This type of lamp is used chiefly in outdoor lighting.

How can we test for the ions of sodium, potassium, and lithium? If a clean platinum wire is dipped into a salt of potassium and then placed in a nonluminous bunsen flame, the flame becomes *violet* in color. The flame of all sodium salts is a distinct *yellow;* that of all lithium salts is *red;* cesium gives a bright *blue* flame. Since the presence of even a trace of a sodium salt will obscure the violet color of potassium, the flame of a potassium salt can frequently be detected only when viewed through a piece of blue cobalt glass, which absorbs yellow light rays.

(left) Removing a sodium brick from a shipping drum. (right) Making sodium pellets for laboratory use. Note the protective equipment in each case.

Ethyl Corporation





Photographs, Bausch and Lomb Optical Company

The bright line spectrum of lubricating oil (left) and of low-grade coal.

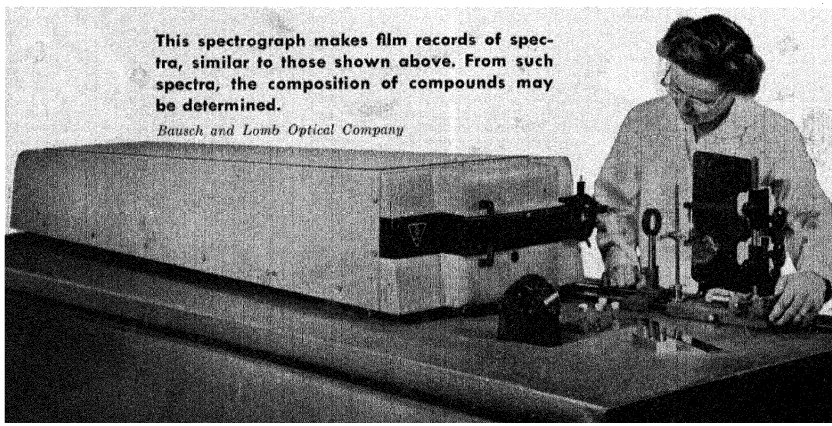
Such *flame tests* are used on other metals besides the alkali metals. Thus, heated copper imparts a *green* color to the flame, and calcium gives the flame an *orange-red* coloration.

How is a spectroscope used? In 1854, David Alter, a Pennsylvania physician, described a method of detecting an element by the color that it imparts to a flame. He also predicted the use of this method in determining the presence of elements in the sun.

Five years later, Bunsen and Kirchhoff (kĭrk'hôf) devised an instrument called the *spectroscope,* which has since become a very powerful tool in the hands of chemists, physicists, and astronomers. In 1860, with the aid of this instrument, two new elements, cesium and rubidium, were detected by Bunsen in a few grams of salt obtained by the evaporation of 40 tons of spring water.

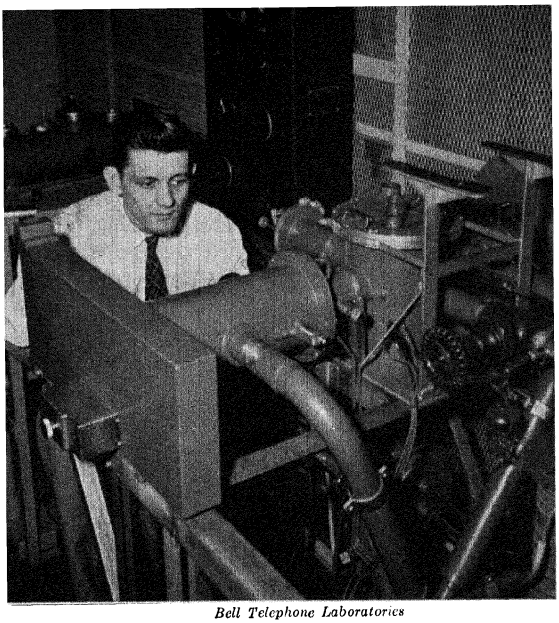
Nine years later, the element helium was discovered with the aid of the spectroscope by Janssen and Lockyer independently. Helium was found not on the earth, but in the sun, more than 90 million miles away. Before the close of the century, this new element was found on our own planet by Ramsay.

With the aid of the spectroscope, other elements, present in such minute quantities that they had heretofore escaped discovery by even the most delicate instruments of science, were finally brought to light. Today, the spectroscope is used also in the study of the complex structure of the atom.



This spectrograph makes film records of spectra, similar to those shown above. From such spectra, the composition of compounds may be determined.

Bausch and Lomb Optical Company



An analytical chemist using electron diffraction equipment to identify crystalline material such as nickel oxide. Beams of electrons aimed at the sample break into a pattern which is made visible by the equipment.

Bell Telephone Laboratories

The principle of the spectroscope. To understand the principle of the spectroscope, we must understand a few things about light. Isaac Newton, in 1672, performed a classic experiment. He let a beam of sunlight pass through a narrow slit into a dark room and placed a glass prism in its path. A band of colors called the *spectrum* was formed. This can be explained by remembering that light is a form of energy which is transmitted by waves.

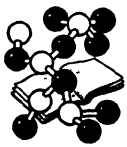
Sunlight is made up of light of various colors. Each color has a different wave-length. Red has the longest wave-length (0.000068 cm.), and violet has the shortest wave-length (0.000040 cm.). The glass prism bent and split up, or *refracted,* the sunlight. The light which was refracted, or bent, least was the red, and that which was refracted most was the violet. Study the spectrum shown in the illustration in color following page 382.

Though some self-luminous sources, such as the sun, have a *continuous spectrum,* as shown in the illustration, an incandescent vapor or gas, such as heated sodium vapor or electrified neon gas, has a discontinuous, or *bright-line,* spectrum. The glowing vapor of each element has its own characteristic colored band of light. Thus, sodium vapor has one bright yellow line, lithium has one red and one yellow line, and the vapor of iron has several hundred lines.

The spectroscope, the most essential part of which is a glass prism, makes possible the quick analysis of incandescent vapors, and the detection of the smallest trace of an element. Less than a millionth

of a milligram of sodium, and minute traces of poisons in blood can be detected by *spectroscopic analysis.* A spectroscope is thus a most useful tool to the chemists who specialize in the analysis of many kinds of substances. Such specialists are called *analytical chemists.*

Spectroscopic work of great precision is carried on today by means of the *spectrograph.* This instrument differs from an ordinary spectroscope in that the observing telescope is replaced by a camera, which makes a photographic record of the spectrum under examination. This permanent photographic record makes possible a more careful analysis of the spectrum. Spectographic analysis is used in steel and other alloys and compares favorably with the usual routine quantitative analysis. Analysis of matter by the study of spectra is called *spectrum analysis.* Because chemical manipulations are unnecessary, all measurements may be made quickly.

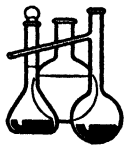


YOU WILL ENJOY READING

Chemistry, Jan., 1945, pp. 37–43, and May, 1952. Published by Science Service, Washington, D.C. Contain the original papers describing the discovery of lithium, sodium, potassium, cesium, and rubidium, and more information on the other elements.

Mills, John. *Electronics: Today and Tomorrow,* pp. 84–94. D. Van Nostrand Co., New York, 1944. Tells the story of the photoelectric cell.

Pough, Frederick H. *A Field Guide to Rocks and Minerals.* Houghton Mifflin Co., Boston, 1953. An excellent book for the boy or girl interested in mineral-collecting as a hobby. Attractively illustrated.



USEFUL IDEAS DEVELOPED

1. A metal is an element that lends electrons. It has a positive valence, and its oxide is a basic anhydride.

2. An ore is a mineral from which an element may be profitably extracted.

3. Ore-dressing is the separation of a mineral from the valueless rock, or gangue, with which it is mixed.

4. Metallurgy is the process of extracting a metal from its ore. The four chief metallurgical processes are (1) electrolysis, (2) reduction by means of carbon, (3) roasting, or heating,

the ore to change it to its oxide, and (4) aluminothermy, using aluminum powder.

5. Metals have certain characteristic physical properties. A metal is (1) lustrous, (2) malleable, (3) ductile, (4) a good conductor of heat, (5) a good conductor of electricity, (6) a solid – mercury is an exception, (7) crystalline, and (8) variable tensile strength.

6. Metals have certain characteristic chemical properties. Some (1) unite with oyxgen, forming oxides which are basic anhydrides, (2) unite with water, forming either bases or oxides with the liberation of hydrogen, (3) decompose acids, liberating either hydrogen or some other gas, (4) combine with nonmetals, forming salts, and (5) unite with bases, liberating hydrogen.

7. Metals may be so arranged in a replacement series that each metal in the list will replace each metal below it from a solution of its salt. According to the electron theory, this behavior is explained by the fact that the metals at the top of the list lose electrons more easily than those at the bottom, and hence go into solution more readily. The metals lower on the list take these lost electrons, become electrically neutral, and precipitate out as free metals.

8. Some nonmetals, such as the halogens, may also be arranged in a replacement series. According to the electron theory, chlorine has a greater tendency to borrow electrons than the other halogens and, hence, borrows electrons from those below it in the series.

9. The flame test for identifying a metal consists of heating a metal or one of its salts in a flame and noticing the color that it imparts to the flame

10. The spectroscope is an instrument devised by Bunsen and Kirchhoff. It is used to detect minute traces of elements in incandescent vapors. The most essential part of a spectroscope is a glass prism, which disperses or breaks up the light into colored lines which are characteristic for each element.

11. Spectrum analysis has been used in detecting the presence of rare elements, such as the inert gases of the atmosphere. It is also used in the study of the structure of the atom.



USING WHAT YOU HAVE LEARNED

Group A

1. According to the electron theory, how do metals differ from nonmetals?

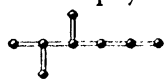
2. What are four typical nonmetals and four typical metals?

3. (a) Name a few metals that occur free. (b) Compare their chemical activity with the chemical activity of metals found combined.

4. (a) In what way does a mineral differ from an ore? (b) Give an example of each. (c) Do minerals ever become ores? (d) Illustrate.

5. (a) What are the four most general methods used in metallurgy? (b) Give an example of an element extracted by each of these methods.

6. What are the characteristic physical properties of metals?



7. (a) Arrange these eight metals in a replacement series: Zn, H, Cu, Na, K, Pt, Au, and Pb. (b) On your list, check those that will replace the hydrogen of dilute HCl.

8. Arrange the number of each metal opposite the letter of the property of which it is an outstanding example.

a) Best conductor of electricity	1) Cu
b) Extremely ductile	2) Au
c) Most malleable of all	3) Li
d) Lightest metal	4) Hg
e) Heaviest metal	5) W
f) Liquid metal	6) Os
g) Extremely high melting point	7) Ag
h) Reddish luster	8) Pt
	9) Na

9. (a) Write five equations illustrating five chemical properties of metals. (b) In each case state the property.

10. According to the electron theory, why does an iron nail become coated with Cu when placed in a solution of $CuSO_4$?

11. In which of the following would a replacement reaction take place? Complete the equations for such replacements.

a) $Zn + Hg(NO_3)_2 \rightarrow$	e) $Cu + AgNO_3 \rightarrow$
b) $Zn + CuSO_4 \rightarrow$	f) $Cu + ZnSO_4 \rightarrow$
c) $Zn + AgNO_3 \rightarrow$	g) $Cu + Hg(NO_3)_2 \rightarrow$
d) $Zn + Pb(NO_3)_2 \rightarrow$	h) $Cu + Pb(NO_3)_2 \rightarrow$

12. Arrange a replacement series of some nonmetals you have studied.

13. According to the electron theory, explain why Br_2 liberates free I_2 from a solution of KI.

14. An element *X* is not found free. It attacks warm water, liberating H_2, and tarnishes readily in air. Where would you place it in the replacement list of metals? See Table 12.

15. (a) What are two elements other than Na that belong to the sodium family? (b) Why are they called *alkali metals*?



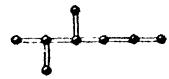
16. (a) How and by whom were Na and K first isolated? (b) How was the news of this achievement received?

17. (a) What are three ways in which Na is similar to K? (b) one way in which it is different?

18. By a diagram, show the present method of obtaining free Na.

19. Make a diagram of the atom of Li, and, from this diagram, state its (a) valence, (b) chemical activity, and (c) atomic number.

20. Using an equation, describe the action of Na on H_2O.



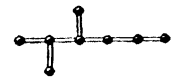
21. What weight of NaOH must be decomposed to produce 69 g. of pure Na?

22. A piece of Na is placed in H_2O, and 336 ml. of H_2 are collected. What weight of Na took part in this chemical change?

23. Which will require more H_2O in dissolving completely: 45 g. of Na or 79 g. of K?

24. Copy and complete. Do not write in this book. Na is stored under .... When Na is exposed to air, the formula of the compound formed is .... Na is used as a catalyst in the preparation of .... An instrument that makes use of the ease with which Cs loses electrons is the .... The color imparted to a flame by K vapor is ..., Li a ... color, and Na a ... color.

25. (a) List four uses of sodium, and (b) three uses of other alkali metals.



26. How is the spectroscope used in astronomy?

27. Name three elements discovered by means of the spectroscope.

28. How can the spectrum of sunlight be obtained?

29. What is the difference in the appearance of the spectrum of a luminous solid and the spectrum of an incandescent vapor?

30. Hydrogen is included in the replacement series of the metals. Why?

Group B

31. Zn appears higher than Fe in the replacement series. What is the reason for coating Fe with Zn to prevent corrosion?

32. Devise an experiment for obtaining Cu from $CuSO_4$ solution.

33. Na and K kept under kerosene for some time lose their silvery luster. Explain.

34. Discuss the use of spectroscopy in crime detection.



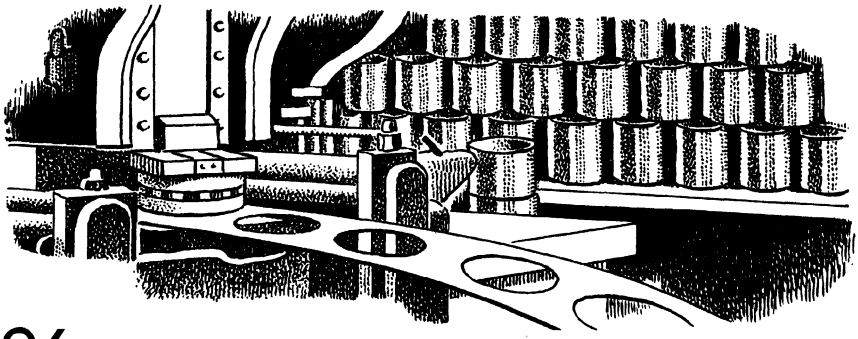
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Purchase or borrow a photoelectric cell and connect it in such a way that, when a flashlight is directed against it, a bell will ring. Explain its action to the class. What use would you make of a photoelectric cell?

2. Make your own replacement series of some or all of the following metals: aluminum, copper, chromium, lead, tin, zinc, and calcium (if you can obtain a small piece from your teacher). Use whatever suitable chemicals you can find around the house such as vinegar. Report your results.

3. Prepare an illustrated ten-minute talk on mineral-collecting as a hobby. Bring some of your specimens to class.

4. Write a 300–500 word essay on one of the various analytical methods used by chemists today such as (a) wet method, (b) spectrophotometry, (c) chromatography, (d) tracer technique.



26 ALUMINUM: MOST COMMON OF LIGHT METALS

. . . I believe I speak for the vast majority of all scientific men. Our object is not to make jobs and dividends. These are a means to an end, merely incidental. We wish to abolish drudgery, discomfort, and want from the lives of men, and bring them pleasure, comfort, leisure and beauty. Harold C. Urey, 1934

The world receives a valuable gift. In 1825, Hans Christian Oersted (ûr'stĕth), a Danish scientist, announced that he had isolated aluminum by gently heating aluminum chloride and potassium amalgam. In 1827 Woehler repeated Oersted's experiments without success. Woehler finally obtained aluminum by substituting metallic potassium for the potassium amalgam used by Oersted.

One of the first of Woehler's American students in Germany was Professor Jewett, of Oberlin College. He brought back to America the story of Woehler's isolation of that extremely light, silvery metal, aluminum. Jewett was fond of talking to his classes of this strange metal, which no one had as yet been able to obtain inexpensively in spite of its great abundance in minerals.

One day, as Professor Jewett spoke of the fortune that awaited the man who was able to develop a simple method for extracting aluminum, one of the students nudged his young classmate, Charles Martin Hall. Chemistry had captivated Hall, and his classmates had known him to make all sorts of experiments, hoping to make a great discovery some day. Here was his chance. His response to that nudge was, "I am going after that metal," and Hall went to work at once in his father's woodshed.

Hall attacked his problem scientifically. He knew that only the most active metals, such as sodium and potassium, were reducing agents strong enough to liberate aluminum from aluminum chloride.

$$AlCl_3 + 3K \rightarrow 3KCl + Al$$

Potassium had been used in the method developed by Oersted and used later by Woehler, and sodium had been substituted for potassium by the French chemist, Henri Sainte-Claire Deville (săNt-klâr′ dē-vēl′). But both potassium and sodium were too expensive to use in a commercial method. Hall finally discarded all methods that depended upon the action of a reducing agent and turned to electrolysis, in spite of his knowledge that Davy, who had isolated the alkali metals by electrolysis, had failed to get pure aluminum in this way.

Aluminum oxide, called *alumina*, was the natural starting point. Alumina in hydrated form is the chief component of *bauxite*, the richest ore of aluminum. But alumina has an extremely high melting point. To melt alumina was commercially impracticable. But if an electric current was to liberate free aluminum from it, alumina had to be either melted or dissolved. Perhaps (the thought came to Hall in one of those flashes of genius) some mineral that would act as a solvent for aluminum oxide might be found. After trying a number of minerals, he came across a milky-white, glassy solid called *cryolite*. He melted this with some difficulty and then threw in some alumina. The alumina dissolved readily. He passed a current through the solution of alumina in cryolite and, to his intense joy, found that metallic aluminum was deposited at the cathode.

On February 23, 1886, he burst excitedly into the laboratory of Professor Jewett and, holding a few aluminum "buttons," exclaimed,

Aluminum Company of America



Charles Martin Hall, the discoverer of the electrolytic process of producing aluminum.

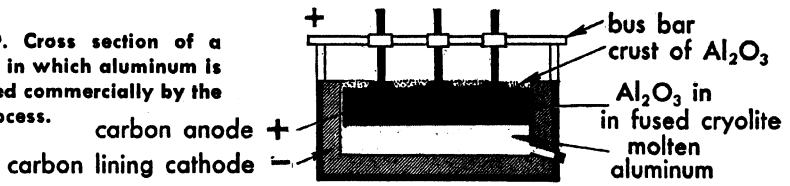


Fig. 89. Cross section of a furnace in which aluminum is produced commercially by the Hall process.

"I've got it!" Hall soon obtained a patent on his process and two years later the Pittsburgh Reduction Company, which later became the Aluminum Company of America, was founded. In 1914 Hall died, world-famous and a multimillionaire. He left most of his fortune to Oberlin College and other educational institutions.

Discoveries often result from social needs. Hall was 22 when he produced aluminum. Exactly two months after Hall had handed his teacher the first samples of his aluminum, another chemist, Paul Heroult (ā-rōōlt'), also 22 years of age, applied for a patent in France on an identical commercial method of preparing aluminum.

This is not a rare example of simultaneous discoveries in the history of science. Advances in science often are made in different parts of the world at almost the same time. They are frequently the final step in a long series of experiments conducted by many research workers in widely separated laboratories. The scientist who is fortunate enough to publish his discovery first is recognized as the hero of a battle in which many other soldiers have been engaged. The heroes of science, on the whole, concede this element of good fortune. Can you think of another such instance in the story of scientific advance?

Metallurgy of aluminum by the Hall process. Hall's process is still in use. The electric furnace used is an open cell about 25 to 30 feet long, lined with carbon, which constitutes the cathode. Powdered cryolite mined in Greenland or made synthetically is placed in the cell, and as the current passes through it, it melts. Aluminium oxide, or alumina, is a white powder obtained by refining bauxite ore. It is added to the molten cryolite and immediately dissolves. The aluminum oxide dissociates, forming positive aluminum ions and negative oxygen ions.

$$Al_2O_3 \rightarrow 2Al^{+++} + 3O^{--}$$

Carbon rods are suspended in the molten aluminum oxide solution and act as the anode. When the circuit is closed, the aluminum ions travel to the cathode, where they obtain electrons which change them from aluminum ions to free aluminum. This free molten aluminum then settles to the bottom of the cell. Later, a hole at the

bottom of the cell is unplugged, and the molten aluminum is tapped off into large ladles and cast in molds, in which it solidifies as *pig aluminum*. The oxygen ions, in the meantime, have traveled to the anode, given up their electrons, and changed to free oxygen. This oxygen combines with the carbon of the anode and forms carbon dioxide, given off as a gas.

$$C + O_2 \rightarrow CO_2 \uparrow$$

The process is continuous. Aluminum oxide is added, aluminum is removed, and the carbon anodes are replaced from time to time. The original cryolite, Na_3AlF_6, though it contains aluminum, does not decompose. It acts only as a solvent. Many of these electrolytic cells are joined in series. Commercial cells produce about 500 pounds of 99+ percent pure aluminum per day.

Bauxite, found in large amounts in Surinam (Dutch Guiana), and British Guiana — Arkansas leads the United States in the production of this ore — contains a fair percentage of the oxides of iron, silicon, and titanium. If these impurities are not removed before the bauxite is added in the electric furnace, the aluminum produced is impure.

After the aluminum is drawn from the electrolytic cells, the pig metal is remelted so that the nonmetallic impurities may be skimmed off. If aluminum alloys, rather than pure aluminum, are desired, the alloying may be done during the remelting. The chief alloying elements include copper, magnesium, manganese, silicon, zinc, iron, nickel, and chromium.

The physical properties of aluminum. Aluminum is silvery white in color and is one of the lightest of the common metals. It is only one-third as heavy as iron. It is very malleable and ductile and compares well with both silver and copper in the ease with which it conducts both heat and electricity. It can be worked readily; that is, it can be cast, rolled, forged, extruded, machined, or drawn. Parts can be joined by welding, brazing, and riveting.

The chemical properties of aluminum. The atomic weight of alumium is 27. Its atomic number is 13; hence it has only three electrons in its outside ring. It is, therefore, a metal with a valence of plus three. Aluminum is an amphoteric element and may act as either an acid or a base. It is attacked by strong bases as follows:

$$2Al + 2NaOH + 2H_2O \rightarrow 3H_2 \uparrow + 2NaAlO_2 \text{ (sodium aluminate)}$$

This sodium aluminate is the salt of aluminic acid, H_3AlO_3. Because of the reaction between aluminum and the strong bases, or

substances with basic reactions, such as washing soda, care should be taken not to heat such substances in aluminumware.

Aluminum is attacked by nearly all acids, forming aluminum salts.

$$2Al + 6HCl \rightarrow 3H_2 \uparrow + 2AlCl_3$$

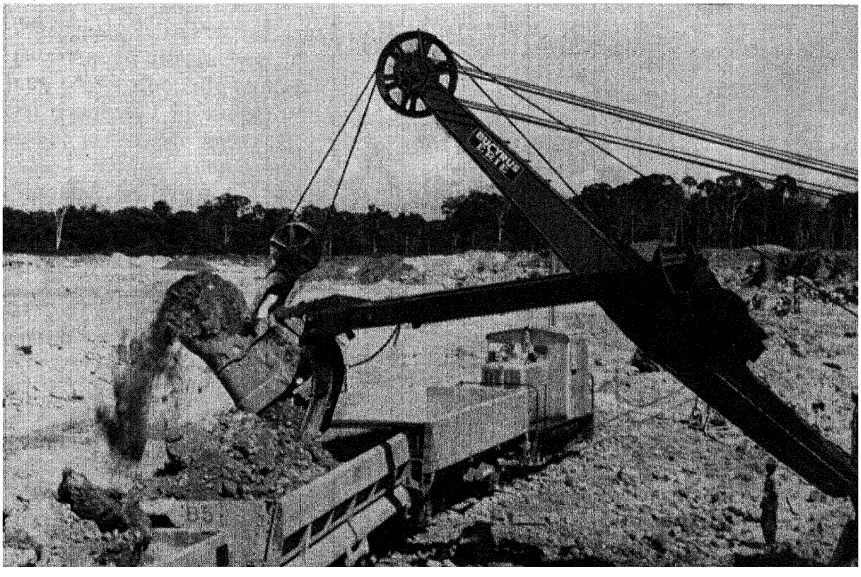
The surface of aluminum oxidizes rapidly in air, forming aluminum oxide, Al_2O_3. This extremely thin, transparent, but tough film acts as an excellent protective coating and, unlike iron rust, adheres firmly to the surface of the metal, thus preventing further oxidation unless the coating is perforated. *Alclad* is a sheet of aluminum alloy such as duralumin covered with a layer of aluminum. It resists corrosion very well.

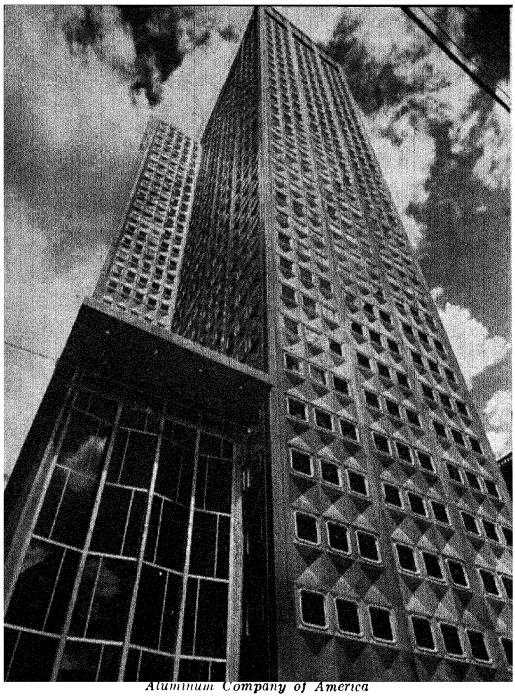
Tremendous growth of the aluminum industry. Before the Hall process was introduced, aluminum was not used widely, because of the great cost of preparing it. It is a far cry from the world production of two tons of aluminum in 1859 at 17 dollars per pound to the more than one million tons of this metal produced in the United States and Canada alone in a recent year at about 20 cents a pound.

The Hall process gives *primary aluminum,* that is, metal produced directly from an ore or ores. But a significant and perhaps increasing source of aluminum, and other metals as well, lies in *secondary sources,* that is, sources from which a metal is recoverable from one use for reuse in another. *Secondary or scrap aluminum* is a very large source of pure aluminum. Production of metals from

Surface mining of bauxite in Surinam. Over-lying earth is first removed. The exposed ore is then loosened by blasting and loaded into the mine cars.

Aluminum Company of America





Aluminum Company of America

An "aluminum skyscraper" in Pittsburgh, Pa. This 30-story building is constructed of aluminum panels mounted on a steel framework. The ceilings, wiring, ventilation ducts, doors, hardware and most of the plumbing are made of aluminum.

secondary sources is one phase of an intelligent metals conservation program. Such a program can do much to conserve natural resources.

By far the largest users of aluminum are the transportation industries. Great quantities of the "metal with wings" are used in the construction of airplanes, streetcars, railroad cars, locomotives, steamships, motorships, automobiles, trucks, buses, bicycles, and motorcycles.

Through decreasing the weight of such carriers as airplanes, railroad cars, and trucks, payload and, thereby, revenue can be increased. At the same time, if the reduction in weight applies only to the total gross weight of the vehicle, as in an automobile or bus, much less energy is required to attain and maintain speed, much less energy is lost in stopping, and operating costs are thereby reduced.

Electricity and aluminum. The electric industries use thousands of tons of aluminum yearly in lines for the transmission of electricity over long distances. For this purpose, aluminum cable with a steel reinforcing core is used instead of copper. Since aluminum is lighter than copper, fewer towers are required to support the cables. More than 1.5 million miles of aluminum transmission cables carry electricity to almost all parts of this nation. Aluminum is used also in the production of parts for electric equipment of many kinds, such as

vacuum cleaners and various household appliances, and particularly in parts for radios and other electronic equipment.

Aluminum in the kitchen. One use of aluminum goes back to 1890, when the first aluminum cooking utensils were produced. Since aluminum is an excellent conductor of heat, and at the same time is very light, aluminum cooking utensils are very popular.

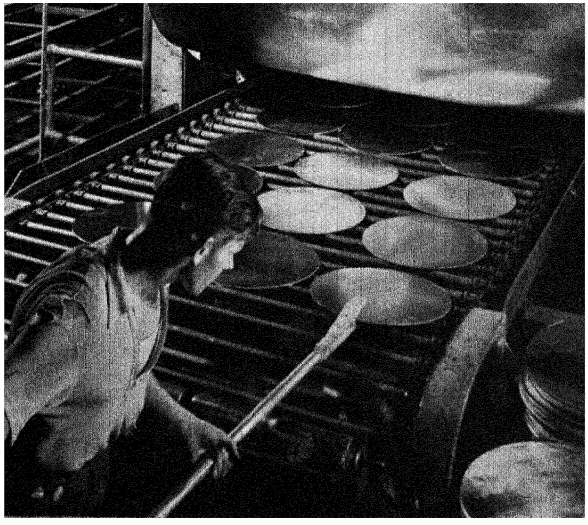
Certain alkaline foods and waters heated in aluminum may produce a superficial discoloration, which is harmless and readily removed by a mild abrasive cleaner. Do not permit all the cooking liquid in a lightweight aluminum utensil to boil off, for if this occurs, a hole may be "burned" in the bottom of the utensil as a result of the relatively low melting point of aluminum.

Because strong alkalies attack the protective coating of aluminum oxide that forms on the surface of aluminum as well as the aluminum itself, cooking utensils made of the metal should not be scrubbed or polished with harsh alkali cleaners. To clean aluminum utensils use soap and water or mild abrasive cleansers only.

Other uses of aluminum. In the packaging of foods and other commodities, aluminum foil has almost entirely replaced tin foil. Candy bars, chewing gum, cream cheese, camera film, and countless other articles go to market in shining dress. Aluminum foil coated with a plastic film is suitable for the packaging of almost any kind of food. Aluminum leaf is used in photoflash lamps.

Collapsible tubes made of aluminum carry such items as shaving cream, tooth paste, and cosmetics, while vital serums and various other pharmaceutical preparations are packed in glass bottles with aluminum seals. Aluminum paints are widely used for protecting both wood and metal. Aluminum foil is used for home insulation.

Aluminum Company of America



Circular aluminum blanks being removed from the conveyor of an annealing furnace. These blanks will be used in the manufacture of cooking utensils.

Much furniture and many decorative articles for the household are made of aluminum.

The buildings of Rockefeller Center in New York contain more than 1000 tons of aluminum in the vertical panels between windows. In the finishing of steel, large quantities of aluminum are used in removing oxides from the molten steel. The largest use of aluminum is in the form of alloys of much greater strength than pure aluminum.

Thermit is used in welding. Attempts to reduce aluminum oxide with carbon failed because of the great attraction of aluminum for oxygen. Aluminum is a powerful reducing agent, especially when it is in the form of a fine powder. Because a powder has a much greater reacting surface than a solid, a powder makes possible a more intense chemical reaction than the same weight of the same solid in larger pieces.

When a mixture of powdered aluminum and iron oxide is ignited by means of a fuse, such as a strip of magnesium ribbon, a chemical reaction takes place at once in which the aluminum takes the oxygen away from the iron oxide, leaving a residue of pure iron.

$$8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$$

The heat of this reaction is so great that the iron formed is molten. This mixture of aluminum and iron oxide, known as *thermit,* is used in welding broken propeller shafts, rudder frames, locomotive parts, and in situations where repairs must be made on the spot. It is also used in one type of incendiary bomb.

The metals chromium and manganese (and wolfram, vanadium, molybdenum, silicon and boron) may be extracted from their oxides or ores by aluminothermy, an aluminum reduction similar to the thermit reaction. The equations for the reduction of chromium and manganese ore are:

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$
$$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$$

This is a common way of manufacturing or producing such metals.

What are alums? When potassium sulfate is dissolved in a solution of aluminum sulfate, the two salts combine and crystallize out as potassium aluminum sulfate.

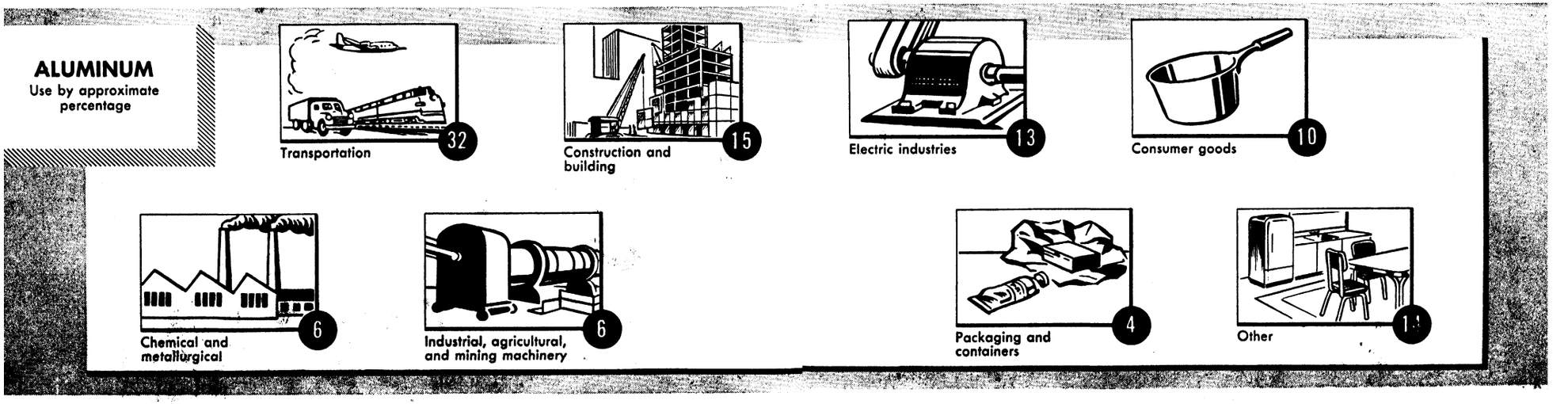
$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow 2KAl(SO_4)_2 \cdot 12H_2O$$

This compound is called *common alum.* It is one of a group of salts, called the *alums,* which resemble one another in the eight-sided form of their crystals, in their solubility in water, and in their type formula. The type formula of an alum is $XY(SO_4)_2 \cdot 12H_2O$. In it X may be K, Na, or NH_4, and Y may be a trivalent element, such as Al, Fe, or Cr. An alum is a *double salt,* that is, a salt containing two metals and one acid radical.

Common alum has a sweetish taste and is used in "Foamite," mordanting (see page 605), and water purification. Alum is used also in making alum baking powder and as an *astringent,* a substance that contracts skin tissues. It is used in the sizing of paper. Chrome alum is used in the *tanning* of leather, during which skins or hides are made softer, and more resistant to the action of bacteria.

Aluminum hydroxide, its preparation and properties. When any soluble aluminum salt is added to water or to ammonium hydroxide, aluminum hydroxide, a white, gelatinous precipitate, may be formed. The aluminum salt is said to hydrolyze, since, as in the case of the solution of aluminum chloride in water, an acid and a base are formed.

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3\downarrow + 3(NH_4)_2SO_4$$
$$AlCl_3 + 3H_2O \rightarrow 3HCl + Al(OH)_3\downarrow$$



Aluminum hydroxide may act either as an acid or as a base. When it comes in contact with a base, it acts as a weak acid and combines with the base.

$$H_3AlO_3 + NaOH \rightarrow NaAlO_2 \text{ (sodium aluminate)} + 2H_2O$$

$AlCl_3$ is the active constituent, about 15 percent, of many body *deodorants* and *antiperspirants.*

Aluminum sulfate in the purification of water. As you know, aluminum sulfate, when it is added to water, hydrolyzes, forming jelly-like aluminum hydroxide.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 3H_2SO_4$$

This aluminum hydroxide gradually settles to the bottom and carries down with it any particles that are floating in the water, including bacteria, industrial wastes, and fine clay. This process, used in the purification of water, is called *coagulation* and is the first step in clearing water of its turbidity. Coagulation does not remove *dissolved* impurities.

Ferrous sulfate is sometimes used instead of aluminum sulfate, because it also forms a gelatinous precipitate, ferrous hydroxide, in water. But ferrous hydroxide rapidly oxidizes to ferric hydroxide, which is also gelatinous. Hence, it is the ferric hydroxide that actually reduces the turbidity, or clarifies the water.

$$FeSO_4 + 2H_2O \rightarrow H_2SO_4 + Fe(OH)_2\downarrow \text{ (ferrous hydroxide)}$$

Aluminum oxide — ore, gem, abrasive, refractory. When aluminum hydroxide is heated, it forms a white, insoluble oxide of aluminum, which melts above 3600°F.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

As hydrated oxides, $Al_2O_3 \cdot 3H_2O$ and $Al_2O_3 \cdot H_2O$ are found widely distributed in the aluminum ore, bauxite. The precious gem stones *ruby* and *sapphire* are composed of alumina, colored by the presence of small amounts of metal oxides. Successful methods have been developed to prepare synthetic rubies and sapphires by melting pure aluminum oxide in the heat of an oxyhydrogen flame. These synthetic stones cannot easily be distinguished from natural gems.

The production of synthetic rubies and sapphires is increasingly important, for they are used as bearings in watches, electric indicators, sensitive electric relays, and in thousands of other kinds of precision instruments.

Emery is a natural aluminum oxide, which is extremely hard and can be used as an abrasive for grinding, polishing, drilling, and cutting. It is almost as hard as diamond. Fused alumina, for use as an abrasive, is prepared in large quantities by the fusion of alumina in an electric furnace. One trademark for such fused alumina is "Alundum."

Not only is fused alumina a good abrasive, but because of its high melting point, it is an excellent *refractory*. A refractory is a substance which, because it melts at a high temperature and is chemically inert, can be used for furnace linings and in similar installations which must withstand extreme heat. Fused alumina refractories are therefore used in making bricks, spark plugs, crucibles, cements for high-temperature work, and high-temperature thermometers called *pyrometers*. Because alumina is quite inert chemically, it is employed as a catalyst support, and for some laboratory ware such as porous plates used in filtering chemical solutions.

Activated alumina is a highly porous Al_2O_3 which is used to adsorb moisture in air conditioning, and to dry such gases as propane and butane.

Newcomers, the light alloys of aluminum. The American Society for Testing Materials defines an *alloy* as: *A substance consisting of two or more metallic elements or of metallic and nonmetallic elements which are soluble in each other when molten, and which do not separate into distinct layers when solid.* The art of making alloys is very old. One of the oldest alloys is bronze. This alloy gave its name to an era of human progress, the Bronze Age, which began about 2500 B.C., and gave way to the Iron Age some 15 to 20 centuries later.

Alloys are in many cases neither true solutions nor compounds. Whereas, for example, Cu and Au mix in all proportions, others have a limited solubility. Some alloys consist of metals present in almost constant proportions such as $NaZn_{11}$. The properties of an alloy may differ radically from those of the elements that compose it. An alloy is usually harder and more resistant than any of its constituents. For these reasons, alloys are extremely important. By mixing two or more metals, we may obtain an alloy whose properties are immensely more valuable than those of any of its ingredients. For example, the *tensile strength* of many aluminum alloys is greater than that of pure aluminum.

Some of the alloys of aluminum containing copper, manganese, magnesium, or other metals are light, strong, and easily machined. Such alloys make ideal materials for the framework of the wings and

fuselages, and landing gear and propellers of airplanes, and for certain parts of automobiles and railway cars. "Duralumin," was one of the first strong aluminum alloys to be given additional strength by heat treatment. Other alloys, stronger, tougher, and more durable, have largely replaced it.

Some of the modern alloys of aluminum are actually stronger than structural steel, and much lighter. Manufacturers of aluminum alloys call their products by many different names. Aluminum alloys of the Aluminum Company of America are called "Alcoa" alloys, and usually a number indicates the particular "Alcoa" alloy.

Whereas there are about 40 metals in common use, more than 6000 alloys have helped make possible our modern industrial world. If we try to escape from alloys, we escape from civilization. Steel, the most important single alloy of all, is discussed in Chapter 27.

Magnesium, lightweight of the structural metals. Magnesium is one of the metals most commonly alloyed with aluminum. It can also be used for many of the same purposes as aluminum with which it has become competitive.

World War II, with its tremendous military demand for light metals, saw the infant magnesium industry grow from a healthy baby to a full-grown adult almost overnight. Production of magnesium jumped in the five years following 1939 from 3500 tons to a high of nearly 200,000 tons. Volume for volume, magnesium in 1953 at 26.5 cents a pound was less expensive than aluminum selling at 20.9 cents a pound.

Magnesium is a soft, silvery-white metal about 60 percent as heavy as aluminum. In pure form it has little structural strength, but when properly alloyed, the resulting materials have good structural strength. Although the strengths of magnesium alloys are less than those of the heavier structural metals, by using slightly greater thicknesses of the alloys, structural shapes as strong as steel, but with only a fraction of the weight of steel, may be made.

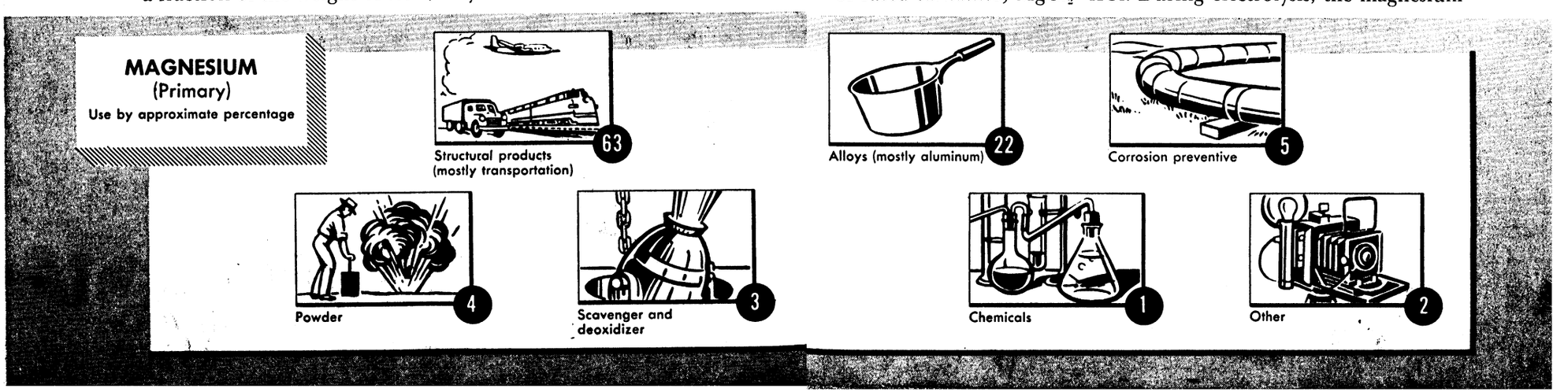
"Dowmetal" is the trademark of a family of magnesium alloys made by the Dow Chemical Company, pioneer producers of magnesium. All "Dowmetals" are composed of magnesium and varying percentages of other metals such as manganese, aluminum, or zinc. The percentages of these metals in the alloys vary with the characteristics desired in the alloy. For example, "Dowmetal A" contains eight percent aluminum and 92 percent magnesium. "Dowmetal G" contains ten percent aluminum, 0.1 percent manganese, and 89.9 percent magnesium. A similar series of magnesium alloys is manufactured by the American Magnesium Corporation. Such alloys are designated by number, for example, "AM3S" or "AM57S." Magnelite, used in kitchenware, contains Al, Mg, and silicon.

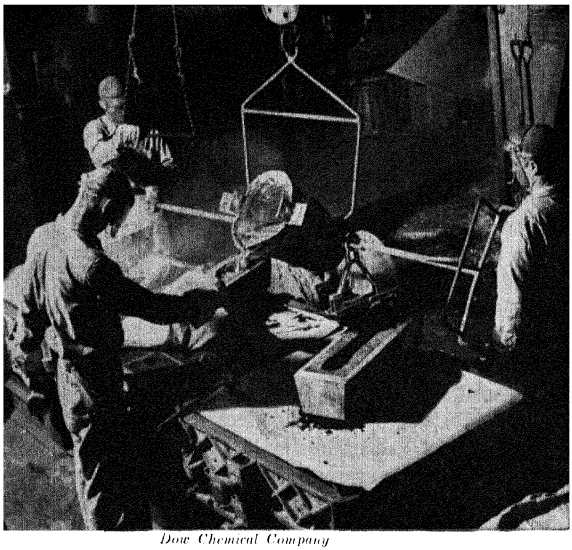
Chemical properties of magnesium. Magnesium is high in the replacement series of metals, but pure magnesium and some of its alloys corrode relatively slowly even in moist air. Like aluminum, magnesium is a self-protecting metal. The protective film is probably a basic carbonate. Powdered magnesium or thin strips of magnesium burn in air when ignited, forming magnesium oxide. Hot magnesium burns in CO_2 to form MgO and C.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

Fused magnesium oxide under the name of "magnorite" is a refractory.

Magnesium from the sea. Magnesium is one of the most abundant industrial metals in the earth's crust. There is an almost unlimited supply of it in the sea, for one cubic mile of sea water contains nine billion pounds of this metal in the form of $MgCl_2$. The brine wells, such as those near Midland, Michigan, are another source of magnesium chloride. Until rather recently, magnesium production in the United States was limited almost completely to the electrolysis of molten magnesium chloride obtained from the sea or salt wells, or of fused *carnallite,* $MgCl_2 \cdot KCl$. During electrolysis, the magnesium



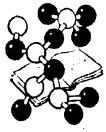


Dow Chemical Company

These workmen are pouring molten magnesium into a mold. Magnesium can be cast, molded, extruded, and worked by many of the common methods of the metals industries.

collects at the cathode, and chlorine at the anode. Magnesium is thus the first structural metal obtained from the sea.

Another source of magnesium is *dolomite,* $MgCO_3 \cdot CaCO_3$, which is very widely distributed throughout the world, forming entire mountain ranges. Magnesium has been obtained from this ore by roasting it to form MgO, and then reducing the magnesium oxide at high temperatures with carbon.

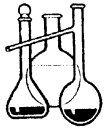


YOU WILL ENJOY READING

Holmes, Harry N. *Out of the Test Tube.* Emerson Books, New York, 1945. "Three Light Metals" are discussed in this very popular science book.

Forbes, R. J. *Man, the Maker.* Harry Schuman, New York, 1950. An excellent and compact history of technology and engineering including a short account of the Hall process.

Wade, Frank B. "Man-Made Gems." *Journal of Chemical Education,* June, 1931, pp. 1015–1026. Describes the manufacture of artificial rubies and sapphires, and the methods used in detecting differences between natural and artificial gems.

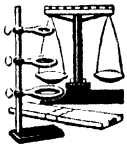


USEFUL IDEAS DEVELOPED

1. An alloy is a substance consisting of two or more metallic elements or of metallic and nonmetallic elements that are soluble in each other when molten and do not separate into distinct layers when solid.

2. A double salt is a salt that contains two metals and one acid radical.

3. Frequently, scientific discoveries and inventions are made independently and simultaneously in different laboratories.



USING WHAT YOU HAVE LEARNED

Group A

1. By whom was Al isolated in 1825?

2. (a) When and by whom was the first successful commercial method of producing Al devised? (b) What were the circumstances surrounding his solution of this problem?

3. Name five elements that are prepared by electrolysis.

4. Write an equation showing how Woehler obtained pure Al.

5. In the metallurgy of Fe, C is used to reduce Fe_2O_3. Why is C not used to liberate Al from its oxide?



6. (a) Make a labeled diagram of the electrolytic cell in which Al is freed from its oxide. (b) Discuss in detail the chemistry of the extraction of Al by the Hall process.

7. (a) What is the function of Na_3AlF_6 in the Hall process? (b) What evidence is there that the Na_3AlF_6 does not supply some of the Al formed at the cathode?

8. (a) Is bauxite just as it comes from the mines used in extracting Al by the Hall process? (b) Explain.

9. Give reasons why each of the following statements is either true or false: (a) O_2 is liberated at the anode of the aluminum cell. (b) The carbon anodes of the aluminum cell must be replaced from time to time. (c) Much Al is produced from alumina in plants located near Niagara Falls.

10. Find the percentage of Al in (a) pure alumina and (b) in pure Na_3AlF_6.



11. Aluminum hydroxide may be written $Al(OH)_3$ or H_3AlO_3. Explain.

12. Lustrous Al becomes covered with a coating in air. Explain this chemical change.

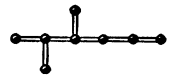
13. Al is higher in the replacement series of the metals than Fe, but it corrodes much less than Fe. Explain.

14. Write the equations for: (a) Action of hydrochloric acid on aluminum. (b) Action of a strong base on aluminum. (c) What precautions are necessary in using aluminumware because of this action of bases?

15. 300 lb. of powdered Fe_3O_4 are available. How much thermit mixture can be prepared from this Fe_3O_4?

16. (a) What properties of Al make it a satisfactory material for use in construction work? (b) Why cannot Al displace steel completely in construction work?

17. (a) What are the most important uses of Al? (b) Opposite each use write the properties that make this use possible.



18. Make a list of ten articles used by you every day which contain Al.

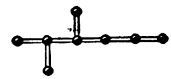
19. (a) What is an alloy? (b) Give three examples.

20. What are the composition and uses of one of the chief alloys of Al?

21. How is a photoflash bulb constructed?

22. (a) Of what is thermit composed? (b) For what is it used? (c) Write the equation for the reaction that takes place when thermit is ignited. (d) What is the source of the heat produced? (The temperature is so high that Fe, which melts at 1530°C., becomes liquid.)

23. (a) What two metals are extracted from their ores by the use of Al? (b) Explain, using an equation.



24. (a) What is a double salt? (b) Give one illustration.

25. Explain how it is possible to have an alum that does not contain Al.

26. Write an equation showing how aluminum hydroxide is prepared in the laboratory.

27. (a) What property of $Al(OH)_3$ makes it useful in purifying water? (b) Of what kind of impurities does it free the water? (c) How? (d) What is added to the water to form the $Al(OH)_3$?

28. Explain how artificial rubies are prepared.

29. (a) How is fused alumina made? (b) What is activated alumina? (c) What are some of its uses?

30. (a) Describe two chemical properties of Mg. (b) For what is Mg used?

31. (a) What metal is the chief competitor of Al? (b) Why?

Group B

32. (a) What is the effect of $Al_2(SO_4)_3$ on moist blue litmus paper? (b) Explain.

33. Describe one industrial process for the production of Mg.

34. (a) What is a refractory? (b) Name two refractories that are used commercially in large quantities.

35. Mg is a very abundant metal. Why has it only lately come into widespread use?

36. One cu. ft. of pure water weighs 62.5 lb. What does one cu. ft. of pure Al weigh?

37. Washing soda should not be boiled in aluminum utensils. Why?

38. Name three chemical discoveries that were made by young men. Do not include Hall's discovery.

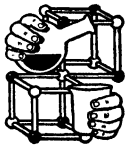
39. Compare the properties of an alloy with the properties of (a) a compound, (b) a solution, and (c) a mixture.

40. (a) What kind of salts hydrolyze in H_2O? (b) Explain.

41. Al is the most abundant metal in the earth's crust. However, Fe costs less than Al. Explain.

42. (a) Write the reaction that occurs when $Al_2(SO_4)_3$ is placed in water. (b) Write the reaction that occurs when Na_2CO_3 is placed in water. (c) What ions exist in each of these solutions? Why? (d) If we add $Al_2(SO_4)_3$ to a solution of Na_2CO_3, we get $Al(OH)_3$ and not $Al_2(CO_3)_3$. Why?

43. The thermit process has been called a vestpocket blast furnace. Explain this comparison.



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make a small model of the electrolytic cell used in making pure aluminum.

2. Make a collection of articles or samples of alloys containing aluminum. Report to the class on the composition and use of each item collected.

3. At the hundredth anniversary of the opening of the U.S. Patent Office (1936) the 12 greatest inventions made in this country were listed. Low-cost aluminum was included. Make a list of 11 other inventions which you might have included in such a list. Consult your teacher of history.



27 IRON AND STEEL

To an extent not generally appreciated, U.S. industrial strength is based on an accident of nature: the unique geographical combination of Minnesota and Michigan ore, Appalachian coking coal and the Great Lakes highway. On this triple gift of nature rests our towering steel industry. To it we owe, in the final analysis, our standard of living. Leonard Engel in *Scientific American*, May, 1948

Importance of steel in our machine age. In a recent year, more than 100 million tons of steel were produced to satisfy the appetite of the machine age. The iron produced in an entire year a hundred years ago would meet our present needs for just one day. This fact is easy to understand when we think of the great skyscrapers, the thousands of miles of rails, the millions of automobiles, the thousands of locomotives, ships, and bridges, and the great numbers of machines made from iron which man did not have even a century ago. Iron ranks first among the metals in tonnage used and, next to aluminum, it is the most abundant metal in the earth's crust.

Where does this iron come from? Iron is not found free, except in meteorites that have fallen on the earth as visitors from outer space. Iron ores, however, are numerous and widely distributed. The most important iron ore deposits (chiefly *hematite*, composed largely of Fe_2O_3) occur in the "ranges" near Lake Superior. The discovery of these huge deposits of iron had a greater effect on American life than the more romantic discovery of gold in 1849. One of the iron mines in the Mesabi range yields every two weeks a volume of iron equal to the Great Pyramid. Here the ore, containing about

50–55 percent iron, is mined in open cuts by power shovels; but elsewhere underground mining is generally employed.

These Mesabi range mines are about 1000 miles from coke- and steel-producing centers. In the metallurgy of iron "the ore generally comes to meet the coal." Why? At the mines, therefore, the ore is loaded into railroad cars of 60-ton capacity, and hauled to the Great Lakes port. Here, ore boats open their hatches, and a load of 10,000 tons of ore is emptied into each boat in half an hour. After the long haul down the Great Lakes to lower lake ports, huge grab buckets scoop out the ore and drop it on a stock pile near the furnaces, which transform these mountains of ore into rails and other products.

A smaller steel industry is located around Birmingham, Alabama, where a geological revolution once laid down coal, limestone, and iron ore. This region supplies about ten percent of our steel.

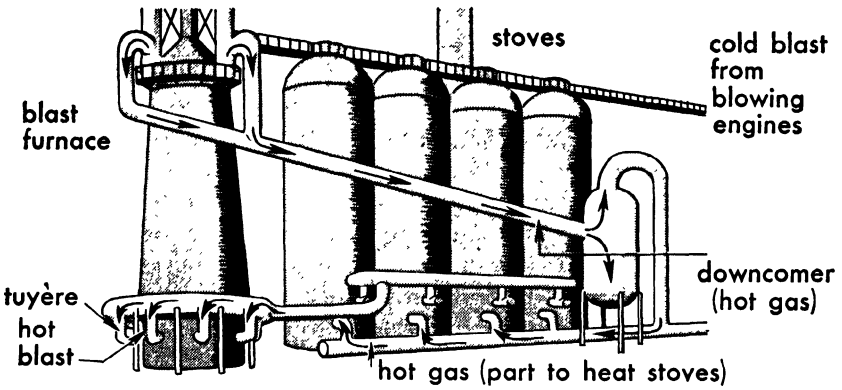
Next in importance to the American iron ore deposits are those of the Ruhr and of Sweden, which also help to supply the furnaces of France, Germany, Belgium, and Luxembourg. The deposits in northeastern England and Spain are valuable also. Russia, too, has many rich deposits of iron ore. Magnitogorsk, a city in the Urals, was built in 1928 by the Soviet Union around a mountain of a magnetic iron ore called *magnetite*, Fe_3O_4. Many nations do not have deposits of iron ore. They depend for iron on other nations.

What chemical reactions take place in the metallurgy of iron? The metallurgy of iron consists essentially of the reduction of iron oxide by means of carbon monoxide and heated coke. This reduction takes place in a *blast furnace*. The *charge* that enters the furnace consists of hematite, coke, and *flux*. The hematite supplies the iron; the coke (and CO) reduces the hematite; and the flux removes the impurities by uniting with them, forming a molten *slag* which is drawn off.

Iron Ore [illegible] of Canada



Surface mining of iron ore at Seven Islands, Labrador. The trucks haul the ore to a nearby railroad line to begin the long trip to blast furnaces in the United States.



Adapted from drawing by American Steel and Wire Company

Fig. 90. Blast furnace and stoves. Study this diagram in conjunction with Fig. 91.

The nature of the impurities in the ore determines the kind of flux used. Oxygen from the air that is forced through the charge keeps the coke near the bottom of the furnace actively burning. Equations for the reactions are given in Fig. 91.

A blast furnace in operation. The modern blast furnace, which has been developed from a furnace invented five centuries ago, is cylindrical, about 30 feet in diameter and 110 feet high, and is made of steel plates lined inside with firebrick, a refractory substance which withstands very high temperatures. At the top of each blast furnace is an apparatus through which the charge may be dropped with a minimum loss of heat. About eight feet from the base are 12 pipes, or *tuyères* (twēr's), through which 100 tons of hot air at about 600°C. are forced every hour. The heating of this air is carried out in the *stoves,* cylindrical towers 100 feet high. There are three or four stoves to each blast furnace.

As reduction of the ore proceeds, the lava-like slag floats on the molten iron. The slag is removed about every four hours, just before the iron itself is tapped and poured from a taphole at the bottom of the furnace. The molten iron flows out along a gutter lined with firebrick until it reaches a brick-lined ladle capable of holding 100 tons of metal. This is carried to an endless chain conveyer and poured into metal forms. The early forms into which the iron flowed resembled a litter of feeding pigs, hence the name *pig iron.*

The blast furnace works continuously except when repairs are necessary or business is slack. Often a blast furnace is in operation day and night for many months at a stretch. One blast furnace produces between 600 and 1200 tons of pig iron daily. From the top of

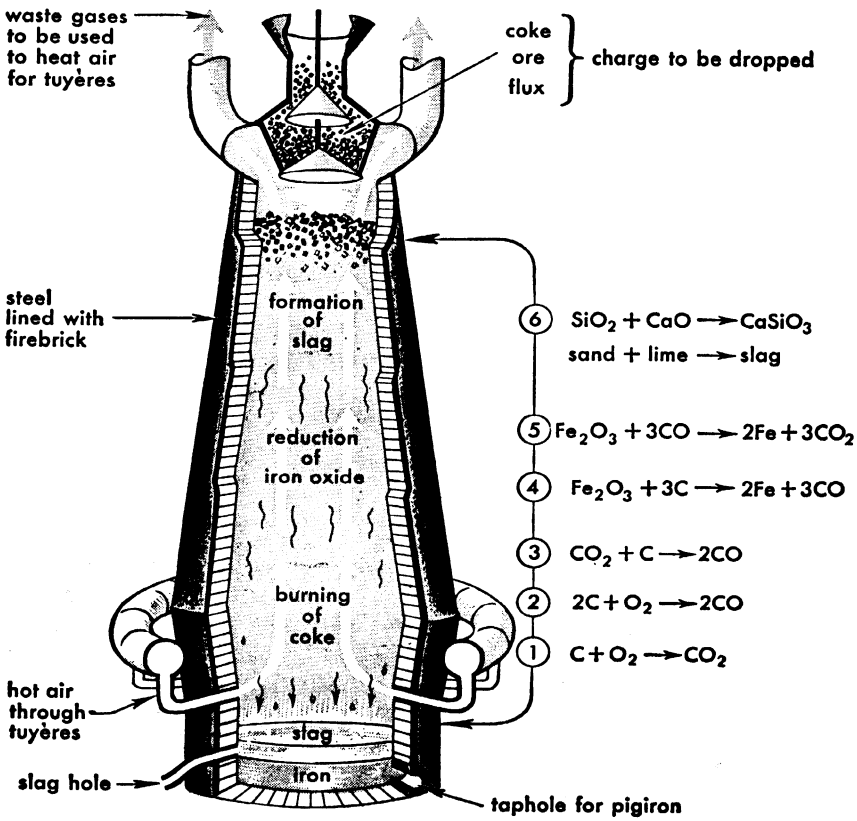
the furnace more than 3000 tons of hot gases issue every day. These gases, which may contain as much as 25 percent carbon monoxide, are gathered and used to heat the blasts of air that enter the tuyères. Blast furnace gas is essentially the same as producer gas.

Composition, properties, and uses of pig iron. Pig iron contains about four percent carbon and smaller amounts of compounds of sulfur, silicon, and phosphorus. These impurities make pig iron a grayish, brittle metal which melts at about 1150°C. It cannot be forged or tempered, but can be cast into objects, such as sash weights, water pipes, stove parts, and radiators, that do not have to withstand great stresses or strains.

Some pig iron is partially purified and changed to *cast iron* by melting it with scrap or wrought iron and then slowly cooling it. Its

Fig. 91. Cross section of a blast furnace. Note the structure of the furnace, the nature of the charge and the chief chemical reactions which occur.

Adapted from drawing by American Iron and Steel Institute



carbon is present as globular particles of graphite. Such cast iron is less expensive than steel, is strong, machinable, and can be welded. It is used for tools, agricultural instruments, and machine parts that are not subjected to severe shocks.

Most pig iron, however, is converted into steel by removing most of its impurities. In fact, in most plants, blast furnaces and steel converters stand side by side.

Wrought iron — oldest form of commercial iron. Up to the fourteenth century the form of iron most commonly used was wrought iron. This is almost pure iron, containing less than 0.1 percent carbon. Wrought iron is soft and tough, and resists shocks and strains very well. Although it has been almost entirely replaced by soft steel, some of it is still used by blacksmiths, and very much more of it is used in the manufacture of chains, anchors, pipes, bolts, and temporary magnets. It resists atmospheric corrosion rather well.

Wrought iron is prepared from pig iron in a shallow furnace holding about 600 pounds of the *melt*. Iron oxide or rusty scrap iron supplies the oxygen that changes the carbon of the pig iron to carbon monoxide.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO\uparrow$$

As the iron becomes purer, its melting point rises and the melt becomes a pasty mass. This is stirred, *puddled*, and then removed in the form of fiery balls at the end of iron rods. These balls are squeezed between hammers, which remove most of the slag, and then rolled to distribute the remaining slag throughout the iron, giving the wrought iron a fibrous structure.

Henry Bessemer and William Kelly usher in the steel age. Both wrought iron and steel have been known for centuries. They were made in small amounts by skilled workers using a slow and expensive process until the invention of the rifled cannon, locomotive, and

Adapted from drawing by American Iron and Steel Institute

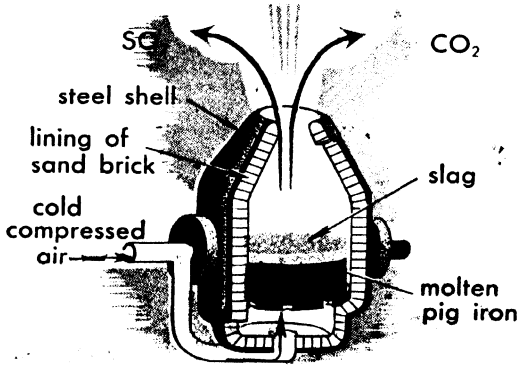


Fig. 92. Cross section of a Bessemer converter. Note the chemical changes which occur as the air passes through the molten iron.

other machines brought an unprecedented and immediate demand for huge quantities of steel.

William Kelly, a Pittsburgher living in Kentucky, got the notion that a blast of air would not chill molten pig iron but would increase its heat by oxidizing its impurities. In this way he planned to make steel quickly and inexpensively. He was scoffed at, and his father-in-law actually questioned his sanity and had a doctor examine him.

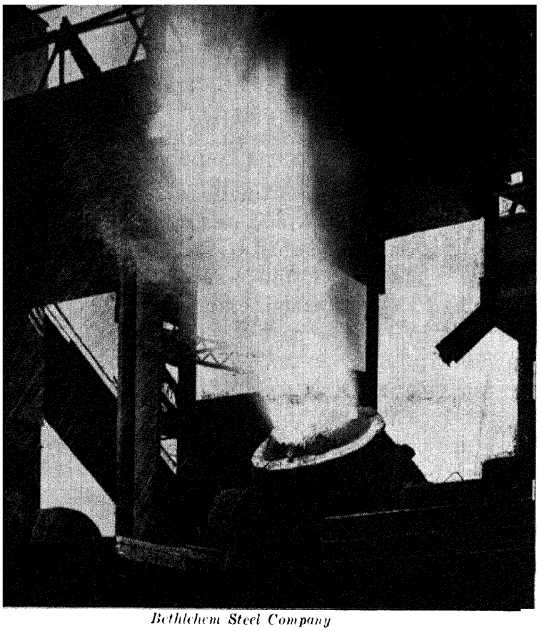
Kelly went right ahead, however, and in 1851 he gave a public demonstration of his process. An eye-witness reported: "We saw a vessel that had a mouth open on one side and near the top. The whole was shaped something like an egg. We saw molten metal poured into the vessel. Then Kelly turned on a blast of cold air. The vessel set up a roaring noise, and fire belched furiously from its mouth, making many colors. But only for a few minutes. The noise and fire died down. We then saw a blacksmith take a small part of the iron which had cooled, and contrived and threw at the feet of the amazed spectators a perfect horseshoe. No one laughed at Kelly now."

While Kelly worked to improve his product, Henry Bessemer in England was discovering the same process independently. During the Crimean War, he had invented a new type of cannon but he could not find an iron strong enough to withstand the high pressures of the expanding gases released. This led him to researches in steel, and in 1855, at the age of 42, he solved the problem and obtained a patent on his process. Kelly then quickly obtained a patent for his own process in the United States. Bessemer built a more efficient furnace and bought out Kelly's patent.

Bessemer was later knighted. This honor came to him not for his invention of the steel furnace but rather for a suggestion he had made when he was 20 years old. He had recommended an improvement for preventing the re-use and counterfeiting of seals and stamps on official documents.

At this time steel was selling at $250 a ton. The world was waiting for an inexpensive steel, and, almost overnight, the iron industry was revolutionized. The first Bessemer furnace, or *converter,* used in the United States was set up at Troy, New York, in 1864. The new process did in ten minutes what the old process took a whole month to accomplish. The old puddling furnaces that produced wrought iron were almost completely scrapped and soon steel took the place of wrought iron almost entirely.

In production, pounds were replaced by tons. By 1870 steel production had forged ahead so rapidly that it equalled the production



Bethlehem Steel Company

One of the most spectacular displays in industry—a Bessemer converter during a "blow."

of wrought iron. At present, wrought iron represents only about one percent of the total output of pure iron in this country. The highly skilled ironworker with his small furnace has given way to hundreds of trained men handling huge furnaces turning out steel on a gigantic mass-production scale.

The acid Bessemer process, a fiery spectacle. The present-day Bessemer converter used in the United States is a barrel-shaped pot of wrought steel about ten feet in diameter and 20 feet deep, lined to a thickness of 1.5 feet with heat-resisting brick made up largely of sand, SiO_2, an *acid anhydride*. Fifteen tons of a fiery broth of molten pig iron, whose chief impurities are carbon and silicon, are poured into the Bessemer converter from the blast furnace.

Through this molten mass blasts of cold air are forced under about 25 pounds pressure, through holes at the bottom of the converter. This *blow* lasts between ten and 20 minutes. The oxygen in the blasts of air oxidizes the iron it strikes, first forming ferrous oxide, which in turn reacts with the silicon impurity, forming silicon dioxide and iron:

$$2Fe + O_2 \rightarrow 2FeO$$
$$Si + 2FeO \rightarrow SiO_2 + 2Fe$$

Silicon dioxide, insoluble in the molten iron, accumulates as slag.

As the blow continues, the carbon impurities begin to burn. A roaring boil then takes place in the converter. The carbon monoxide

burns at the mouth of the converter, and countless flying sparks of metal and slag add to the spectacle.

$$C + O_2 \rightarrow CO_2$$
$$CO_2 + C \rightarrow 2CO$$
$$2CO + O_2 \rightarrow 2CO_2$$

In a few minutes the carbon is gone; the flame flickers and contracts. This is the signal to stop the blast by turning the converter vessel over on its side.

Inside the converter, a seething mass of molten iron is covered with a thin layer of slag. The metal, however, contains some dissolved gases and, if solidified at this point, would be spongy. So a predetermined amount of carbon and manganese is added in the form of iron alloys, such as *ferromanganese,* which contains about 70 percent manganese, or *spiegeleisen,* which contains about 20 percent manganese. About 14 pounds of manganese are used for every ton of steel produced. The manganese unites with any dissolved air or combined oxygen, and in addition strengthens the steel by its presence.

The chemical reactions that take place in the converter when spiegeleisen is added are:

1) **The action of the manganese:** $\begin{cases} Mn + 2FeO \rightarrow MnO_2 + 2Fe \\ Mn + O_2 \rightarrow MnO_2 \end{cases}$

2) **The action of the added carbon:**

$$3Fe + C \rightarrow Fe_3C \text{ (iron carbide)}$$

The converter is then tipped completely over and its charge of liquid steel is poured into a waiting mold.

The basic open-hearth process. Pig iron containing sulfur and phosphorus cannot be treated in the *acid* Bessemer converter, since this type of furnace cannot remove these impurities. Phosphorus is oxidized during the blow, but it will not enter the slag and become part of it.

The basic open-hearth furnace, however, completely removes both sulfur and phosphorus (*acid impurities*) by means of lime and a lining made of the oxides of calcium and magnesium which are basic anhydrides. In England and on the Continent the Bessemer furnace lined with these basic oxides is used in the treatment of iron ores containing sulfur and phosphorus.

The open-hearth furnace was invented by Charles W. Siemens (zē'mĕns), who left Germany to become a citizen of England. He patented his furnace five years after the Bessemer furnace was invented. In 1873 the first open-hearth furnace was built in the United States.

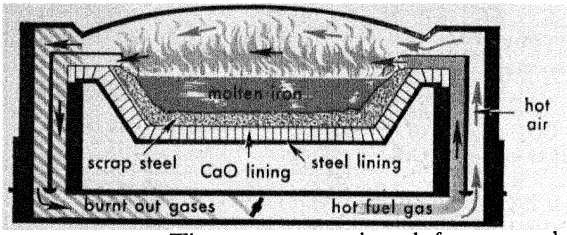


Fig. 93. Open-hearth furnace (greatly simplified) showing the nature of the charge and lining and the flow of the hot gases.

The present open-hearth furnace, as large as an eight-room house, contains a shallow, oblong steel basin about 50 feet long by 15 feet wide encased in brickwork. The charge consists of about equal amounts of scrap iron and molten pig iron, with a small amount of iron ore placed over a layer of limestone, $CaCO_3$. The scrap iron consists of old, discarded factory and farm machinery, junked cars, and so forth. This is cheaper than pig iron, contains less carbon, and conserves our reserves of raw material. Burning fuel and hot air enter at one end, are deflected down from the low roof made of refractory brick, and heat the charge just as a gigantic blast lamp might; the waste gases finally leave at the other end of the furnace. Such a furnace in which the charge is heated by flames deflected from the roof is called a *reverberatory furnace*. By a regenerative process, all the heat of the gases is used by reversing their flow at regular intervals. The following reactions take place:

1) Carbon is burned out by the oxygen of the air

$$2C + O_2 \rightarrow 2CO$$

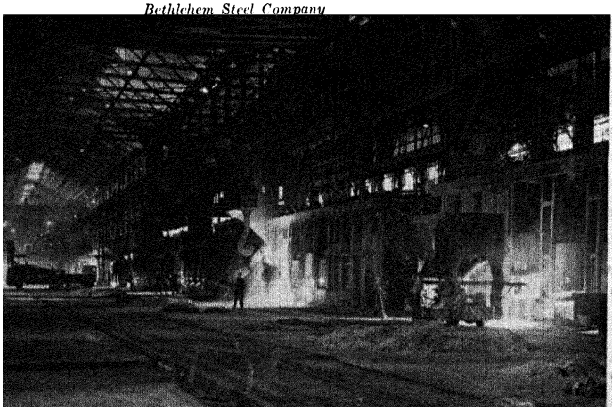
and by the oxygen of the rusty scrap iron, and ore.

$$3C + Fe_2O_3 \rightarrow 3CO + 2Fe$$

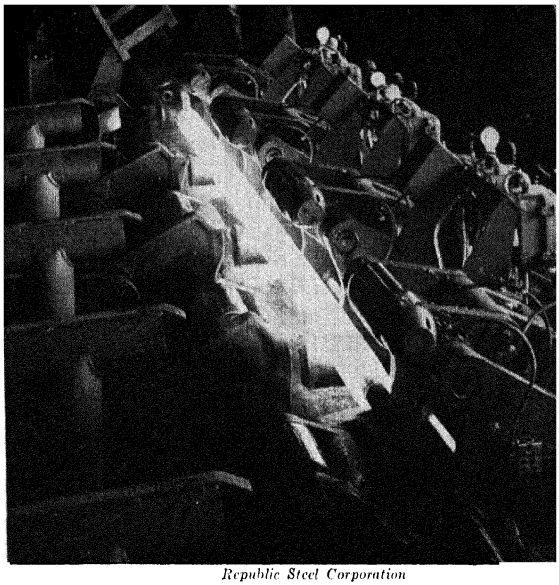
2) The limestone decomposes, forming carbon dioxide, which bubbles up rapidly through the melt. This bubbling produces a vigorous stirring and leaves a basic lining of CaO.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

Bethlehem Steel Company



The open-hearth department of a steel mill. Open-hearth furnaces, located behind the wall at the right, are charged with molten iron from the blast furnace, scrap iron, and limestone. About 12 hours are required to complete a "heat" of 250 tons of steel.



A special machine for the manufacture of seamless steel tubing. Shown is a length of white-hot tubing just after piercing. During the manufacturing process a steel billet eight feet long is converted to a tube 35 feet long.

Republic Steel Corporation

3) Some sulfur is liberated as sulfur dioxide.

$$FeS + 2FeO \rightarrow 3Fe + SO_2 \uparrow$$

4) The calcium oxide combines with the phosphorus and silicon oxides, forming a slag, which rises to the top.

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

From time to time, samples of the 200- to 500-ton pool of liquid are removed and quickly analyzed for carbon content so that the composition of the steel may be controlled carefully. This open-hearth process is longer and may be controlled more easily than the acid Bessemer process, and takes about 12 hours for 200-ton heats.

In spite of its slightly higher price, basic open-hearth steel is in great demand in this country because of its generally higher uniformity and quality. In fact, less than five percent of the steel made in the United States today is prepared by the acid Bessemer process. Open-hearth steel is used for rails, structural steel, machinery, and plates for boilers and ships; Bessemer steel for sheets, pipes, and bars.

From converter to rail, girder, sheet, and pipe. When the steel is ready to be tapped, a hole is opened in the rear of the furnace, and the steel drains into a huge brick-lined ladle. The lighter slag flows out last and *overruns,* or overflows, the filled ladle. Between five and 15 tons of steel from this ladle are poured into square, round, or rectangular cast iron molds called *ingot molds.* The molds are

stripped from the ingots, which are then lowered into underground furnaces or soaking pits, where they are heated for six hours to a uniform rolling temperature of about 2400°F.

All steel begins in the ingot. While still red hot, the ingot, as tall as a man, is first *deseamed,* that is, cleaned of all surface scale and seams. Then it is changed into smaller sizes and different shapes in *rolling mills* or under hammers and presses. In the continuous-sheet rolling mill slabs of hot or cold steel are rolled down to specified widths and thicknesses in one uninterrupted operation at a rate of about 1000 feet per minute. In the *blooming mills,* a pair of heavy steel rolls, built like a huge clothes wringer, flatten and shape the ingot into a *bloom,* which may then be converted into a rail. The rail travels on another roller line to a *hot saw,* where it is cut into 33-foot-6½-inch lengths. When cold, each piece becomes a standard rail 33 feet long. Steel rails at the mill cost about 4.5 cents a pound. Similarly, other steel ingots are sent from one machine to another and finally emerge as rods, bars, plates, girders, wire, and tubing.

Composition and properties of steel. Steel contains from 0.05 percent to 1.7 percent carbon, the percentage being regulated according to the use to which the steel is to be put. Most steel does not contain sulfur or phosphorus, for sulfur makes the steel brittle when hot, and phosphorus makes it brittle when cold. Steel is hard, silvery in color, ductile, magnetic, and can be welded, forged, and tempered.

Tempering is one way to change the properties of steel. The *percentage* of carbon in steel and the *form* in which the carbon is present determine the properties of the steel. The carbon may be present as free carbon or as iron carbide, Fe_3C. It may be present either in solution or as crystals. A steel rich in dissolved iron carbide is very hard and brittle, while one containing a large amount of crystalline iron carbide is comparatively soft.

The percentage of free and dissolved iron carbide in steel may be varied by heat treatment. This treatment of a metal to vary its hardness, strength, and toughness is called *tempering.* Rapid cooling or *quenching* in cold water or brine produces a hard but brittle steel. By quenching in boiling water or hot oil, a slower rate of cooling is obtained, resulting in partial crystallization in the hard steel and producing a soft but tough steel.

Heat without flame, and almost without wires. Another method for heat-treating steel is by means of an *induction furnace.* No flame of any kind is involved, nor are there direct connections to a source of electricity. Moreover, instead of being heated chiefly on the surface, as in most kinds of heating, a substance placed in an induction

furnace is heated from within. Thus, the heating is very rapid, easily controlled, and applied only where it is needed. A small induction furnace using 600 kilowatt hours of electricity is capable of melting one ton of steel per hour.

An induction furnace acts as a transformer. Alternating current of high frequency flows in the primary coil, and the material to be heated is placed in much the same position as if it were the core of a transformer within the secondary coil. As the transformer operates, the core becomes warm. If the frequency of the current fed into the primary coil is increased greatly, the core becomes hot. This heating effect comes from eddy currents set up within the core as a result of the changing magnetic fields produced by the rapidly alternating current.

Steel alloys, another way to change the properties of steel. Heat-treating is not the only method of improving steel. The addition of small amounts of other metals changes the properties of steel and widens the range of uses of the *alloy steels.* It must be remembered that steel itself is an alloy of iron and carbon.

With the development of the railroad, automobile, and the airplane, engineers raised a cry for more alloys. Transportation needed strong, flexible, rust-resisting alloys. Out of the chemist's crucible came hundreds of such new alloys for thousands of different uses. On the wings of this new age of alloys came *molybdenum* and *vanadium* steels for axles, springs, gears, and rails; *wolfram, molybdenum,* and *chromium* steels for high-speed cutting tools; *nickel-chrome* steels for armor plate; *cobalt* steel for turbine blades, tail cones, and combustion chamber linings of jet planes; and *manganese* steel for brake shoes, burglar-proof safes, the jaws of rock crushers, and non-magnetic binnacles of ships.

A far-reaching development in steels is the large-scale production of *stainless steels.* These alloys, first used for making stainless kitchen utensils, are employed in a multitude of ways. For example, the Empire State and Chrysler buildings in New York City are sheathed in

Adapted from a drawing by American Iron and Steel Institute

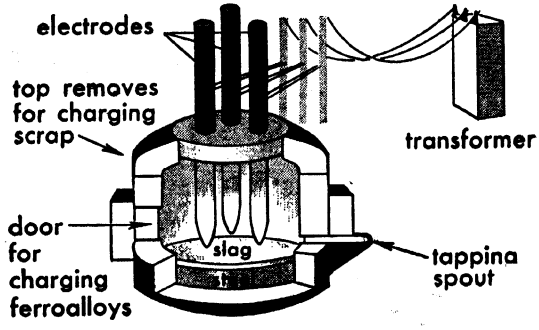


Fig. 94. Cross section of an electric furnace for the production of alloy steels. The chemical reactions involved are essentially the same as those of the open-hearth process.

rustless steel that needs neither paint nor any other coating to protect it against corrosion.

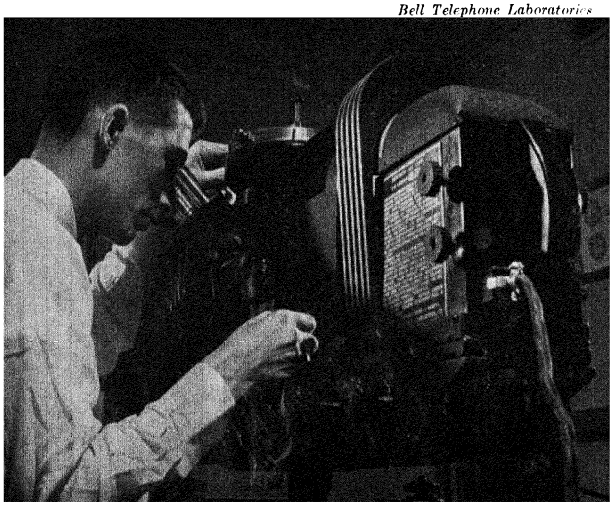
A typical stainless steel is "USS 18–8" which, besides iron, contains about 18 percent chromium and eight percent nickel as well as 0.5 percent manganese, 0.5 percent silicon, and about 0.1 percent carbon. The trademarks of two other stainless steels are "Enduro KA2" and "Rezistal." The metal *niobium* is also added to stainless steel. Small amounts of silver added to stainless steel decrease salt-water corrosion of this alloy. "Duriron," which resists acid corrosion very well, contains about 15 percent silicon. "USS Cor-Ten" contains copper and is a very corrosion-resistant steel used widely in railroad passenger cars.

Some high-grade steel, used for special purposes such as razors, springs, and pens, is made in small amounts in *electric arc furnaces* from ingot iron and steel plus the necessary alloying elements. The electricity serves to supply the high temperature required for the purification of this fine steel. The process can be rigidly regulated.

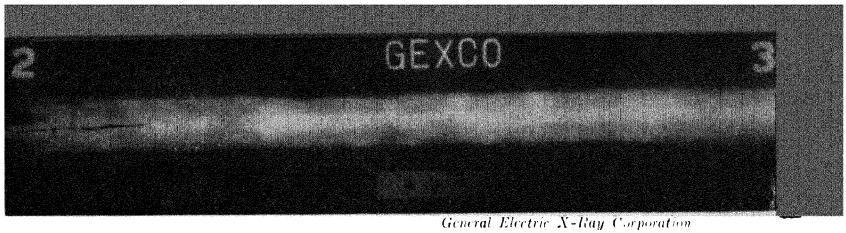
What is case-hardening? In the process called *carburizing,* wrought iron or soft steel is heated in contact with coke or charcoal. The carbon forms a layer of very hard, high-carbon steel over the softer low-carbon metal. This gives a hard skin or exterior and a tough interior —a condition ideal for gears and carving knives. This method was the one used by the skilled artisans who fashioned swords, armor, and guns from wrought iron hundreds of years before Bessemer steel came into use.

Case-hardening is also accomplished by the use of ammonia and sodium cyanide. In this process, called *nitriding,* ammonia gas at high temperatures or NaCN reacts with special steels in airtight containers. Very hard nitrides are formed on the surface of the steel.

Bell Telephone Laboratories



Tiny flaws and defects in metal are detected by this instrument called a Metallograph. The Metallograph takes photomicrographs of the surface of a metal magnified up to 2,000 times.



General Electric X-Ray Corporation

A radiograph of a weld shows a crack (left) in the internal weld metal. The numerals are used to identify the location of defects.

How steel is analyzed. Even traces of impurities or slight defects in the inner structure of steel alloys may weaken them. Many railroad wrecks and explosions have been laid at the door of defective steel. Great strides have been made in the analysis of the structure of steel. *Metallography* is the name given to this field of study. Various methods of testing steels are used. Besides testing the physical properties of steel, including strength, ductility, and hardness, accurate chemical analyses give its composition.

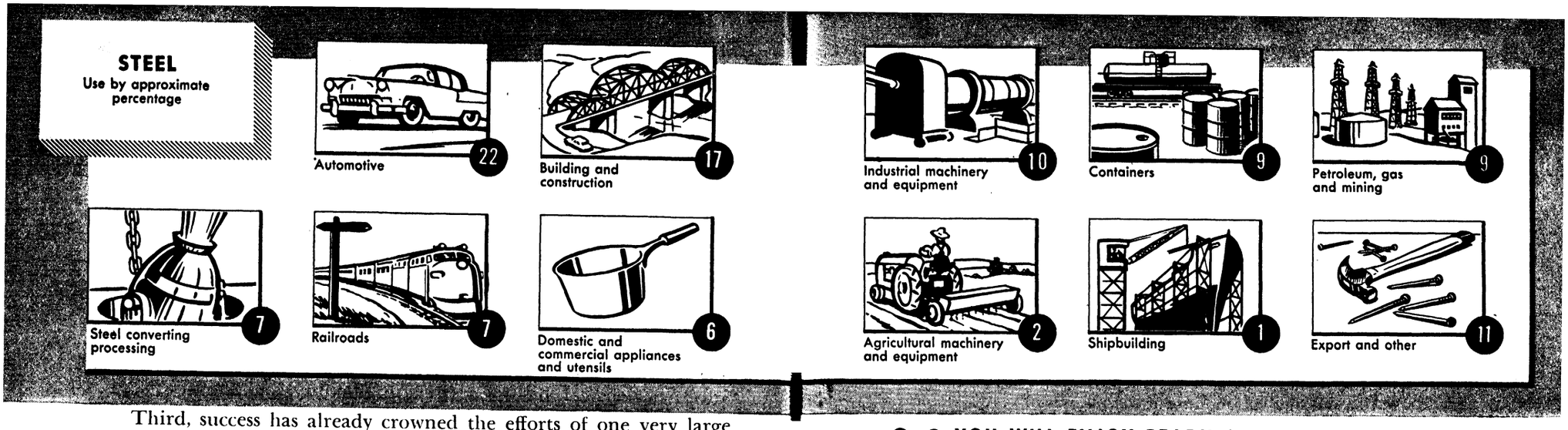
By etching the carefully polished surface of a sample of an alloy with a dilute acid, the irregularly pitted surface, photographed under a special microscope, will show poor welds, cracks, blowholes, sandholes, and any other weaknesses. Whether the alloying metal has formed a compound or is merely in solution can also be determined from these *photomicrographs.*

X-ray photography is also used in the examination of steel. Portable x-ray machines have been developed that are powerful enough to affect a photographic film behind solid steel one foot thick. Structural defects in castings or welds are thus easily detected. Special railway cars carrying x-ray machines and other equipment examine thousands of miles of railroad track each year.

New horizons in the steel industry. Several major innovations are now taking shape in the steel industry.

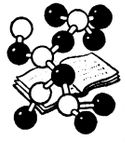
First, in an effort to raise steel production with present plants and equipment, *air enriched with pure oxygen* is being used instead of ordinary air in a few blast furnaces and steel converters. Oxygen-enriched air in the blast furnace hastens the melt by raising the temperature several hundred degrees. In the open-hearth and Bessemer furnaces, the addition of pure oxygen to the air shortens the production time by accelerating the removal of carbon. Cheaper oxygen may accelerate this new development.

Second, *high pressure operation* in the blast furnace saves time and increases the daily output of pig iron. By means of a carefully worked-out system of valves, the pressure inside the blast furnace can be carefully increased and regulated so that the rate of the blast can be stepped up. This results in increasing the daily output of pig iron and also reduces the consumption of coke by about ten percent.



Third, success has already crowned the efforts of one very large steel company in this country in its long attempt to substitute a quicker, cheaper, and more compact method of converting the molten steel of the converter directly into semi-finished steel products. The method, announced in 1948, is known as the *continuous casting process*. This process eliminates the most expensive and intricate machinery now used in processing steel. All finished steel products formerly began as ingots. However, continuous casting makes use of a relatively small casting machine which forms billets of iron, cools them, and then cuts them to any desired length up to 35 feet. It eliminates hammering, pressing, rolling, and reheating. Not only does this process cut costs and increase production, it also makes possible smaller and less costly plants. In time this development may help decentralize the steel industry and allow even greater expansion.

Finally, work is progressing to meet the ever-increasing threat of a shortage of top-grade iron ore containing 60–65 percent iron. With the already rapid depletion of this rich iron ore of the Mesabi range mines, iron men are studying how to concentrate and utilize low-grade iron ores containing only 25 percent iron found plentifully in many parts of the United States. For example, northern New York iron mines, abandoned almost half a century ago, are being reexamined. Inferior iron ores (magnetic taconite) from the Mesabi range, have been ground, impurities removed magnetically or by flotation, heated into walnut-sized pellets containing 65 percent iron, and then used in blast furnaces. If successful, such beneficiation of low-grade ores will give us a plentiful supply of iron for many years to come. In the meantime, we have begun to import rich iron ores containing as high as 67 percent iron from Labrador, Venezuela, Brazil, The Dominican Republic, and even Liberia.



YOU WILL ENJOY READING

de Kruif, Paul. *Seven Iron Men.* Harcourt, Brace & Co., New York, 1929. The author of *Microbe Hunters* tells the story of the iron-hunting Merritt family, pioneers in the Minnesota iron industry.

Lyans, R. C. "Student-Made Visual Aids." *Journal of Chemical Education,* May, 1944, pp. 241–242. Includes the blast and open-hearth furnaces.

Morrow, Martha G. "Steel for War and Peace." *Chemistry,* April, 1945, pp. 1–8. Well written and beautifully illustrated.

Parker, Charles M. "Panorama of Steel." *Journal of Chemical Education,* May, 1951, pp. 236–242. An illustrated article on recent developments in steel.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) Where does Fe rank with respect to usefulness among the metals? (b) Where does Fe rank with respect to tonnage used?

2. (a) Where and (b) in what form does Fe occur in the United States? (c) in Europe?

3. (a) Why are the mines of the Mesabi range so valuable? (b) How is this ore mined? (c) Where are the reduction furnaces? (d) Why?

4. Make a diagram of a blast furnace and label: the place where the charge enters, the tuyères, the hotter parts of the furnace, the cooler parts, the place where the slag collects and is tapped, and the place where the Fe collects and is tapped.

5. (a) Of what is the solid charge in the blast furnace composed? (b) What is the function of each constituent of the charge? (c) What other substance must be used in the furnace in large quantities? (d) For what purpose?

6. (a) Describe what takes place in a blast furnace. (b) Write equations for the chemical reactions that occur.

7. (a) What valuable gaseous product is formed during the operation of the blast furnace? (b) For what is it used?



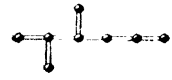
8. Copy and complete. Do not write in this book. Blast furnace iron is also called ... iron. It contains about ... percent of ... and smaller amounts of compounds of ..., ..., and .... The impurities of the pig iron are removed by either the ... process or the ... process.

9. (a) What properties of pig iron make it useless for many of the purposes for which steel is made? (b) For what is pig iron used?

10. (a) Name two men who helped usher in the steel age. (b) At what important period of American history did the steel age begin?

11. Using a labeled diagram, describe the acid Bessemer converter.

12. (a) Why must a Bessemer converter tilt easily? (b) How does the operator know when to tilt it?



13. What is the source of the highest temperature reached by the contents of the converter?

14. (a) How are the impurities of pig iron in the Bessemer converter removed? (b) Write equations for the reactions.

15. A function of the Bessemer process is to remove almost all C, yet C is added at the end of the process. Explain.

16. What is the function of spiegeleisen in the operation of the Bessemer converter?

17. The acid Bessemer process removes all objectionable impurities from only one kind of ore. Explain.



18. Make a drawing of the basic open-hearth furnace. Label: the layer of slag, the place where the molten steel collects, the place from which the steel drops into the ladle. Show by arrows the path of the air and the combustible gases.

19. (a) Why is the open-hearth process called *basic*? (b) What is the source of the great heat produced?

20. (a) Why is the basic open-hearth process said to be regenerative? (b) Why is the furnace called a *reverberatory* furnace?

21. (a) Of what does the charge in the basic open-hearth process consist? (b) Why is scrap iron used?

22. Show, by equations, the three most important chemical changes that take place in the basic open-hearth furnace.

23. Compare acid Bessemer and basic open-hearth steel by making a table listing (a) quality, (b) cost, (c) uses, (d) tonnage, (e) time required for the process.



24. Compare the properties and composition of steel and pig iron.

25. Why must most steel be free from S and P?

26. Name two general methods for changing the properties of steel.

27. (a) What is tempering? (b) How is it done?

28. What physical and chemical changes take place in steel during tempering?

29. (a) What is an alloy? (b) How does it differ from a compound?

30. Steel itself is an alloy. (a) Explain. (b) Name four steel alloys and (c) tell for what use each is suited.



31. How is steel made in electric furnaces?

32. A sample of hematite contains 75 percent Fe_2O_3. What weight of wrought iron can be made from 250,000 tons of this ore?

33. What volume of air is required to oxidize all the C present in 500 tons of pig iron containing four percent C?

34. What are three tests used in testing the quality of a sample of steel?

35. (a) What is the oldest form of commercial Fe? (b) How does it compare in composition and properties with steel?



36. What is the chief chemical reaction that takes place during the making of wrought iron?

37. Why does the wrought iron in the puddling furnace become pasty?

38. How do you account for the fact that fairly pure Fe has been known for 5000 years, although Fe is never found free?

39. Why does the manufacture of basic open-hearth steel outrun Bessemer steel about 13 to one?

40. When would the addition of flux in a blast furnace be unnecessary?

41. What is the difference between an acid lining and a basic lining?

42. (a) State four new developments in the steel industry. (b) Describe one of them in detail.

Group B

43. Of what use is slag from a blast furnace?

44. (a) Name and give the formulas of three ores of iron other than hematite. (b) What is fool's gold?

45. 19 g. of Fe yielded 27.2 g. of Fe_2O_3. Calculate the atomic weight of Fe.

46. What four factors help to determine the location of plants for the production of iron and steel?

47. (a) Give the names and formulas of two iron oxides used as pigments in paints. (b) What property makes them ideal for this purpose?

48. Why does the molten metal not run out of the holes in the false bottom of the Bessemer converter?

49. Describe the induction furnace and its operation and use.

50. What is the difference between carburizing and nitriding?

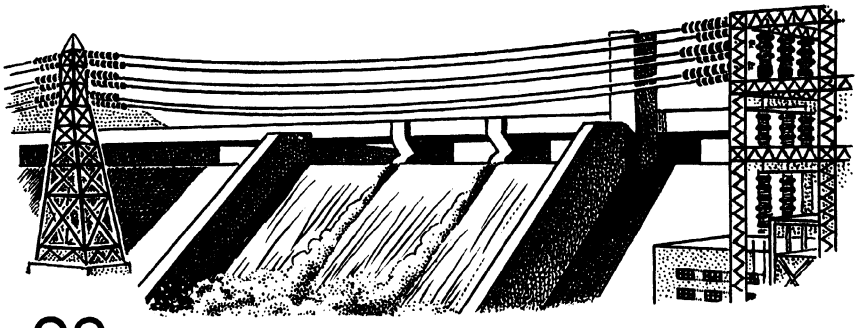


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make a list of the different metals that enter into the manufacture of an automobile. From this list pick out those metals that must be imported. Why must these metals be imported? Of what significance is this fact?

2. On an outline map of the United States indicate the location of the largest steel mills and the richest coal deposits in this country. Show also the location of most of the iron mines and the routes over which both coal and iron are sent to the steel plants. What relationships do you discover?

3. Construct a model of an open hearth or blast furnace.



28 COPPER: NERVES OF THE MACHINE AGE

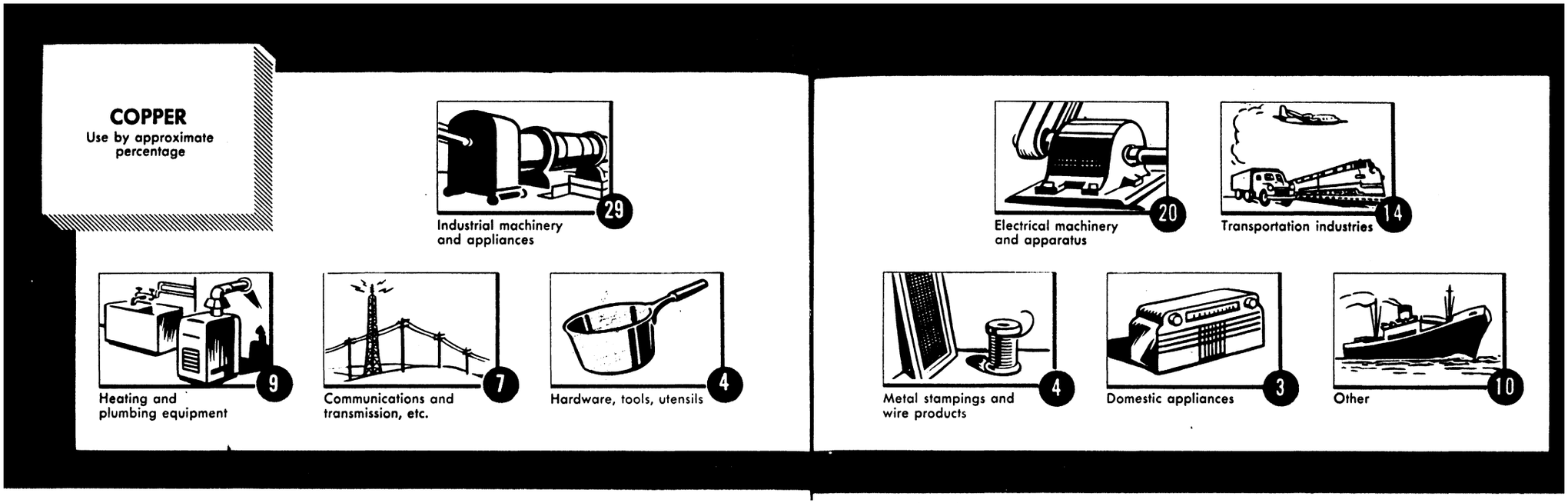
. . . Berthelot analyzed a small votive figure from the excavations of ancient Chaldea and found it to consist of nearly pure copper. The age of this figure is variously estimated at from 3000 to 4000 B.C. *A small metal cylinder from Egypt of a period estimated at about 4000* B.C. *was also of copper. Thus the mining and metallurgy of copper is at least 5000 years old.* J. M. Stillman, 1919

Copper, the most important nonferrous metal. In 1831 Michael Faraday performed an immortal experiment. By moving a magnet through a coil of copper wire, he discovered that an electric current could be produced in a wire. This was the beginning of the electric age, with its generators, motors, electric wires, cables, and thousands of electric instruments. The manufacture of all copper items in the United States consumes over one million tons of copper each year.

If steel is the backbone of the machine age, then copper is its nervous system, for along copper wires travel the electron impulses that animate our huge machines. Next to silver, copper is the best conductor of electricity.

Copper, the red metal, was the first metal used by man. It was used during the Bronze Age long before iron, mainly because copper was found free. Copper is soft, has a high tensile strength, and melts at about 1100°C. The ancients used copper and its alloys for implements and decorations.

Copper "nerves" carry electricity throughout the world. Copper is such an excellent conductor of electricity that millions of miles of copper wire are used to carry electric power. Great quantities of copper are used also in the construction of telephone and telegraph



wires and cables and in underwater cables for use in transoceanic communication. Parts for electric motors, electronic devices, and other equipment using electricity require great quantities of copper.

Alloys of copper. *Bronze,* composed of copper, zinc, and tin, and *brass,* composed of copper and zinc, are among the most widely used alloys of copper. *Nickel silver,* or *German silver,* is an alloy of copper, zinc, and nickel. "Monel metal" is composed of copper, nickel, and iron. This alloy is widely used in the production of noncorrosive sinks, cooking utensils, and food and chemical processing equipment.

Copper is used in varying amounts in the production of many of the alloys of steel, aluminum, and magnesium. Our one-cent piece is made of a copper alloy, and other coins contain copper.

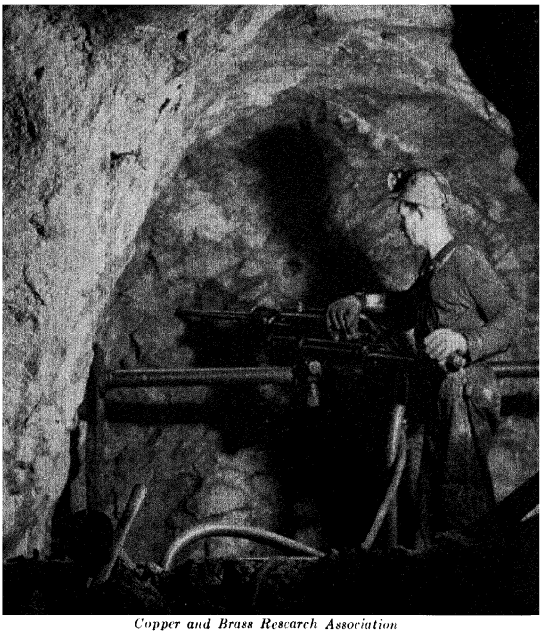
Copper in construction. Because copper and its alloys form self-protecting films on exposure to moist air (see page 431), and are of relatively high tensile strength, they are widely used in the construction industries. Gutters, downspouts, valleys, and flashings made of copper or copper alloys usually last as long as the house or other building on which they are installed and require a minimum of maintenance. Copper sheathings and copper roofs are also used. Copper sheathing frequently is used as a covering to protect the hulls of wooden ships.

Brass pipe and copper tubing are often specified by architects in plumbing and heating installations; and faucets, valves, and other plumbing fixtures are usually made of brass. Hardware and screens made of copper alloys resist corrosion and last longer than those made of most lower cost metals.

Copper and the processing industries. The processing industries convert raw materials into finished or semifinished products. Many of the processes involved are chemical in nature and must be carried out in vats, reaction chambers, cookers, and similar equipment that will withstand, without corrosion, the chemical reactions, the high temperatures and pressures, and various other factors that may be present. Copper and copper alloys are often ideally suited to the requirements of a particular processing situation, and great quantities are used in the production of processing equipment. Copper and copper alloys are used also in the production of household utensils. Copper-bottomed stainless-steel cooking utensils are very popular.

How copper is freed from its ores. When copper occurs free, as it does in the Lake Superior region, its ore is melted, and the copper flows away from its impurities. In the Lake Superior region, most of the copper ore occurs as small particles of free copper embedded in gangue, from which it must be separated.

Though lumps of native copper weighing 500 pounds have been found, the metal occurs chiefly in the combined state. Formerly, mines in the Keweenaw Peninsula of Michigan supplied much of our domestic copper, but now most of it is mined in Arizona, Montana, Nevada, New Mexico, and Utah. In these western areas copper usually occurs as the sulfide, Cu_2S, together with iron sulfide and copper oxide.



Copper and Brass Research Association

In an underground Montana copper mine, a miner drills blast holes with a pneumatic drill.

The metallurgy of sulfide ores is very complex. It involves first the process of roasting, during which the crushed ore is heated in the presence of air and changed into cuprous oxide.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow$$

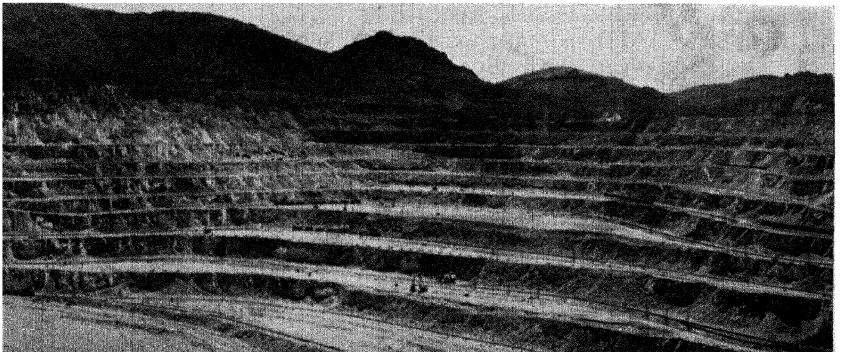
This cuprous oxide is then transferred to a reverberatory furnace where coke or powdered charcoal reduces the copper oxide to copper.

$$Cu_2O + C \rightarrow 2Cu + CO \uparrow$$

Matte from blast or reverberatory furnaces contains copper and iron sulfides. The matte is treated in a furnace resembling the Bessemer converter, where oxygen from blasts of air unites with the sulfur

An open-pit copper mine in New Mexico.

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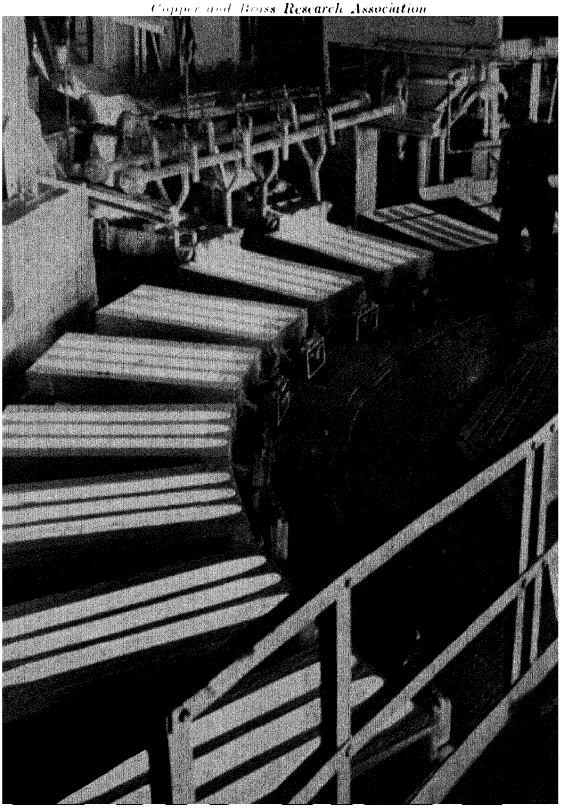


in the matte, forming sulfur dioxide. The iron oxide remaining in the furnace combines with the silicon dioxide lining of the furnace, forming ferrous silicate slag, $FeSiO_3$. The copper that results from this process is called *blister* copper, because it has cavities and other defects caused by escaping gases. Blister copper may contain as much as 99 percent copper.

How blister copper is refined electrolytically. Most copper ores contain small amounts of silver, gold, zinc, arsenic, and other metals. Since the presence of minute amounts of certain of these substances greatly decreases the ability of the copper to conduct electricity (0.03 percent of arsenic lowers it 14 percent), blister copper is purified electrolytically. Plates of blister copper about three feet square and one inch thick are suspended as anodes in tanks containing a warm solution of copper sulfate and sulfuric acid, which is stirred mechanically. The cathodes consist of very thin sheets of pure copper.

Impure copper passes into solution at the anode, producing copper ions. The two electrons thus released reach the cathode, where they join a copper ion and convert it into free copper, which is

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Pouring molten copper into wire bars from which electric wires are drawn.

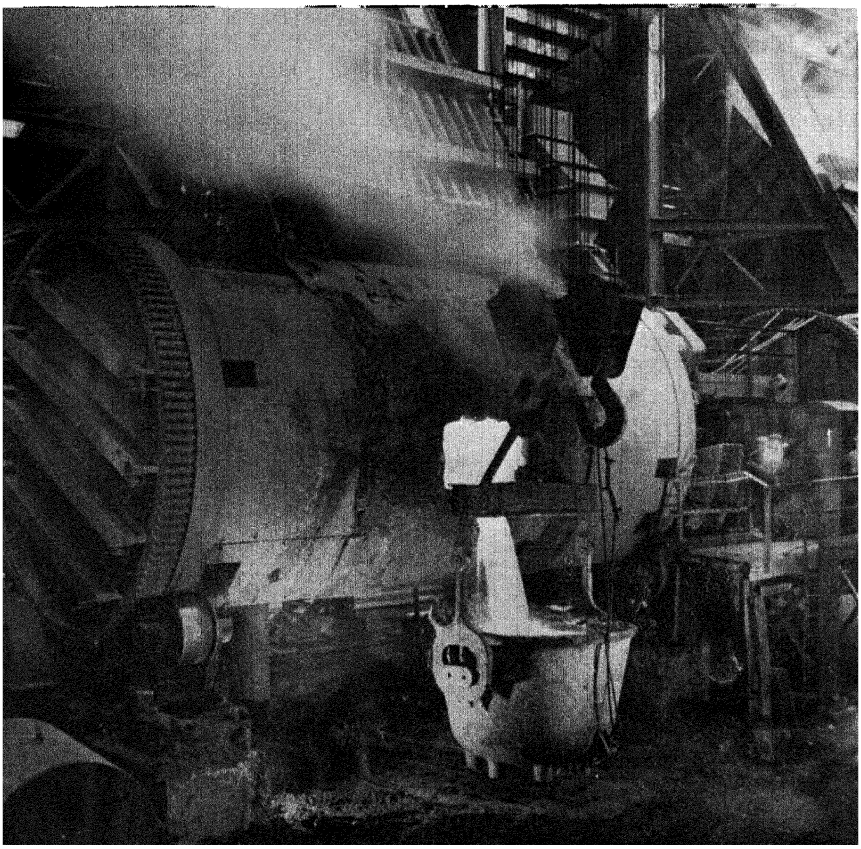
deposited on the cathode. Negative sulfate ions, under the influence of a direct current, travel to the anode, give up their extra electrons, and unite with the copper of the anode, forming more copper sulfate. Thus, while copper from the anode is gradually transferred to the cathode, the concentration of the copper sulfate bath does not change (see Fig. 95).

$$Cu^0 - 2\epsilon \rightarrow Cu^{++}; \quad Cu^{++} + 2\epsilon \rightarrow Cu^0$$

Because copper is higher than either silver or gold in the replacement series, it loses electrons more easily than either of these rarer metals. Hence, while copper goes into solution and is carried to the cathode, the silver and gold do not ionize but sink to the bottom of the tank as sludge. Zinc goes into solution, and arsenic also collects in this sludge. These metals are present in much smaller amounts than copper and require a higher voltage to reduce their ions and

A copper converter in which matte is reduced to form slightly impure, or blister, copper.

Copper and Brass Research Association



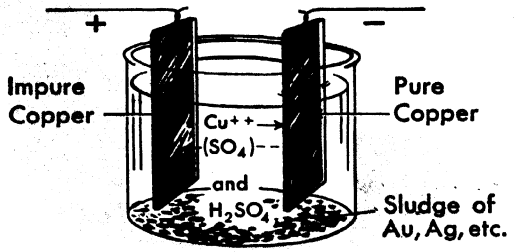


Fig. 95. Electrolytic process for refining copper. How should this diagram be altered to illustrate the copper-plating process?

precipitate them out on the copper cathode. Huge amounts of gold and silver are later extracted from the sludge.

The principle involved in this *electrorefining* of copper is used also in *copper-plating.* The object to be plated is hung from the cathode; the anode consists of a slab of pure copper. As dissociation occurs, a coating of copper gradually builds up on the cathode.

Flotation, a widely used ore-dressing process. One of the most important metallurgical operations introduced in recent years in ore dressing is *flotation,* which was developed in an attempt to concentrate copper ore and get rid of most of the gangue before the ore is chemically treated to obtain its copper. Ores containing as little as one percent copper are processed in the United States. Flotation makes possible economical mining of such ores.

In the flotation process, the ore is crushed and placed in a tank containing water and two chemical agents. The first of these is a frothing agent, such as pine oil, the purpose of which is to create oil-coated air bubbles, when air is blown into the tank. The second chemical is a collecting agent which forms a water repellent film around the particles of metal. The particles attach themselves to the

Adapted from a drawing of Denver Equipment Company

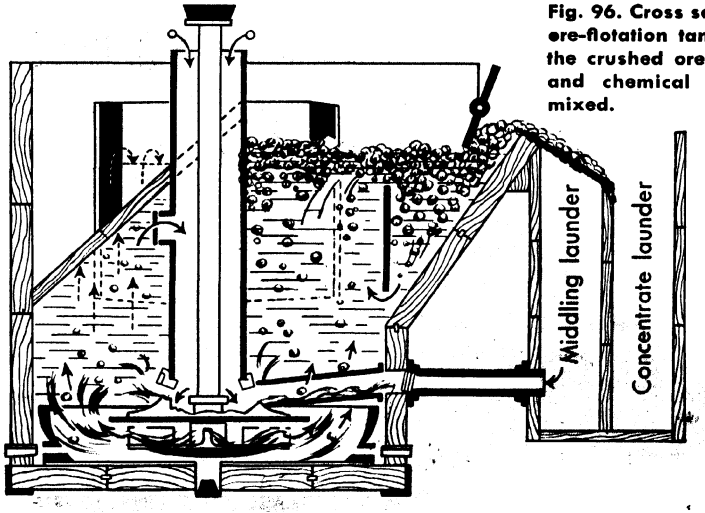
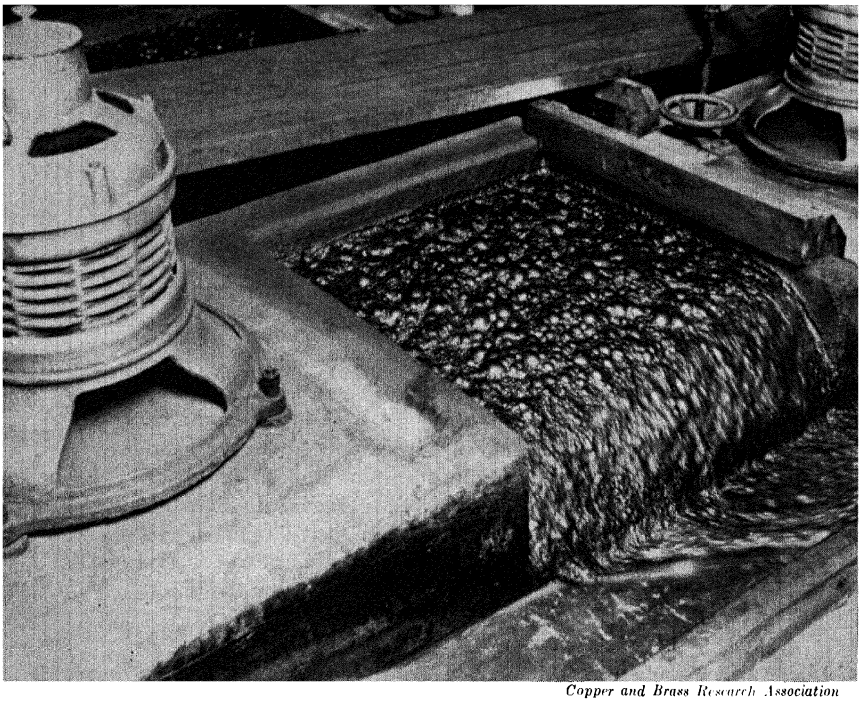


Fig. 96. Cross section of an ore-flotation tank in which the crushed ore, air, water, and chemical agents are mixed.



Copper and Brass Research Association

An ore-flotation tank in operation.

air bubbles and ride to the surface. The froth is then skimmed off and treated chemically to obtain its copper.

One of the pioneers in the discovery of the "affinity of oils and fatty substances for mineral particles" was an American woman, Mrs. Carrie Billings Everson. She patented this process in 1886.

Chemical properties of copper. Copper occurs just below hydrogen in the replacement series. Therefore, it loses electrons less easily than iron, zinc, tin, and the other metals above hydrogen, but more easily than silver, mercury, and gold. Therefore a piece of iron placed in a solution of copper sulfate becomes coated with copper. The copper takes the electrons lost by the atoms of iron which have gone into solution. A strip of silver, on the other hand, when placed in a solution of copper sulfate, remains unchanged.

$$Cu^{++} + SO_4^{--} + Fe^0 \rightarrow Fe^{++} + SO_4^{--} + Cu^0$$
$$Cu^{++} + SO_4^{--} + Ag^0 \rightarrow \text{no reaction}$$

This is made use of in the recovery of thousands of tons of copper each year. Water from the mines containing $CuSO_4$ is passed over scrap iron which is replaced by pure copper.

Dry air hardly affects copper. But when copper is exposed to moist air, it first becomes coated with a thin layer of red cuprous oxide, Cu_2O. The water vapor and carbon dioxide of the air react with this Cu_2O, forming a dull greenish layer of basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$. The greenish coating, or *patina,* on copper roofs, copper pipes, and bronze statues is generally considered to be a basic copper carbonate accounted for by this chemical change and a basic copper sulfate. Both copper oxide and basic copper carbonate act as protective films that prevent deeper corrosion.

Copper unites with nearly all the nonmetals, especially at high temperatures, forming copper salts. Thus, heated copper burns in an atmosphere of chlorine, forming thick clouds of copper chloride.

$$Cu + Cl_2 \rightarrow CuCl_2$$

Since copper occurs below hydrogen in the replacement series, it cannot replace hydrogen in acids. For this reason, hydrochloric acid and dilute sulfuric acid do not attack copper. The oxidizing acids, nitric and concentrated sulfuric, react with copper, yielding not hydrogen, but reduction products of the acids, thus:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow$$
$$Cu + 2H_2SO_4 \text{ (hot conc.)} \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

Why copper exhibits two valences. Copper has two valences, plus one and plus two. The electron theory offers the following interesting explanation of these two valences: in the atom of a heavier element, the electrons are not always arranged in the manner we would expect from its atomic number. For example, in the case of copper (atomic number 29), the 29 electrons outside the nucleus may be distributed as follows:

Cu: Valence of 1	Cu: Valence of 2
2 electrons in first ring	2 electrons in first ring
8 electrons in second ring	8 electrons in second ring
18 electrons in third ring	17 electrons in third ring
1 electron in last ring	2 electrons in last ring

This arrangement occurs because the heavier elements, having larger nuclei, have the power to stabilize more than the normal number of electrons in their inner rings (see page 160). Iron, for example, has valences of two and three, and mercury has valences of one and two.

Because copper has two different valences, it forms *two* series of salts. *Cuprous* salts contain monovalent copper; *cupric* salts contain

divalent copper. The cuprous ion is almost colorless; the cupric ion is bright blue. Under ordinary conditions, cuprous salts are less stable than cupric salts, but at high temperatures, cuprous salts are the more stable.

$$\underset{\text{red}}{2Cu_2O} + O_2 \rightleftarrows \underset{\text{black}}{4CuO}$$

Cupric oxide is used in removing sulfur compounds from crude oil by a method invented by Frasch.

How to test for the cupric and cuprous ions. A simple test for detecting a cupric salt in a solution is to place an iron nail in the solution. A layer of red copper deposited on the nail indicates the presence of the divalent copper ion. Why?

Another test involves the use of ammonia, which immediately turns cupric salts deep blue. Cuprous salts in solution may be identified also by the addition of ammonia water. Cuprous salts will show no color change until the solution is shaken in contact with air. As the cuprous ion oxidizes to the cupric ion, the blue color gradually grows darker.

Copper sulfate, the most important salt of copper. Anhydrous copper sulfate is white, but when it is crystallized from water solution, it unites with five molecules of water and appears as a blue crystal.* When heated, this hydrate loses its water of crystallization (water of hydration), and becomes a white powder. This reaction is reversible.

$$CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 + 5H_2O$$

Copper sulfate is prepared by moving a perforated bucket containing copper in and out of dilute sulfuric acid. Although dilute sulfuric acid has no effect on pure copper, the oxygen of the air reacts with the copper, forming copper oxide, which in turn reacts with the dilute sulfuric acid, forming copper sulfate.

Minute amounts of copper are almost universally found in living cells. Without it man gets anemia, and plants cannot synthesize chlorophyll. In large quantities, however, it is poisonous to lower forms of life. When copper sulfate is added to water, algae and other small water plants are killed. Therefore it is used in the purification of water. Cloth bags containing copper sulfate often are suspended from a boat and pulled through outdoor reservoirs in which drinking water is stored.

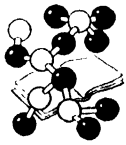
* The names *bluestone* and *blue vitriol* for crystallized copper sulfate are now considered archaic.

An excellent fungicide, it is used also (mixed with calcium hydroxide as *bordeaux mixture*) in spraying fruit trees and potato plants. Copper sulfate is used also in refining blister copper and in copper-plating (see page 427).

How copper is used in printing. The words on a page of this book are first set in type. But type metal is so soft that it wears down in printing more than 25,000 or 50,000 copies. Therefore, a mold of a type page is made in wax. This mold is carefully dusted with a thin coating of graphite. The graphite-covered mold is then hung as the cathode in an electroplating tank. A plate or bar of pure copper is used as the anode and a solution of copper sulfate as the electrolyte.

A direct current of electricity is turned on until a very thin coating of copper has been deposited on the graphite-covered mold. The mold with the attached copper shell is removed from the tank and the wax is melted away. The thin copper shell is backed with an alloy of lead, or type metal, making a plate strong enough to be used in printing. This process of using electricity and copper to make a printing plate from type is called *electrotyping*. The finished plate, known as an *electrotype*, can print more than 100,000 copies.

For long press service or for resistance to abrasive inks, a thin deposit of nickel is made against the graphite-covered wax-mold surface before the copper shell is formed. Such nickel-faced electrotypes are known as *nickeltypes*. Copper or nickel electrotypes may be chromium plated for extremely long press runs or severe service.



YOU WILL ENJOY READING

Doolittle, Dortha B. "Women in Science." *Journal of Chemical Education*, April, 1945, pp. 171–174. Discusses work of Maria Mitchell, Ellen H. Richards, Florence Sabin, Caroline Herschel, and many others.

Thorpe, T. E. *Essays on Historical Chemistry*, pp. 185–205. The Macmillan Co., New York, 1923. The life and work of Michael Faraday are included.



USING WHAT YOU HAVE LEARNED

Group A

1. What properties make Cu the most widely used nonferrous metal?

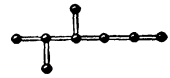
2. (a) What is the chief use of Cu? (b) Why must Cu for most industrial uses be close to 100 percent pure?

3. (a) What are the three most common alloys of Cu? (b) What is the general composition of each?

4. (a) What four areas of the United States produce most of our Cu? (b) In the United States where does Cu occur in the free state?

5. (a) What four steps are necessary to obtain Cu from a Cu_2S ore? (b) Write equations indicating the reactions involved.

6. What are (a) matte, (b) blister copper, and (c) copper sludge?



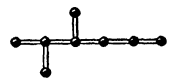
7. (a) Using a diagram and the electron theory, explain the electrorefining of Cu. (b) From what four metals is Cu completely freed by this process? (c) Why does electrorefining of Cu remove these metals? Explain.

8. Describe the ore-flotation process.

9. (a) Under what conditions do bronze statues or copper roofs get a green coating? (b) What compounds of Cu form on their surface?

10. Why is aluminumware often preferred to copperware for kitchen use?

11. HCl has no effect on Cu, whereas HNO_3 dissolves it readily. Why?



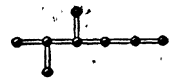
12. On the basis of the electron theory, how are the two valences of Cu explained?

13. How would you tell a solution of a cuprous salt from a solution of a cupric salt?

14. What happens to certain cuprous salts when they are exposed to air?

15. (a) What is the difference between anhydrous $CuSO_4$ and its hydrate, crystallized copper sulfate? (b) How can one of these salts be changed to the other?

16. How do you account for the liberation of SO_2 when H_2SO_4 acts on Cu?



17. How does $CuSO_4$ help in the purification of water?

18. (a) What is bordeaux mixture? (b) For what is it used?

19. Explain the steps in the making of the plates for printing this book.

20. Show how the two oxides of Cu illustrate the law of multiple proportions.

21. Cu is used in making silver coins. Why?

22. What volume of NO is formed by the action of Cu on 126 g. of nitric acid containing 60 percent HNO_3?

23. What is the percentage of Cu in an ore containing 80 percent malachite, $Cu_2(OH)_2CO_3$?

24. What simple method is used to reclaim Cu from the waste water from copper-mining operations?

Group B

25. In plating sheet iron with Ni, why is it necessary to plate the Fe first with Cu?

26. How would you test for the presence of Cu in an aluminum-copper alloy?

27. Using the electron theory, explain why Cu is so effective in reducing HNO_3 to NO.

28. Cu is not attacked by dilute H_2SO_4, yet $CuSO_4$ is prepared commercially by dipping Cu in this acid. Explain.

29. In the electrolytic refining of Cu, why does the Zn impurity not precipitate on the pure Cu cathode?

30. Explain the "transmutation" of Fe into Au as "practiced" by certain unscrupulous alchemists.



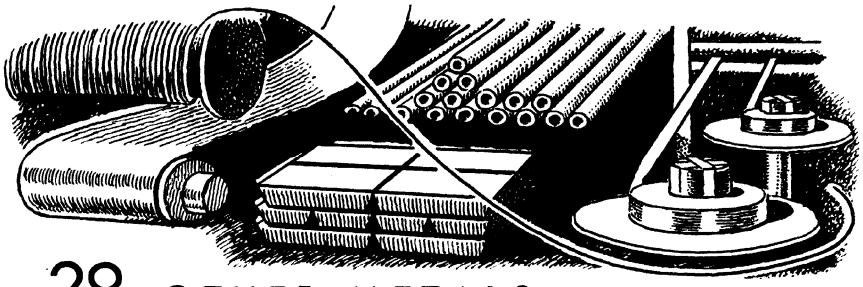
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. In the market quotations of your daily newspaper, find how copper compares in price with steel, Al, Zn, Pb, Sn, Ni, and Cr. Make a graph showing price fluctuations of Cu over a period of a month. Give reasons for this fluctuation.

2. Set up a small copper-plating tank, and demonstrate the process of copper-plating to your class. Why is this process important?

3. Name as many household articles as you can that are made either of pure Cu or of copper alloys. Is Cu indispensable in making such articles? Give reasons for your answers.

4. Write a two- or three-page report on the life of Michael Faraday and his discovery of the principle of the dynamo. How has this discovery affected our way of living?



29 OTHER METALS AND THEIR USES

. . . Iron breathes the air, burns itself up in oxygen and so gives its life that we may live. John Ruskin, 1819–1900

. . . Rust and corrosion mean an enormous loss to Americans, greater than that caused by fire and flood combined, a loss of at least several billion dollars a year. Rust is a skin disease. Corrosion is an infectious internal disease like tuberculosis. Iron Trade.

Have all the elements been discovered? Seventy of the 92 natural elements are metals. Between 1923 and 1945, the six elements necessary to complete Mendeleyeff's periodic table were discovered. Of these, five turned out to be metals. Two Italian investigators, C. Perrier and Emilio Segre, obtained element 43, *technetium,* in 1937. This was the first synthetic element ever created. In 1940, element 85, *astatine,* was produced in the cyclotron, and during the research on nuclear fission, 1940–1954, eight new elements (Nos. 93–100) were produced in the United States (see page 187). Three of the most widely used metals — iron, copper, and aluminum — have already been discussed. In this chapter we shall not consider most of the remaining metals, many of which are extremely rare and from our point of view relatively unimportant, but shall focus our attention upon those whose abundance, properties, and uses make them more or less familiar.

How science fights corrosion of metals. Rust and corrosion are two great destroyers of property. As soon as most metals are exposed to air, water, or chemicals, an attack is launched upon them. Rust attacks their surfaces, and corrosion eats its way into most metals.

Science battles corrosion and rust with various weapons, the most important of which are: (1) putting a coating of a more resistant

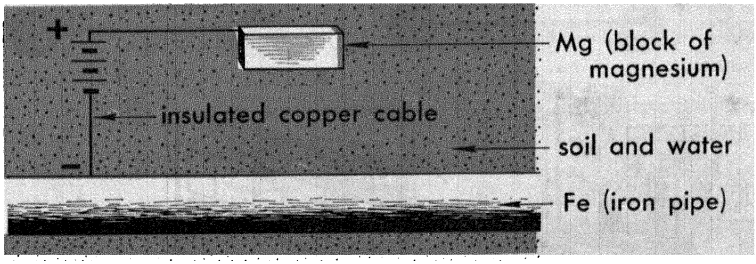
metal such as zinc, tin, chromium, nickel, silver, cadmium, and gold, over a less resistant one; (2) alloying a metal to form a product that is more resistant; (3) covering a metal with a thin film of its oxide or with a coating of paint, lacquer, or enamel; (4) adding some organic inhibitor such as sodium chrome glucosate to the radiator of a car to prevent corrosion of the cooling system; and (5) sacrificing one metal to protect another in *cathodic protection.* The active metal magnesium protects the less active metal iron from corrosion due to small, local electric currents. Buried iron pipelines are protected from corrosion by attaching to the iron pipes blocks of magnesium metal by means of an insulated copper cable (see Fig. 97). Magnesium anodes or an impressed electric current is used to protect canal gates, water tanks, and the metal bottoms of our moth-ball fleet lying in several waters.

A powerful film to protect sheet iron. Tin is a soft, white metal that melts at a comparatively low temperature (232°C.) but, compared with other metals, it is highly resistant to oxidation by air and to acids found in certain kinds of foods, such as fruit and tomatoes. Furthermore, tin is scarcely affected by dilute hydrochloric or sulfuric acids.

Because of its chemical inactivity, tin is used extensively in covering light-gauge sheet steel to protect it from corrosion. First, the steel is scoured with sand, then pickled in dilute sulfuric acid, and washed thoroughly to remove the acid. It is then dipped in a bath of molten tin, on which is a layer of oil that prevents any oxidation of the steel during the tin-plating process. Most of this *tin plate* is used in the manufacture of tin cans for food canning and the oil industry. The weight of tin in a tin can produced by this *hot dip process* is hardly more than one percent of the weight of the can.

Tin plate is also produced electrolytically by a new process developed as a result of the tin shortage during World War II. This process is much faster than the older hot dip process and deposits the

Fig. 97. Cathodic protection of buried iron pipe.



tin in thinner, more even coatings, thus saving more than one million pounds of tin a year. In this process, tin anodes are used to supply the tin for plating the cold-rolled steel strip that forms the cathode. As much as 1000 feet a minute can be coated with a film only 30-millionths of an inch thick.

Tin is used also in making bronze, solder, Babbitt metal, and *pewter,* an alloy of 75 percent tin and 25 percent lead used commonly during Colonial days for tableware. The comparatively high cost of tin prevents its more extensive use. Tin salts are used for weighting silk.

Little or no tin is mined in the United States; we are dependent for our entire tin supply on mines in Bolivia, Indonesia, and British Malaya.

Tin has two valences. The *stannous* ion has a valence of two and the *stannic* a valence of four. (Consult Table 14 for other facts about the metals discussed in this chapter.)

Nickel and nickel-plating. Nickel, a silvery-white metal, is not oxidized by dry air and is only slowly attacked by moist air. It is therefore used extensively for plating. Nickel resembles tin in that it is scarcely affected by hydrochloric or sulfuric acids. Nickel-plating is done electrolytically, using a nickel anode, and a nickel salt as electrolyte. The metal is used also as a catalyst in the hydrogenation of oils, in the nickel-alkali storage battery (*Edison cell*), and in the cadmium-nickel alkaline storage battery.

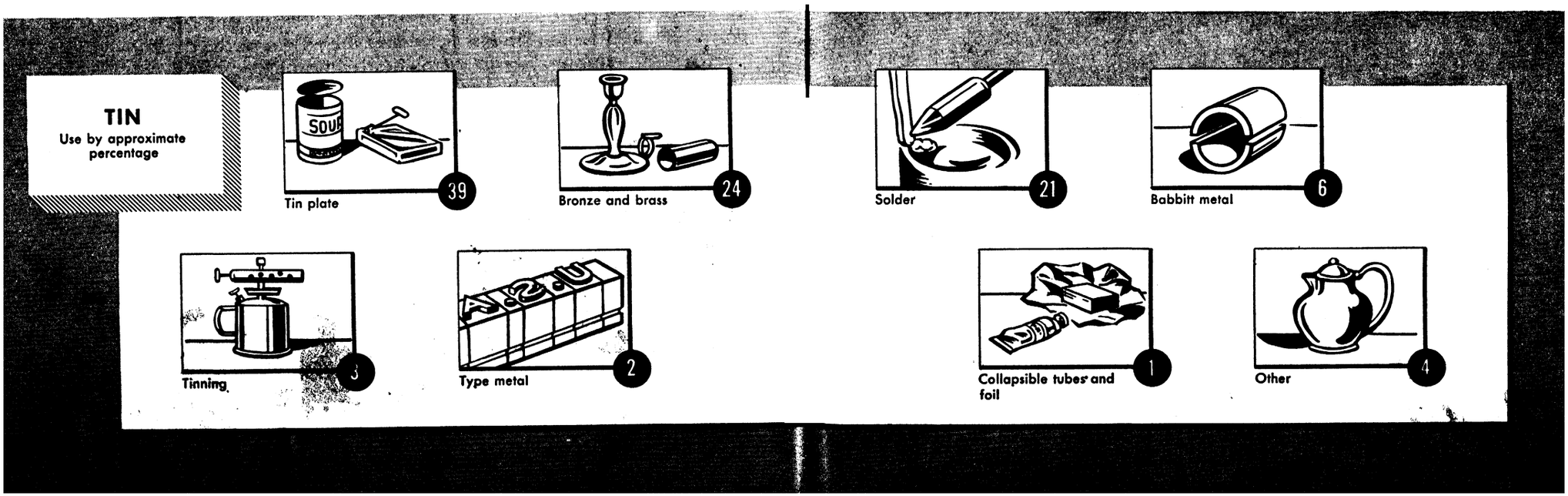
Nickel alloys and cobalt are important. "Monel metal," which contains 70 percent nickel, 28 percent copper, and two percent iron, is a

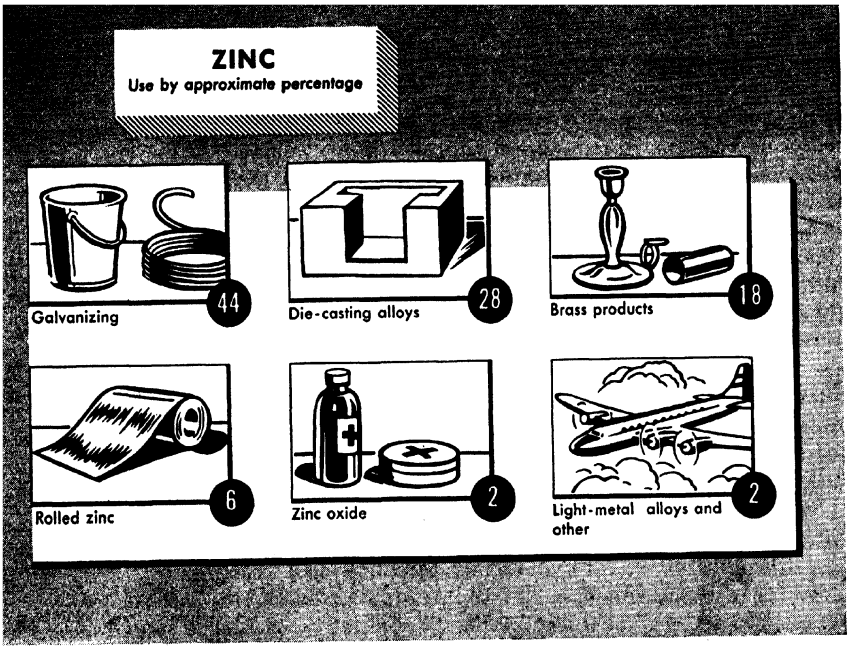
strong, acid-resisting alloy used extensively. It is only one of the many important nickel allies on the nonrust battlefield. Our own five-cent piece contains 25 percent nickel alloyed with copper. Coins used in more than 20 countries are pure nickel.

Many steel alloys contain nickel. "Invar," which expands very little on heating and is therefore used for lead-in wires in electric-light bulbs, and in instruments that measure accurately, is a steel alloy containing 35 percent nickel. "Permalloy" and "Hipernik" are steel alloys containing high percentages of nickel. Because these alloys are more magnetic than iron, they are used in transformers. "Alnico," a family of nickel alloys that contain nickel, iron, cobalt, and aluminum, can lift 500 times their own weight of iron. Alnico magnets are used in radio and TV receivers, and in magnetic tape recorders.

An even more powerful magnet is made of platinum and cobalt, a metal closely related to nickel. Cobalt is a very strategic metal used in many important alloys. The *stellites* made of cobalt, chromium, and wolfram are used for high-temperature, high-speed cutting tools. *Vitallium* containing cobalt, chromium, and molybdenum is used in jet engines and gas turbines which are subjected to extremely high temperatures.

Chromium, the tarnishproof plating. Chromium is used in a number of very important steel alloys. Its extreme hardness, high luster, and very high resistance to corrosion, have brought chromium to the forefront as a plating metal. Automobile headlight shells, bathroom fixtures, and tarnishproof jewelry, are only a few of the articles now plated with chromium rather than with nickel. The electrolyte used





in this plating is chromic acid containing a catalytic agent. Nichrome is an alloy of nickel, iron, manganese, and 11 percent chromium.

Chromium is obtained by reducing chromite, $Cr_2O_3 \cdot FeO$, with aluminum

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$ (see *thermit process*)

or by electron reduction. Though neither fuming nitric acid nor even aqua regia attacks chromium, warm dilute sulfuric acid or hydrochloric acid reacts with it, liberating hydrogen.

$$2HCl + Cr \rightarrow CrCl_2 + H_2 \uparrow$$

Chromium has several different valences, ranging from two to six. Most chromium salts are highly colored (*chroma* means *color*).

Zinc and galvanized iron. One of the oldest methods of protecting iron from rust and corrosion is to coat it with zinc. This is done in one of three ways: (1) immersing sheet iron that has been pickled and then thoroughly cleaned in a bath of molten zinc; (2) depositing zinc on the iron electrolytically; (3) packing the article to be coated in zinc dust and heating to about 300°C., a process called *sherardizing*. The zinc condenses onto the metal.

Although zinc is higher in the replacement series than iron, it acts as a protective coating, because the thin layer of zinc oxide or zinc carbonate that forms on exposure to air sticks to the metal.

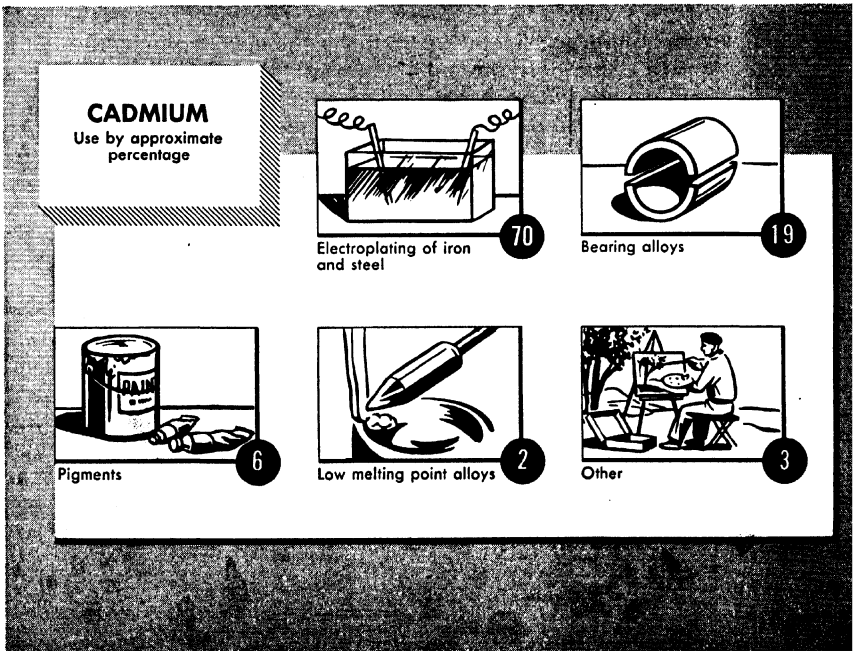
This coating prevents further corrosive action, thus protecting the easily corroded iron. Iron coated with zinc is the familiar *galvanized iron* used in making pails, cans, and pipes. The cathode of all dry cells is made of zinc. Large quantities of zinc are used also in the alloys bronze, brass, and nickel (German) silver.

Zinc dust catches fire when heated and burns with a bright light, forming zinc oxide, ZnO. This oxide, under the name *zinc white,* is used in making paints and in the manufacture of automobile tires — its high heat-conductivity helps to keep the tire cooler and thus prolongs its life. It is also used in zinc ointments, face powders, deodorants, and similar cosmetics where it furnishes covering and antiacid and adhesive properties.

How zinc is freed from its ores. Zinc is not found free. Its chief ore is *zinc blende,* ZnS. Its metallurgy is simple. After first concentrating the ore by flotation, the ZnS is roasted to convert it into the oxide. This oxide is then mixed with finely powdered coal and heated in clay retorts. This process reduces the zinc oxide to zinc. The zinc vaporizes, and is then condensed into a solid, melted, poured into ingots, and sold as *spelter.*

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \uparrow$$
$$ZnO + C \rightarrow Zn + CO \uparrow$$

Natural gas, instead of coal, is also used as the reducing agent. The advantages of this newer process are: (1) natural gas is found



nearer zinc mines than coal; (2) a lower temperature is sufficient to reduce the ZnO; (3) the process is continuous rather than intermittent. The chief chemical reaction is:

$$ZnO + CH_4 \rightarrow Zn + CO\uparrow + 2H_2\uparrow$$

Cadmium resembles zinc. Many zinc ores contain from one to two percent of a metal that closely resembles zinc in appearance and properties. This metal, cadmium (Cd), is freed from its ores in the same manner as zinc. Cadmium is somewhat harder than zinc and is superior to zinc as a plating metal, because the finished plate is free from the pinholes so frequently found in zinc plate. Why do pinholes lessen the effectiveness of zinc-plating?

The chief use of cadmium is in electroplating. Coatings of cadmium one-third as thick as zinc provide as much protection. It is used also in making the yellow pigment, CdS, for paints and printing inks. Alloys of cadmium are used extensively in making bearings and for other uses in which a relatively low melting point is desired.

Silver, the noble white metal. Silver, which is very low in the replacement series, occurs free (usually alloyed with gold) as well as in a variety of ores, chief of which is the sulfide of silver, *argentite*. This ore is roasted, and the oxide is reduced with charcoal.

When silver is found as part of a lead sulfide ore, it is separated from the lead by the *Parkes process,* in which the ore is roasted and then reduced to a silver-lead alloy. To this molten alloy about two percent of zinc is added. Silver, being very much more soluble in zinc than in lead at the temperature of the molten alloy, mixes with the zinc and rises to the top of the melt. The silver-zinc mixture is then skimmed off and heated, and the zinc is distilled off.

Silver is called the *white metal* because it can be obtained as tiny white crystals. It is the best-known conductor of heat and electricity and, next to gold, the most malleable and ductile of all metals. Oxygen has no effect upon it, but ozone oxidizes it. Why?

$$6Ag + O_3 \rightarrow 3Ag_2O$$

Removing tarnish from silverware. The tarnishing of silver exposed to air is caused by the formation of a film of brownish-black silver sulfide, Ag_2S, formed by the action of the sulfur or sulfur compounds in air or in food (yolk of eggs, mustard). This tarnish may be removed by heating the tarnished silverware in a water solution of table salt, and washing soda, Na_2CO_3, in contact with aluminum. Because an aluminum pan is badly stained by this process, it is

preferable to use either a piece of aluminum in an enameled pan or else a cheap aluminum pan. The hydrogen that is liberated reduces the silver sulfide to pure silver. The cleansing action may be represented by the following chemical equations:

$$3Na_2CO_3 + 3H_2O + 2Al \rightarrow 2Na_3AlO_3 + 3CO_2 + 3H_2$$
$$H_2 + Ag_2S \rightarrow 2Ag + H_2S \uparrow$$

Flannel cloth impregnated with silver phosphate protects silverware wrapped in it. H_2S attacks the silver phosphate instead of the silverware. Silver behaves like copper in the presence of the common acids (see page 431).

Silver in jewelry and coinage. Because of its high cost and pleasing appearance, silver is used in jewelry and coinage. Because it is too soft to stand hard usage, it is alloyed with copper to make more durable coins. The amount of silver in alloys is stated in terms of *fineness,* which indicates the number of parts of silver in 1000 parts of the alloy. American silver coinage is 900 fine; that is, it contains 90 percent silver and ten percent copper. Sterling silver is 925 fine, containing only 7.5 percent copper.

At one time, China and India required much of the exported silver for use as a monetary standard. What is the present price of silver in the United States?

Silver-plating. The making of silver-plated articles, especially tableware, consumes much of the silver produced annually. The process of silver-plating is similar to copper-plating. The article to be plated is hung from the cathode. A sheet or bar of pure silver is used as the anode. The electrolyte is a solution of silver potassium cyanide which, although extremely poisonous, is used instead of other electrolytes because it gives the most even and durable coating (see illustration on page 444). The manufacture of silver chloride and silver bromide, used in photography, required more than 400 tons of silver in a recent year.

Silver is now employed more widely by industry than by the arts in the United States. Silver alloy brazing of airplane, radar, and radio parts is responsible for this shift.

Gold, the yellow metal that resists corrosion. Gold, which is found in the free state, was known to the earliest civilizations, as evidenced by the golden ornaments of elaborate workmanship which they have left to us. The gold fields of Nubia and of Asia Minor were the sources of the riches of Croesus, wealthy king of ancient Lydia in Asia Minor, who lived about 2500 years ago. Gold is obtained in various parts of the world from quartz veins which must be crushed,

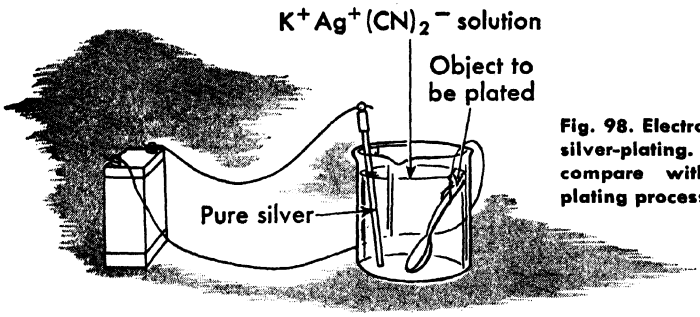


Fig. 98. Electrolytic process of silver-plating. How does this compare with the copper-plating process?

and from river sands or gravels. Today the greatest center of gold production is the Transvaal in Africa.

When gold occurs in river sands or gravels, the mining operation, called *placer mining*, is simple. About three-fourths of the world's gold is obtained by placer mining. The gold prospector tests his "dirt" by panning, that is, stirring the sand with water in a pan to enable the heavy gold to settle to the bottom. A single pan in the Klondike sometimes yielded a pound of pure gold. The largest gold nugget ever found was picked up in Victoria, Australia, in a wagon rut only a few inches below the surface of the ground. It was called *Welcome Stranger*, and weighed 157 pounds.

Gold ores usually contain silver also. The two are separated by adding nitric acid in which only the silver is soluble. Gold is often refined electrolytically (see pages 427–428), the electrolyte being a solution of gold chloride containing some hydrochloric acid.

Gold is not attacked by air, water, or any one of the common acids. Gold dissolves in aqua regia, going into solution as gold chloride. Alkali cyanides, such as highly poisonous sodium cyanide, NaCN, also dissolve it. About 60 percent of the gold in gold ore is extracted by mercury, with which gold forms an *amalgam* (page 446). NaCN is used to remove the remaining gold from the ore.

Gold in jewelry and coinage. Like silver, gold is used in jewelry and coinage. Because of its softness it is alloyed with copper to produce greater hardness. Gold coins formerly used in the United States contained ten percent copper. For 100 years the American gold dollar was backed by 23.22 grains of pure gold (1 troy ounce = 480 grains). Franklin D. Roosevelt in 1934, under powers conferred upon him by the Congress, changed the gold content of the dollar to 13.71 grains, worth slightly more than 59 cents of the former dollar. The price of gold was changed from $20.67 per troy ounce to $35.

The purity of gold is measured in *carats*. Pure gold is 24 carat. Eighteen-carat gold, used extensively in jewelry is 18/24, or 75 percent gold. About one-half of the gold mined each year is stored to back up currency; the rest is used in the arts and crafts.

Gold-plating and other uses of gold. Much jewelry and many other small objects are made of one of the cheaper metals plated with gold. Gold-plating on an object prevents tarnishing and makes possible a brilliant polish. Gold-plating is carried out in the same way as silver-plating. The anode is pure gold and the electrolyte is gold potassium cyanide. *Liquid gold,* used to decorate pottery and earthenware, is an organic salt of gold dissolved in various oils and applied to the surface of the glaze. After firing, a brilliant film of metallic gold is left. *Gold leaf* is used also for decorative purposes, for lettering bookbindings, letters on windows, and the like. *White gold* is an alloy of gold and some other metal such as palladium or nickel. Much gold is used in the production of electric equipment and in color photography.

Mercury, the only liquid metal. Occurring in small amounts in the free state but obtained easily from its ores, the metal mercury was known to the ancients. *Cinnabar,* HgS, a brownish-red compound, is the chief ore of mercury. The chemistry of its extraction is simple. The ore is heated to vaporize the mercury. The vapor is then condensed, purified, and shipped in flasks of 76-pound capacity.

So dense is mercury (density = 13.6 grams per milliliter) that iron floats on it. Mercury remains unchanged in dry air, oxygen, and carbon dioxide.

As you know, when mercury is heated, it changes to red mercuric oxide, HgO, which upon further heating decomposes back into its elements. It was this simple chemical change that led Lavoisier to the true explanation of burning. Dilute nitric acid readily attacks mercury, and, in general, mercury reacts with the acids much as copper does.

$$3Hg + 8HNO_3 \rightarrow 3Hg(NO_3)_2 + 2NO\uparrow + 4H_2O$$

Westinghouse Electric Corporation



A research scientist placing pure gold wire around the valve opening of a vacuum tank used in the production of zirconium. Gold was the only material found satisfactory in making an air-tight, high-temperature, corrosion-resistant seal.

Mercury combines directly with sulfur and the halogens. It is sometimes mixed with metals forming mercury alloys, called *amalgams*. One such amalgam contains silver, and is used by dentists to fill teeth.

Adding one valence electron produces a poison. The element mercury has two valences and hence forms two series of salts. Mercurous chloride, HgCl, is a white crystalline salt, *calomel,* used in medicine. Mercuric chloride, $HgCl_2$, also is a white crystalline compound. It is a violent poison and is known as *bichloride of mercury,* or *corrosive sublimate.* It is such a powerful germicide that it destroys all known bacteria. The Hg^{++} ion is poisonous, but the Hg^{+} ion is not. Mercury compounds, formerly used in hatmaking, produced mental disturbances. Hence the term "mad as a hatter." "Mercurochrome" is an antiseptic consisting of a complex organic compound containing 23 percent mercury.

From measuring instruments to turbines. Mercury, also known as *quicksilver,* is commonly used in thermometers, barometers, and other scientific instruments. It is used in preparing the mercury salts mentioned above as well as in making *mercury fulminate,* $Hg(CNO)_2$, an unstable compound used as a *detonator* for explosives (see page 270).

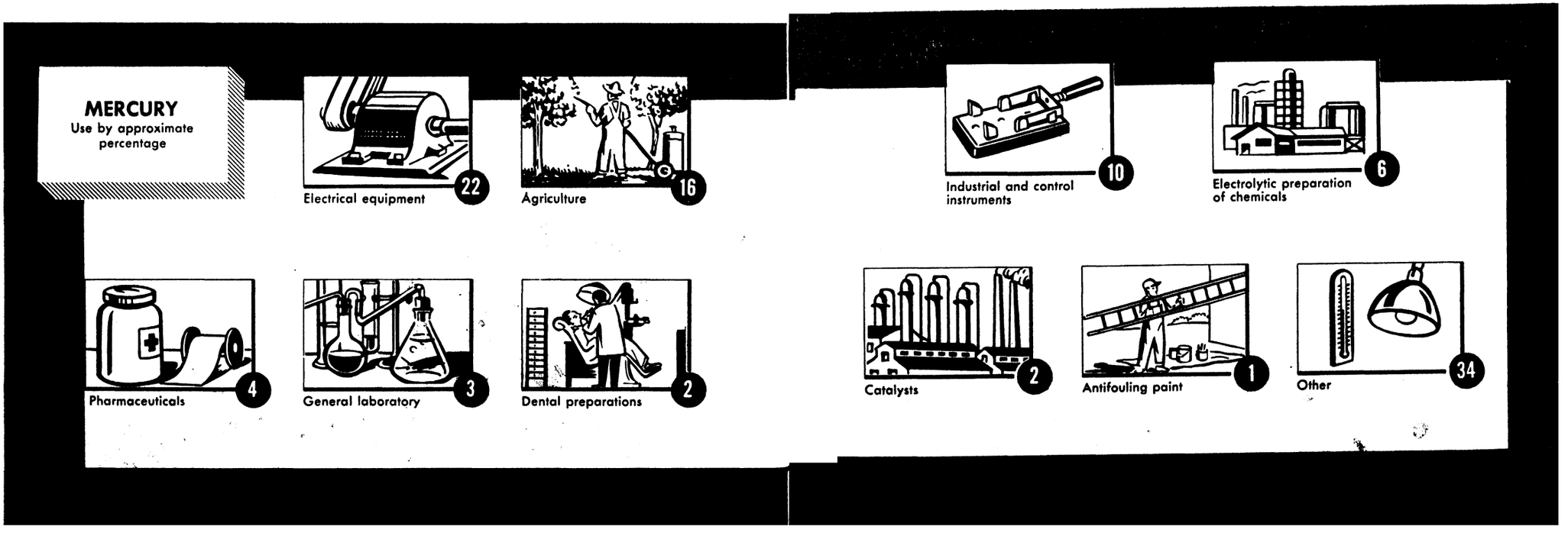
Mercury may be used in boilers and turbines. A huge electric generator using mercury vapor instead of steam, is in operation in Schenectady, New York. The mercury vaporizes at high temperatures

and its vapor drives a turbine. The exhaust mercury vapor passes through a steam boiler in which its high temperature produces superheated steam, which, in turn, drives a steam turbine. The system is *closed* and the process is continuous; mercury is condensed, returns to the mercury boiler, and is again vaporized.

Sunlight and fluorescent lamps. Other uses of mercury are in sunlight and fluorescent lamps. In the sunlight lamp an arc is formed between two wolfram electrodes in the bulb, and the pool of mercury that is vaporized gives off light rich in ultraviolet radiations, which have health-promoting value. Radiations from such lamps also kill airborne and surface bacteria.

Mercury is used in the mercury vapor lamp employed in photography and in mercury vapor vacuum tubes that are used as *rectifiers* to convert alternating current (ac) to direct current (dc). Such tubes are used in storage-battery chargers, in a-c radios, and in other installations requiring the conversion of alternating current to direct current.

The fluorescent lamp is one form of "electric discharge" light source. It consists of a tubular bulb with an electrode sealed in each end. A flow of electricity takes place through a drop of mercury that has been vaporized. The ultraviolet light produced causes certain powders, called *phosphors,* that adhere to the walls of the tube to *fluoresce,* that is, to emit visible light while absorbing the invisible ultraviolet radiations. Almost any color or tint can be produced by



mixing these *phosphors,* such as zinc silicate or magnesium tungstate. Phosphors are also used to coat TV, radar, and x-ray screens. A moving beam of electrons excite and light up the phosphors.

Fluorescent lamps are much more efficient than hot-filament lamps. The hot-filament, or *incandescent,* lamp is really more a heater than a light source. Light is produced only by heating the filament to incandescence. More than 90 percent of the electricity supplied is consumed in heating the filament and less than ten percent is used in producing light. Fluorescent tubes are more than three times as efficient as incandescent lamps; that is, they give more than three times as much light for the electricity consumed.

Lead and manufacture of white lead. Lead, a slightly lustrous, bluish-white, soft and malleable metal, occurs free very rarely. When exposed to air, it is quickly coated with a protective layer of lead oxide or lead sulfide. Lead reacts slowly with most corrosive acids.

Excessive amounts of lead salts form cumulative poisons that may affect the entire human body, especially the nervous system. The dangers of lead poisoning were known for a long time. Wedgwood, the famous maker of glazed pottery and friend of Priestley, wrote in 1775, "I will try in earnest to make a glaze without lead," and he did. Lead poisoning, once a serious occupational disease, is now less common, thanks to mechanical safeguards and humanitarian legislation.

The principal uses of lead, listed in order of the quantities consumed, are storage batteries, cable covering, tetraethyl lead for gasoline, and pigments (litharge and white and red lead). Lead is also used for pipes, tank linings, nuclear reaction and x-ray protective plates, shot, reaction chambers for the manufacture of sulfuric acid, and in alloys such as solder, type metal, Babbit metal and terne metal (sheet iron covered with a layer of lead-tin alloy).

The manufacture of white lead was carried on as early as 300 B.C. From an old manuscript of this time, the following description is given: "Lead is placed in earthen vessels over vinegar, and after it has acquired a rust, they open the vessel and scrape it off. Then they beat it to a powder and boil it." This is essentially the method used in the *Old Dutch process.* The chemical reactions involved are:

1) Lead reacts with vinegar (acetic acid), forming lead acetate.

2) Lead acetate reacts with carbonic acid, formed by the fermentation of tanbark which is placed over the earthenware pots, and white lead is formed. The average composition of white lead is $Pb(OH)_2 \cdot 2PbCO_3$.

Modern production methods, such as the Carter and Sperry processes, are improvements on the Old Dutch process. These newer



Lead Industries Association

The television tube shown here being welded contains as much as 30 percent lead by weight.

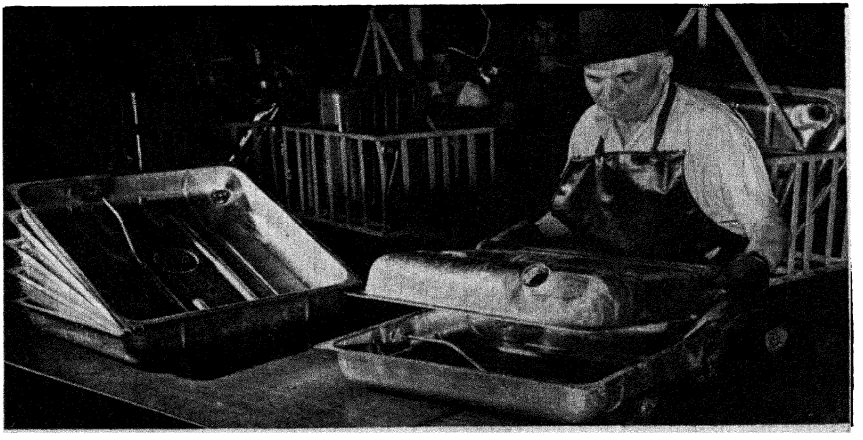
methods have cut down the time required in the manufacture of white lead from a few months to a few hours.

Hiding is desirable in paint. Paint is essentially a mixture of *body pigment* and a *liquid vehicle.* To these may be added a *thinner* to reduce the mixture to painting consistency, a *drier* to accelerate the *drying* of the vehicle, and a *tinting,* or *coloring, pigment.*

Linseed oil, obtained from flaxseed, is the most commonly used vehicle, or *medium.* During the drying process, it polymerizes with the aid of the oxygen of the air, forming an elastic, impervious, horn-like film. Tung oil, from the Chinese tung tree, and soybean oil are

Non-corrosive automobile gasoline tanks, made from terne-plate, a lead-tin alloy.

Lead Industries Association



often used instead of linseed oil. Turpentine is the most commonly used thinner. It evaporates after the paint has been applied. Among the most frequently used driers are certain oxides, such as MnO_2 and Pb_3O_4, and certain metallic soaps, all of which act catalytically to hasten the drying process. Colored pigments include such chemical compounds as yellow cadmium sulfide, CdS; chrome yellow, $PbCrO_4$; Venetian red, Fe_2O_3; carbon black; Prussian blue; and red lead, Pb_3O_4, which is the standard protective paint for iron and steel.

A frequently used body pigment, or base, is white lead. This opaque compound is ground with linseed oil and the required amount of drier, color, and thinner. A *filler,* or *extender,* is an inert material added to paint to give greater bulk and decrease cost. Common fillers are $CaSO_4$, $BaSO_4$, kaolin, fine white sand, and $CaCO_3$. However, when used in excessive amounts, fillers impair the life of the paint film.

In the production of paints, one of the chief objectives is the achievement of hiding power, or the ability to cover completely the underlying surface. For this purpose titanium dioxide, TiO_2, a white pigment with a high whitening power, is added to the paint mixture.

The element titanium occurs abundantly in the United States in the ore *ilmenite,* $FeTiO_3$. Titanium dioxide is produced from ilmenite, without the production of titanium as a metal, by several chemical reactions ending in large rotary kilns. In addition to being used in paints, titanium dioxide is also used extensively in the production of paper products of high opacity, in making linoleums, rubber articles, cosmetics, glass, and so forth.

Lead and storage batteries. The lead storage cell is a device for changing chemical energy into electric energy. In a six-volt storage

battery, there are three cells. It contains a lead plate with pockets of spongy lead as the negative electrode, and a lead plate with pockets of lead peroxide, PbO_2, as the positive electrode.

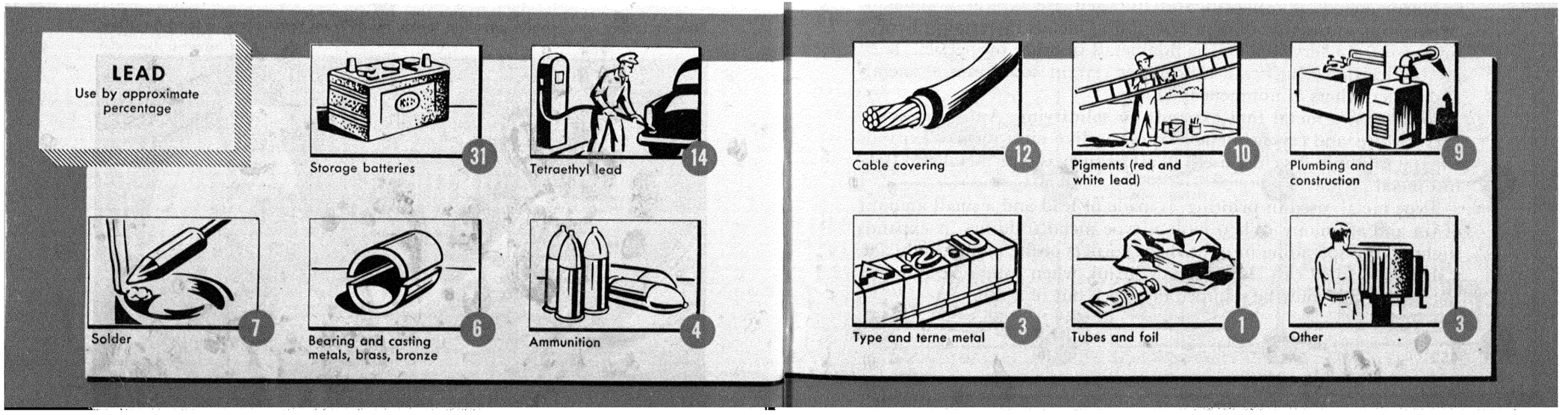
Both plates are immersed in a dilute solution of sulfuric acid (sp. gr. 1.2). When the exterior terminals of the plates are connected by a copper wire, the chemical changes that take place cause a transfer of electrons that produces an electric current. The spongy lead gives up electrons which travel to the PbO_2. We say that the current moves from the plus pole to the minus pole. *Actually, however, the flow of electrons is from the negative to the positive pole.* As the battery is used, both plates become covered with $PbSO_4$. The changes that occur during the *discharge* of the cell are:

Negative plates: $Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2\epsilon$
Positive plates: $PbO_2 + H_2SO_4 + 2H^+ + 2\epsilon \rightarrow PbSO_4 + 2H_2O$

As you can see, each of these reactions removes some H_2SO_4 which changes to H_2O, and the electrolyte, therefore, becomes more and more dilute, and its specific gravity falls. Hence, we can test the strength of the cell by testing the specific gravity of the solution by means of a hydrometer (see Fig. 100). When the cell has run down, as indicated by the dilution of the electrolyte, it can be recharged by passing a direct electric current through it in the opposite direction. This reverses the reactions given above.

A storage battery should not be discharged completely, nor charged or discharged too rapidly. Why? Water must be added to replace the water lost through gradual evaporation, and chemical action.

Bismuth helps fight fire. Bismuth is a white, lustrous, brittle metal with slightly reddish tinge. It occurs both free and combined. It is



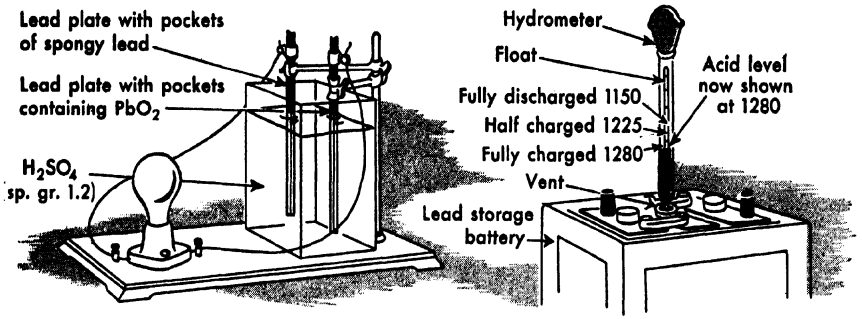


Fig. 99. The lead storage cell. **Fig. 100. Testing a storage battery.**

used chiefly in making low-melting-point alloys such as *Wood's metal,* which contains 50 percent bismuth and melts at 60°C. Electric fuses, safety plugs in boilers, and other automatic devices for protection against fire or explosion contain this metal. If a fire breaks out in a building equipped with automatic water-sprinklers, a temperature of 60°C. is reached quickly. The bismuth alloy in the plug then melts, setting a stream of water loose and at the same time breaking an electric circuit, which sends out a fire alarm.

Bismuth subnitrate, $Bi(OH)_2NO_3$, is used for digestive disturbances, and as a suspension for x-ray of the digestive tract because it is opaque to x-rays. Cosmetics containing bismuth compounds may be dangerous since the compound, bismuth subnitrate, hydrolyzes in contact with perspiration, forming nitric acid. A fungicide spray composed of a bismuth compound is effective against mildew diseases of tobacco, potato, and other plants.

Bismuth, antimony, and arsenic occur in the periodic table (see page 162) in the same group as phosphorus and nitrogen. Bismuth is a true metal; phosphorus and nitrogen are typical nonmetals. Arsenic and antimony, though resembling metals in certain physical properties, are very close to the nonmetals in other properties. They are borderland elements, acting under certain conditions as metals and under others as nonmetals.

Antimony, a metal that expands on solidifying. Antimony is silvery, brittle, and crystalline and, quite unlike most metals, expands when it solidifies. Its chief use is in alloys such as type metal and Babbitt metal.

Type metal, used in printing, is made of lead and a small amount of tin and antimony. When molten type metal solidifies, it expands slightly, thus spreading into the sharp corners of the mold, producing a sharply defined cast. Most metals shrink when solidified and cannot be cast but must be stamped or struck out of a die.

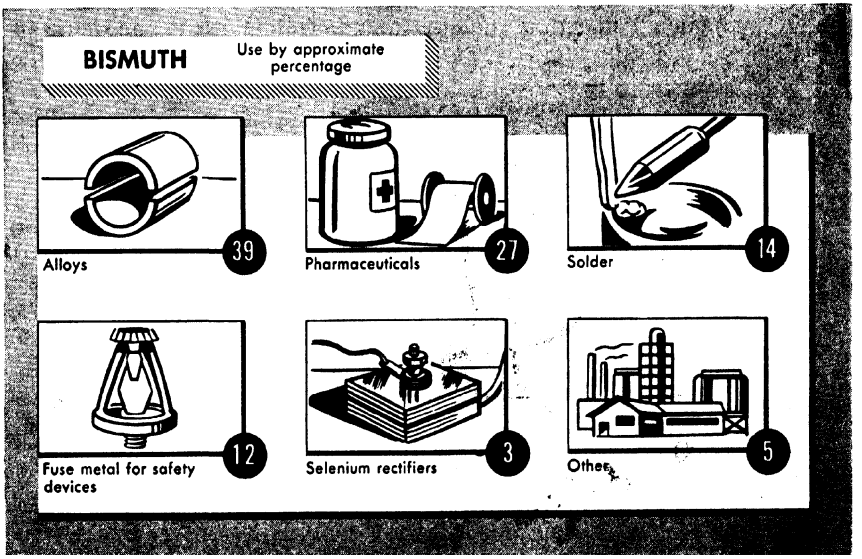
Babbitt metal, named after its American inventor, Isaac Babbitt, contains antimony and tin and a small amount of copper. It is used in making anti-friction bearings for machinery. Compounds of antimony are used to make canvas and other textiles rotproof and fireproof. Antimony preparations were used as medicinal agents back in the Middle Ages.

Arsenic, a poison and a preservative. Arsenic is a steel-gray, brittle, metallic-looking solid that is found both free and combined. Like bismuth, it is seldom used as the pure element. Lead shot is made harder by the presence of one percent of this metal. When heated in air, it forms arsenic trioxide, exhibiting, like bismuth and antimony, a valence of three toward oxygen.

$$4As + 3O_2 \rightarrow 2As_2O_3 \text{ (white arsenic)}$$

White arsenic is a powder that is used in glassmaking and as a preservative in the mounting of skins. The poisonous nature of the compounds of arsenic is used in man's battle against the insect pests which, by attacking his cattle and crops, cause losses of billions of dollars yearly. Insects destroy approximately ten percent of man's food and fiber crops each year. Suspensions of *lead arsenate* and *calcium arsenate* are widely used agricultural insecticides for spraying. *Paris green* is an arsenic salt of copper.

Arsenic compounds are stomach poisons and are used against insects that eat foliage. Contact insecticides such as lime-sulfur and nicotine dust are employed against sucking insects. The great advantage of calcium arsenate is its low price which makes possible its use in cotton fields against the destructive boll weevil. It also kills the



tomato worm. Lead arsenate is effective against insects that attack fruits, flowers, and shrubs. Fruits and vegetables exposed to excessive amounts of such poisonous sprays should be carefully and thoroughly washed before being eaten raw or cooked.

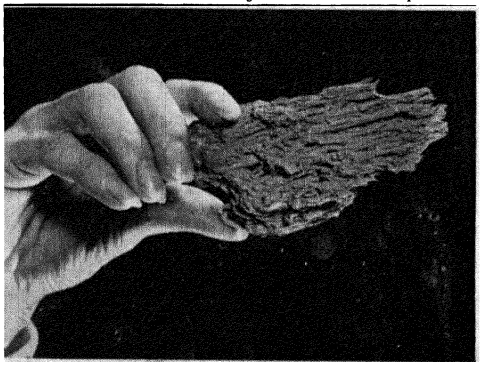
Platinum, one of the very heavy metals. Antonio de Ulloa (dā-o͞ol-yō'ä), 200 years ago, described a strange metal that he had seen in Peru. Because its value was not appreciated then, it was used to adulterate gold. When a heavy gray nugget of this metal was brought to Europe and studied carefully, it was found to be a new element, platinum.

The properties of platinum make it very valuable. It is very resistant to corrosion. Like gold, platinum is attacked only by aqua regia, which dissolves it, forming platinum chloride. Platinum crucibles and dishes should not be used for melting alkalies or metals of low melting point, since platinum is attacked by these substances. Because of its high resistance to the passage of electricity and its high melting point (1750°C.), platinum is used in making electric furnaces, resistance thermometers, spark-plug tips, rayon spinnerets, and x-ray and radio tubes.

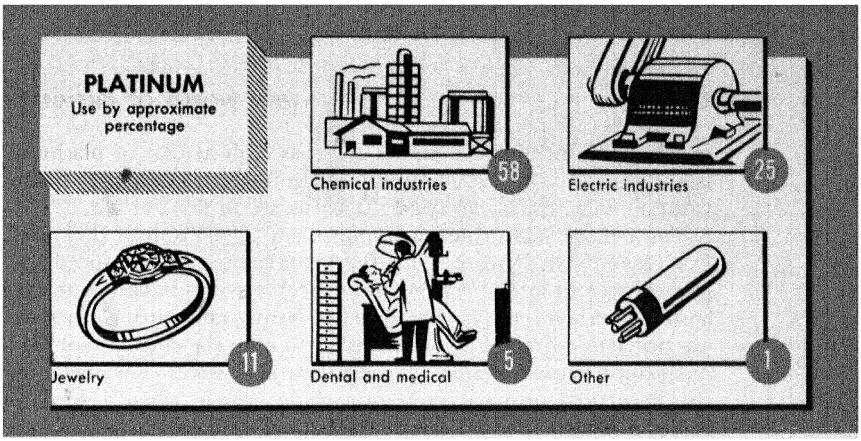
One of platinum's most important uses is as a catalyst in the contact process for manufacturing sulfuric acid, and in making nitric acid by the oxidation of ammonia. Because of the rarity, beauty, and durability of platinum, it is widely used in making jewelry. Surgeons use it to replace parts of bones, and dentists use it in bridgework. Platinum salts are used to make photographic prints more permanent and beautiful than those made by the use of silver salts.

Platinum has a density of 21.45 grams per cubic centimeter. Together with the other members of the heavy metal family (iridium, osmium, ruthenium, rhodium, and palladium), it is mined in the

Westinghouse Electric Corporation



This hard, gray, coke-like lump is titanium sponge, the mid-point in the production of commercially useful titanium metal from rutile, ilmenite, or other ores.



gravels of river beds, chiefly in the Ural Mountains in the Soviet Union and in Canada. Some platinum is mined in Brazil, and in this country in California and Oregon.

In the hope of freeing itself from the necessity of using metals, such as platinum, which are both expensive and subject to wide fluctuations of price, industry has turned to new alloys that are cheaper to produce. This technological war among the metals has multiplied the kinds of materials available for man's use and has ushered in the age of alloys. In this war of the metals, less well-known metals have come into wider use.

Many "rare" metals are really very abundant. Titanium, zirconium, vanadium, wolfram, and tantalum are actually more abundant than lead in the earth's crust. Zirconium is more than twice as abundant as copper, and thirteen times as plentiful as lead. It is highly resistant to many acids and is used in our submarine nuclear reactors because it is a low neutron absorber. Some new casting alloys contain this metal. Titanium, fourth most abundant metal and newest of the structural metals, is about half as heavy as steel, resists seawater corrosion better than steel, and has great tensile strength. Like zirconium, it is highly reactive at high temperatures, becoming brittle and hard to handle. Gallium, 150 times as abundant as silver, melts at body temperature and expands on solidification.

One of the reasons these so-called *rare metals* are still not widely known has been the difficulty of extracting them cheaply from their ores. However, as one recent writer put it, "It is not improbable that many of the present well-known metals may, within the next half century, become outmoded in favor of certain of the relatively more abundant but less-known metals of today."

Wolfram, the metal used in electric-light bulbs. Wolfram's original name was *tungsten*, a misnomer since the element is a metal. This steel-gray, heavy metal, three times as hard as platinum and with a

melting point (3300°C.) almost twice as high as that of platinum, has gradually replaced platinum in the electric industry. Today, wolfram filaments in electric-light bulbs are in general use.

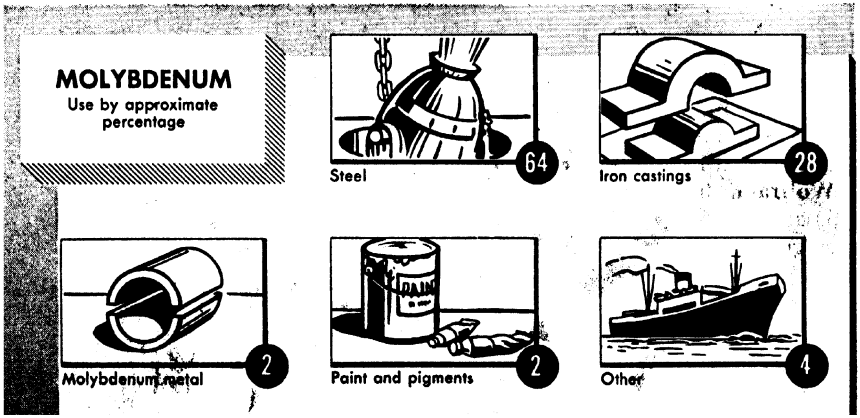
The United States consumed more than 12,000 tons of this metal in a recent year, most of it for the manufacture of high-speed tool steel alloys and machinery. Wolfram steel is not only hard but stays hard even when red hot. The speed of boring and cutting machines was previously limited by our inability to keep the cutting tool cold. As the tools became heated, they lost their keen edges. This metal has also been used to make wolfram carbide, which, when welded together in the form of millions of minute particles (cobalt being the welding agent), makes an excellent abrasive known as "Carboloy."

Molybdenum, tantalum, germanium, and beryllium. Molybdenum (Mo) is similar to wolfram in physical properties, but its melting point is lower (2500°C.), and its lower cost has made it an active competitor of wolfram in the electric field, and in the making of high-speed tool steel alloys. Bartlett Mountain in Colorado holds about 95 percent of all the world's known store of molybdenum.

Tantalum (Ta) is another recent addition in the electric field. It is a corrosion-resisting metal resembling lead. Its price is only one-fifteenth that of platinum, and already uses have been found for it in electron tubes, neon tubes, surgical and dental instruments, acid-proof coils, electric contacts, art metal, and in the spinnerets used in synthetic textile manufacture.

Germanium crystals are used in tiny transistors which have recently replaced vacuum tubes for many uses in electronics.

Beryllium (Be), the fourth lightest element, is another newcomer that has found its greatest use in copper alloys. These alloys are used in making certain tools and springs. Beryllium alloy springs retain their resiliency remarkably well.



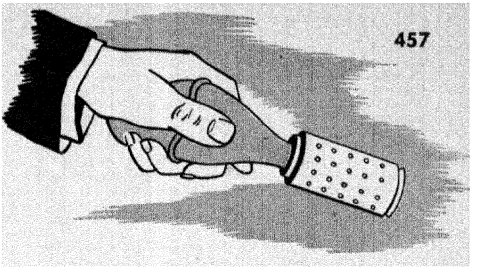
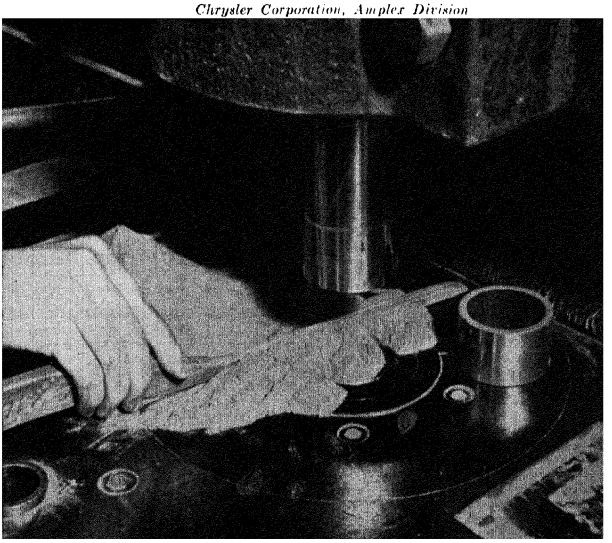


Fig. 101. Demonstration of the principle of oil-retaining bearings. When the aspirator bulb is squeezed, oil wells up in the pores of the bearing to form a protective coating.

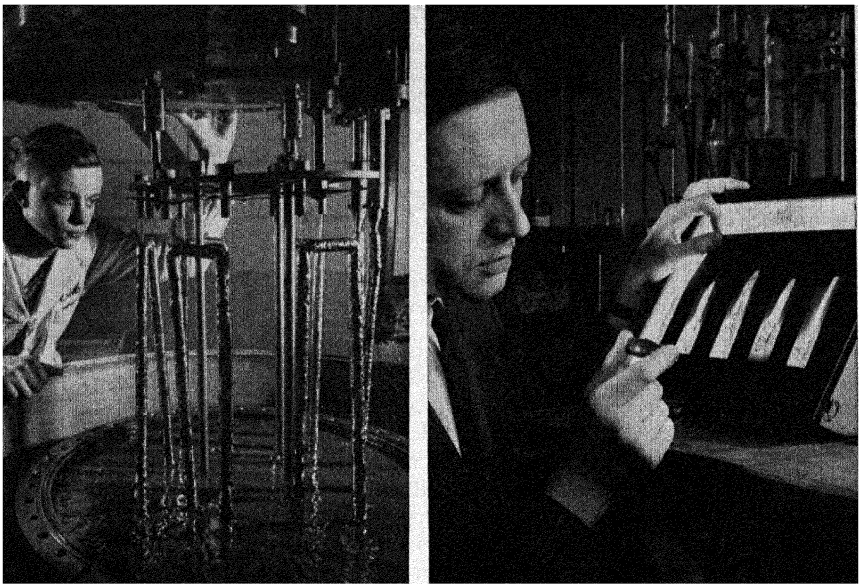
Powder metallurgy. Most metal products are made by casting the molten metal in molds, by machining a block of the metal to the desired shape, or by a combination of casting and machining. But metal products in great quantity are being made by a newer process that consists of (1) pressing metal powder or a mixture of metal powders into form, and (2) baking this compressed metal powder form in a *sintering furnace*. Metal products so produced are porous but of great strength. Wolfram filaments for electric lamps and electron tubes are made by sintering powdered wolfram and hammering the resulting product into very fine but porous wires. Wolfram carbide cutting tools are also made by this process.

Among the many interesting metal products made by sintering are porous bearings that can be filled with oil and yield enough lubrication for the life of the equipment. Squeeze the bearing, and oil wells up from its pores. Release the pressure and the oil flows back into the bearing. Such bearings are called *oil-retaining bearings* and generally are pressed from tin, copper, and graphite. Under great strain, they provide the greatest quantity of lubrication; under slight strain, very little. The oil in the bearings is not affected by extremes of temperature.

Chrysler Corporation, Amplex Division



An operator filling a "die well" with metal powder. When the well is filled with powder, the upper punch will move down, compressing the powder into a cylindrical bearing such as that shown.



Westinghouse Electric Corporation *Bell Telephone Laboratories*

(left) Hairpin-shaped bars of 99.9 percent pure zirconium emerge from the vacuum tank in which they have been produced. (right) A scientist studies x-ray plates to determine the structure of the single crystal of germanium which he holds.

New frontiers in metallurgy. During the first fifty years of the twentieth century, the number of metallic elements used commercially has more than tripled. Research has been responsible for this great surge in the use of metals. For example, our nuclear energy program has resulted in the discovery of new metals such as plutonium and in the commercial production of such metals as zirconium and beryllium; jet engine research has produced a variety of high-temperature alloys using the "new" metals as well as substances known as *cermets,* a combination of metal and glass or other ceramics.

But despite the advances which have been made, metallurgy remains a great challenge to man's ingenuity. Fully a third of the known metals are waiting for the chemist who can contrive methods of producing them in large quantities for the service of mankind.

Nor is the problem provided by metals whose metallurgy is still unsolved the only mystery left. The metals in general use today are never pure. Even the so-called *commercially pure* metals contain small but important amounts of impurities. "Pure" gold, for example, contains as much as 0.4 percent copper and other substances. Only recently have science and industry begun to explore the preparation of truly pure metals in which the impurities may, in some cases, be less than one part in 100 million.

Even a trace of impurity greatly affects the behavior of a metal. Tiny crystals of virtually pure iron produced in the laboratory have been found to be remarkably flexible and to possess a tensile strength of almost a million pounds per square inch, far beyond that of any commercial alloy or metal.

As yet, no simple inexpensive commercial method of producing such pure metals has been developed although many are now under study. Titanium and zirconium, which show the characteristics of commercially valuable metals only when they are extremely pure, are produced by the Kroll process, named for Wilhelm Kroll who developed it for the U.S. Bureau of Mines. The key step in the process is the reduction of a chloride of the metal by molten magnesium in an inert atmosphere or vacuum. This process is still not regarded as entirely satisfactory. If successful methods of producing pure metals in quantity are discovered, it will undoubtedly be possible for metallurgists to create an entirely new series of metal alloys with strength, heat and corrosion resistance, and other properties much superior to anything now produced. The field of the pure metals represents another great frontier in metallurgy to be explored by the chemists of the future and offers a worthwhile inspiration to today's students of chemistry.

Metals are unequally distributed over the earth. Metals were distributed over the earth without regard for nations. Many countries lack essential metals and must import them from foreign sources. The United States, for example, must import part or all its supplies of antimony, chromium, cobalt, manganese, mercury, nickel, platinum, tin, wolfram, and vanadium (see Table 13 below).

This unequal geographical distribution of the metals has in times of peace brought nations closer together in friendly trade. It has also, unfortunately, caused some nations to embark upon imperialistic ventures, during which regions rich in various natural resources have been seized and exploited. It has encouraged conservation and also spurred scientists to find substitutes such as plastics for these essential metals. Shortages of metals have also led to thorough research in the extraction of metals from ores previously considered too poor in metal content.

TABLE 13. METALS NORMALLY IMPORTED BY U. S.
(In Approximate Percentage of Consumption)

Mercury	100	Chromite	90	Manganese	82	Wolfram	80	Antimony	44
Nickel	92	Tin	82	Platinum	81	Cobalt	78	Vanadium	40

TABLE 14. FACTS ABOUT METALS

A study of this table will help you to organize and remember what you have learned about these metals.

METALS		SOURCES	CHIEF ORES	METALLURGY	CHIEF USES	ALLOYS
Antimony	Sb	Mexico, Bolivia, China, U.S.	Sb_2S_3 (stibnite)	Roast, reduce	Type metal	Babbitt metal
Arsenic	As	U.S., Canada	As_2S_3 (orpiment)	Roast, reduce	Insecticides	Lead shot
Bismuth	Bi	Germany, U.S.	Free and combined	(mp 271° C.)	Low mp alloys	Wood's metal
Cadmium	Cd	U.S., Mexico	CdS (greenockite)	Roast, reduce	Electroplating, bearings	Wood's metal
Chromium	Cr	Turkey, Rhodesia, U.S., Philippine Is.	$FeO \cdot Cr_2O_3$ (chromite)	Reduction with Al	Plating	Chrome steel
Cobalt	Co	Belgian Congo, Canada	$CoAs_2$ (smaltite)	Aluminothermy	High temperature alloys	Alnico
Gold	Au	South Africa, U.S.	Free condition	Placer, cyanide	Jewelry, coinage	24 carat (pure)
Lead	Pb	Mexico, U.S.	PbS (galena)	Roast, reduce	Batteries, tetraethyl lead	Type metal, solder
Magnesium	Mg	Available all over the world	Sea water, $KMgCl_3 \cdot 6H_2O$ (carnallite) $MgCO_3 \cdot CaCO_3$ (dolomite)	Electrolytic	Structural products	Aluminum alloys
Manganese	Mn	Russia, South Africa, India, U.S.	MnO_2 (pyrolusite)	Aluminothermy	Steel and aluminum alloys	Dowmetal G
Mercury	Hg	Spain, Italy, U.S.	HgS (cinnabar)	Roast, distill	Thermometers	Amalgams
Nickel	Ni	Canada, New Caledonia, Russia	Complex ores	Heat with CO, decompose $Ni(CO)_4$	Plating, coinage	Monel metal
Platinum	Pt	Russia, Canada, U.S.	Free condition	(mp 1750° C.)	Catalysts	Platinum-iridium
Silver	Ag	Mexico, U.S.	Free and Ag_2S	Parke's process	Coinage, cutlery	Sterling
Tin	Sn	Malay States, Indonesia, Bolivia	SnO_2 (cassiterite)	Reduction (mp 232° C.)	Tinware	Solder, pewter
Titanium	Ti	U.S., India, Norway	$FeTiO_3$ (ilmenite), TiO_2 (rutile)	Kroll process	Pigments, alloys	manganese titanium chromium titanium
Wolfram	W	China, Burma, U.S., Spain, Portugal	Wolframite and scheelite ($CaWO_4$)	(mp 3300° C.)	Electric bulbs, tool steels	Tungsten steel
Vanadium	V	Peru, U.S.	V_2S_5 (patronite)	Reduction	Tool steels	Crocar
Zinc	Zn	U.S., Belgium	ZnS (zinc blende)	Roast, reduce	Galvanizing	Bronze, brass



YOU WILL ENJOY READING

Chemistry, Jan., 1945, pp. 21–22. Contains a very interesting account of several "rare" elements which are plentiful.

U.S. Department of Agriculture. *Painting on the Farm.* Bull. No. 1452. Supt. of Documents, Washington, D.C. 5¢.

Weeks, Mary E. *The Discovery of the Elements.* American Chemical Society, Easton, Pa., 1945. This scholarly and well-illustrated book tells the story of the discovery of the elements and something about the discoverers.



USING WHAT YOU HAVE LEARNED

Group A

1. Copy and complete. Do not write in this book. Eight of the last elements discovered were produced by Americans. The symbols for elements 93–98 are .... Of all the elements ... are metals. The most important metals used for coating other metals are ..., ..., ..., ..., and Au. The chief ore of Sn is .... The most common ore of Pb is .... Hg is usually obtained from cinnabar, whose formula is .... The symbol for wolfram is ....

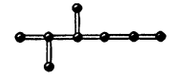
2. What is the difference between rusting and corrosion?

3. (a) What are the three general methods for protecting metals from rusting and corrosion? (b) Why should steel articles be oiled thoroughly before being stored?

4. Compare the process of tin-plating, nickel-plating, and galvanizing.

5. (a) Tin cans are not made of pure Sn. Why? (b) Name two highly magnetic alloys.

6. (a) What is the composition of our silver coins, (b) of gold coins formerly used in the United States, and (c) of sterling silver?



7. What are two reasons for the rapid development and widespread use of chromium-plating?

8. Using an equation, explain the metallurgy of Cr.

9. Using equations, describe the metallurgy of Zn, starting with its sulfide ore.

10. (a) What metal does Cd resemble? (b) For what is it used? (c) Why?

11. Compare the methods used in the purification of Cu, Zn, and Hg.



12. (a) What are five metals that were known to the ancients? (b) Why were these metals known to them?

13. Explain chemically the formation of tarnish on silverware.

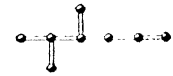
14. Using equations, discuss a chemical method for cleaning silverware.

15. Using a diagram, show how you would silver-plate a spoon.

16. What is placer mining?

17. How does a jeweler tell pure Au from brass?

18. What is 14-carat gold?



19. What are (a) liquid gold, (b) gold leaf, and (c) white gold?

20. What two properties of Pt make it very valuable to industry?

21. For what two reasons have chemists made an effort to find substitutes for Pt?

22. (a) What is the melting point of W? (b) Name its chief uses.

23. Compare the properties of the two chlorides of Hg.

24. (a) How is Hg used in fluorescent lighting? (b) What are the advantages of fluorescent lighting?

25. (a) Describe a recently introduced piece of apparatus that makes use of both Hg and W. (b) What are phosphors?



26. Using word-equations, describe the manufacture of white lead.

27. What types of substances do all paints contain?

28. (a) Name four elements that appear in the nitrogen group in the periodic table. (b) What property have they in common?

29. What effect would the sudden exhaustion of sources of Sb have upon one particular industry?

30. What are three metals in addition to As whose compounds are poisonous?

31. How is Pb used in the chamber process of manufacturing H_2SO_4?

32. Using a diagram, describe the construction of a lead storage battery.

33. How does the use of the word *carat* in connection with Au differ from its use in connection with diamonds?

34. Cu, Ag, and Au appear in the same group of the periodic table. Why?

35. Why are lead paints not used in chemical laboratories?

Group B

36. How would you prepare (a) $ZnSO_4$, (b) $ZnCO_3$, (c) $AuCl_3$, and (d) As_2O_3?

37. Why is it dangerous to smoke around batteries that are being charged?

38. The bottoms of ships are often painted with HgO. Why?

39. What is the function of a flux in soldering?

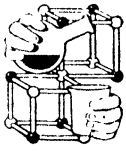
40. Pure Zn does not dissolve in dilute H_2SO_4. Commercial Zn reacts readily with this acid. Explain.

41. The atomic number of Hg is 80, and that of Au is 79. The transmutation of Hg into Au has been accomplished. Explain.

42. For what are the following metals used? (a) Ti, (b) Zr, (c) Be, (d) Ge, (e) Co.

43. (a) Discuss powder metallurgy. (b) For what are the products of this process used?

44. In the fight against metal corrosion the process of cathodic protection has lately been introduced. Explain this process.

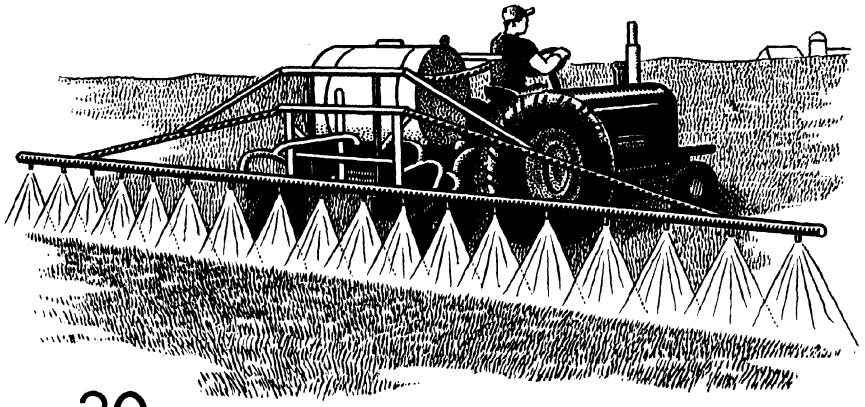


PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make a collection of ores of as many metals as you can find in the community in which you live. What do you conclude from a study of your collection?

2. Consult your teacher of history or economics and write a two- or three-page report on the present gold and silver policies of the United States.

3. Write a report on the way in which you or your father or some friend takes care of the lead storage battery in your car. Include in your report such items as charging and discharging, checking, and testing the specific gravity of the electrolyte.



30 FERTILIZERS AND SALTS OF SODIUM

A farmer with his potash locked up in silicates is like the merchant who has left the key of his safe at home in his other trousers. He may be solvent, but he cannot meet a single draft. It is only solvent potash which plants can use. E. E. Slosson, 1919

Liebig used chemistry in agriculture. Fertilizers, as you know, are composed of substances that must be replenished in the soil to prevent plant starvation. Soils have been fertilized from time immemorial with manure, fish scrap, dried blood, wastes from slaughterhouses, bird excrement (*guano*), and bones. The practice of the ancients was based not upon chemical knowledge but upon their general observation that crops thrived better if grown on land supplied with refuse or decayed organic matter of any kind.

Justus von Liebig, who made many contributions to organic chemistry, and whose name is commonly linked with the Liebig condenser, is generally regarded as the father of agricultural chemistry. In 1840 he tested his new theory of soil fertility on a barren piece of land near Giessen, Germany. Year after year he kept on feeding the soil with only mineral fertilizers, including nitrates, phosphates, and potassium salts, until it was as fertile a spot as could be found in all Germany.

With one blow Liebig overturned the firmly rooted belief that plants thrive only on manure or other organic matter. He proved that they would also thrive on soluble salts containing potassium, phosphorus, and nitrogen. He showed that "since plants assimilate

potassium, nitrogen, and phosphorus, these elements must necessarily be resupplied to the soil." Other men followed this pioneer work. One of these investigators, Sir John Lawes, started the Rothamsted Experiment Station at Harpenden, England, now the most famous agricultural experiment station in the world.

The fight to save topsoil. Erosion and an exhaustive system of cropping have taken terrific toll of the soil in many parts of the United States. Fifty million acres of land in this country have been so ruined. In part, this has been caused by the destruction of forests and the poverty of some farmers who were forced to "eat up" their soil by not returning to it the elements necessary for its fertility.

The practice of *contour farming,* that is, farming around a hill or slope and not in straight lines, holds water as it falls, and helps to prevent further erosion. Strips of close-growing crops, such as grasses, planted between other strips of cultivated crops, such as wheat and corn, also help to hold the topsoil. This is known as *strip cropping.* Plowing under green-manure crops, such as alfalfa and sweet clover, helps both to keep rich soil in good condition and to improve poor soil. In addition, the generous use of irrigation and commercial fertilizers is essential to the success of farming.

Krilium is the trade name for a number of soil conditioners which help erosion control by making clay-like soil porous and friable. It also raises its water-holding capacity and improves root penetration. It is a synthetic, negatively-charged particle which is adsorbed on clay forming small lumps which bind the soil together, and cannot be washed out like most natural soil conditioners.

Potassium salts for fertilizers. Plants require sulfur, iron, calcium, magnesium, manganese, silicon, copper, boron, zinc, and minute

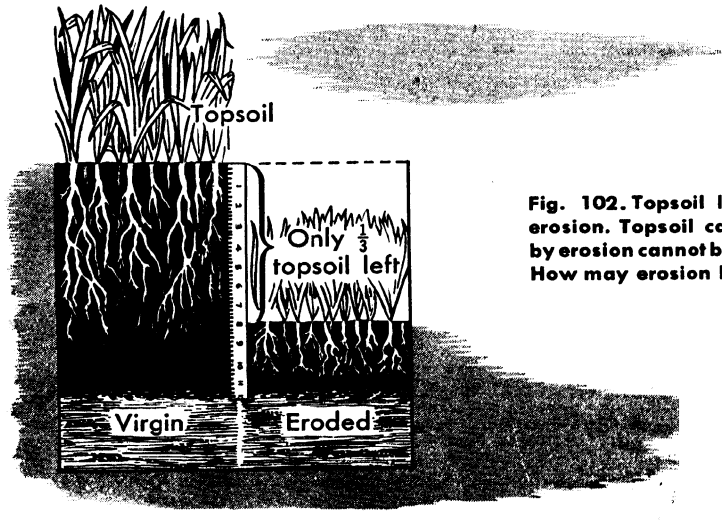


Fig. 102. Topsoil lost through erosion. Topsoil carried away by erosion cannot be recovered. How may erosion be retarded?

quantities (*traces*) of other elements for growth. However, the three elements most often lacking in sufficient quantities are nitrogen, phosphorus, and potassium. For example, if potassium salts in the soil in which potatoes have been planted are insufficient, the resulting crop will illustrate very strikingly the *potash hunger* of the potato.

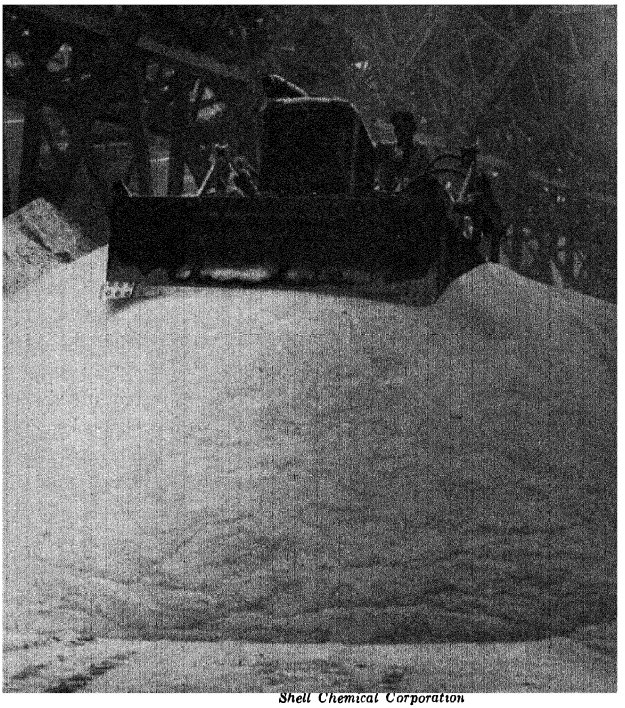
Our potash problem. In early days, because our land was fertile, there was no potash problem. In fact, for many years the principle export commodity of the American Colonies and the newly formed United States was crude potassium carbonate, K_2CO_3, obtained by washing out (leaching) this chemical from wood ashes in pots by means of water. This industry started as early as 1608 in Jamestown, Virginia, and continued until rich European deposits were discovered about the time of the War Between the States. At this time huge deposits of potassium salts began to be developed from the salt mines at Stassfurt, Germany. Here in layers hundreds of feet thick, is an almost inexhaustible supply of soluble potassium in the form of *sylvite*, KCl, and *carnallite*, $KCl \cdot MgCl_2$.

When World War I brought home to us our extreme dependence upon foreign countries for our supplies of potassium salts, we began to look for domestic sources, and found them. In the 25 years between World Wars I and II, the combined efforts of the U.S. Government and private agencies succeeded in building up an industry that freed us from foreign supplies.

Our main sources are the huge underground deposits of KCl and K_2SO_4 in Carlsbad, New Mexico, and Texas. Searles Lake, an inland sea in the Mohave Desert, contains 36 percent salt of which one-fifth is KCl. Other minor sources are the ashes of kelp (a giant seaweed

This demonstration plot shows how fertilizers help crops grow and halt erosion. *U.S. Department of Agriculture*





A stockpile of ammonium sulfate which can be used either as a fertilizer or in the manufacture of other ammonium salts.

Shell Chemical Corporation

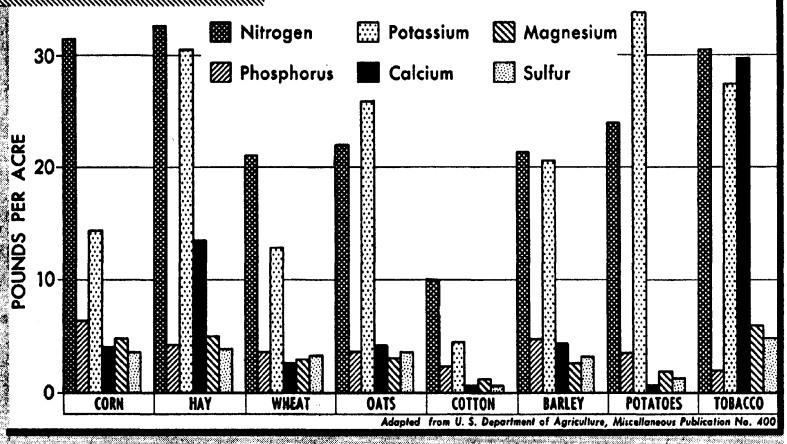
off the coast of California which also contains iodine), sugar beet wastes, basic lining of steel furnaces, and the dust of cement works.

The future of our fertilizer industry. The fertilizer industry is one of our basic industries. Today the fertilizer manufacturer, dependent more and more upon mineral sources, is learning to compound fertilizers from them in order to meet the requirements of each kind of crop. To save freight charges, these fertilizers are being put on the market in a highly concentrated condition.

"Ammophos," ammonium phosphate, made by combining ammonia, NH_3, and phosphorus pentoxide, P_2O_5, is such a fertilizer. Some others, such as potassium ammonium phosphate, contain all three of the elements necessary in a *complete fertilizer.* A complete fertilizer for sugar beets now on the market is a 4-12-6 fertilizer. This means four percent nitrogen, 12 percent P_2O_5, and six percent K_2O.

Will feldspar be a future source of potassium? One of the most common rock-forming minerals in this country is *feldspar,* composed of potassium aluminum silicate, $KAlSi_3O_8$. This mineral is a tremendous untapped storehouse of potassium. Partly because feldspar is insoluble in water, chemists have not yet succeeded in getting its potassium into soluble form inexpensively. A solution to the problem would give us an inexhaustible supply of potassium, and also bring

TABLE 15.
FOOD ELEMENTS REMOVED FROM THE SOIL BY VARIOUS PLANTS



a fortune to the man who finds it. Incidentally, feldspar is rich also in aluminum, but thus far no one has yet been able to devise a method to extract the metal from it at a cost low enough to be competitive with the Hall process.

Potassium nitrate, KNO_3, chief constituent of gunpowder. With the introduction of gunpowder, potassium nitrate became a much needed chemical. Gunpowder is a mixture of carbon, sulfur, and potassium nitrate. When ignited, tremendous volumes of gases and vapors are produced suddenly, thus giving it explosive power. The high temperature at which the reaction occurs increases these tremendous volumes enormously. The equation for the explosion of gunpowder may be written:

$$2KNO_3 + 3C + S \rightarrow K_2S + N_2 + 3CO_2$$

Sodium nitrate cannot be used instead of potassium nitrate in gunpowder because it is *hygroscopic,* that is, it takes up water from the atmosphere.

Potassium nitrate is found in the topsoil of certain sections of India, Persia, and other countries, but the supply is not as great as that of sodium nitrate. From the time that gunpowder began to be used in Europe, the constant warring of nations led to a great demand for this chemical. Among the first papers communicated to the English Royal Society was one that dealt with the manufacture of

saltpeter. Its author declared "the only place where saltpeter is to be found is in stables and pigeon houses."

The East India Company imported nitrate from India as early as 1625. In France and Germany "niter plantations" sprang up. These were heaps of organic material mixed with wood ashes and other alkalies. The putrefaction that went on in these heaps in the open air produced potassium nitrate as one of the products. Up to the time of Lavoisier, officers of the French government had been accustomed to search for niter in wastes in the cellars of private houses, and to confiscate it, both to help supply the needs of the country and to prevent its use in insurrections. But shortly before the French Revolution, Lavoisier, as controller of munitions, abolished this confiscation and at the same time increased the supply of this chemical by improving methods of manufacture.

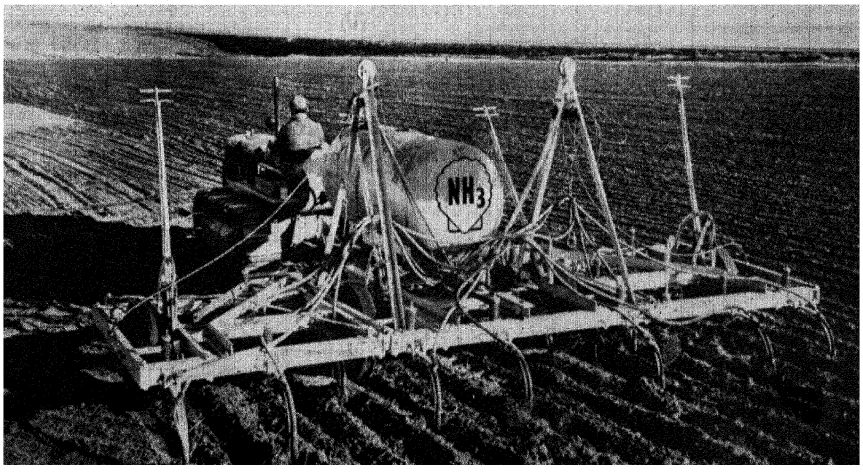
About 1650, Glauber showed that saltpeter could replace manure as a means of restoring the fertility of exhausted soils. It is still widely used as a fertilizer. Today it is prepared from sodium nitrate by the addition of potassium chloride solution, as follows:

$$NaNO_3 + KCl \rightleftarrows NaCl + KNO_3$$

Although this reaction is reversible, the potassium nitrate can be separated out by *fractional crystallization* (see page 473) because potassium nitrate is more than six times as soluble as NaCl in boiling water.

Will *hydroponics* supply our plant foods in the future? *Hydroponics* (from *hydro,* water, and *ponos,* labor) is a method of growing plants in water to which chemicals are added rather than in soil. This growing of crops without soil with the aid of the proper plant

Apparatus for fertilizing the soil by injection of anhydrous ammonia.
Shell Chemical Corporation



nutrients will in some cases increase the yield and improve the product. Tomatoes, beans, cucumbers, and many other plants have already been grown successfully by hydroponics.

It is not likely that science will do away completely with farms, such as we know, in favor of smaller areas filled with tanks and sterile sand beds containing the solutions required to produce various crops. However, much about plants can be learned by using hydroponics as an experimental tool of the agrobiologist.

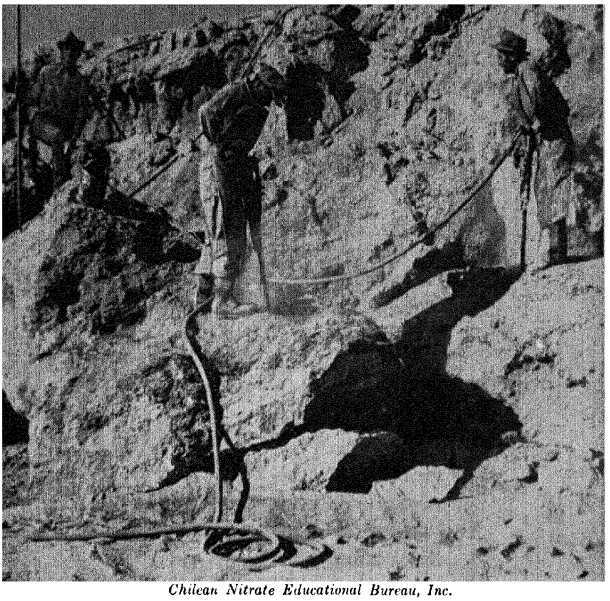
What properties are common to the salts of the alkali metals? Chemists have found that certain characteristics of the salts of the members of a family of elements resemble one another. Hence, they study the salts of such a family together.

We have already learned about some of the salts of potassium and shall continue with the salts of sodium, another important member of the alkali metals. The alkali metals form part of Group I of the periodic table. All their salts are white, crystalline solids. They are all soluble in water. Potassium compounds are just about as abundant as sodium compounds.

After studying the salts of sodium and potassium you will notice their marked resemblance to the ammonium (NH_4) salts. Because of this resemblance and also because NH_4^+ is a univalent, positively charged ion, the NH_4 ion might be considered as belonging to the same family group as sodium and potassium — the alkali metals. Because ammonium hydroxide is a base, and at the same time readily gives off a gas, or *volatilizes,* it is often called *volatile alkali.*

Sodium nitrate, fertilizer from the Andes. The coastal mountains in northern Chile rise abruptly from the floor of the Pacific Ocean. Between this range and the westward slopes of the Andes Mountains at elevations ranging from 4000 to 9000 feet is a desert plateau where only occasional cloudbursts send water into the loose, sandy soil. Most of this plateau is as rainless as any part of the world. In certain sections, annual rainfall is less than an inch.

Below this sandy soil is *caliche,* a rock containing between 50 percent and 75 percent sodium nitrate, $NaNO_3$. This nitrogen-containing mineral probably was formed by the action of nitrifying bacteria on ancient accumulations of seaweeds, guano, and other organic materials as well as by electric fixation during electric storms. The deposits were preserved because of the scarcity of rain. If the rainfall were normal, the deposits would have dissolved and washed into the Pacific Ocean. Another theory explains that these deposits have come from volcanic ash rich in nitrates or accumulated by the minute nitrate content of the underground waters of the region.



Workmen in the Chile nitrate deposits using pneumatic drills to break up large chunks of caliche.

Chilean Nitrate Educational Bureau, Inc.

Here in the Andes is the greatest concentration of nitrate salts in the world, a circumstance which for many years gave Chile a world monopoly of nitrate fertilizer. This monopoly was broken by the development of the synthetic nitrate industry (see page 262). Chile still continues to export this essential chemical in large quantities.

We are no longer dependent upon Chile for our nitrates, and in normal times we actually export some synthetic sodium nitrate to manufacturers and farmers both in Europe and Asia. Nitric acid is first synthesized from the elements of the air, and then the HNO_3 is treated with *soda ash,* forming synthetic $NaNO_3$.

$$2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + H_2O + CO_2$$

Chile saltpeter, another name for sodium nitrate, is used chiefly as a nitrogen fertilizer, and also in making nitric acid and potassium nitrate. A most important byproduct of caliche is iodine, extracted from the sodium iodate, $NaIO_3$, found mixed with sodium nitrate.

Sodium chloride, the best-known salt. Whenever most people speak of salt, they mean sodium chloride, NaCl. Not only has sodium chloride been known from antiquity, but even today it is one of the most abundant and important chemicals in the service of man.

The sea is an inexhaustible salt supply. If the salt of all the oceans could be collected, it would occupy 15 times the volume of Europe above sea level. Sea water contains an average of about three percent solid matter, most of it sodium chloride. The Dead Sea contains

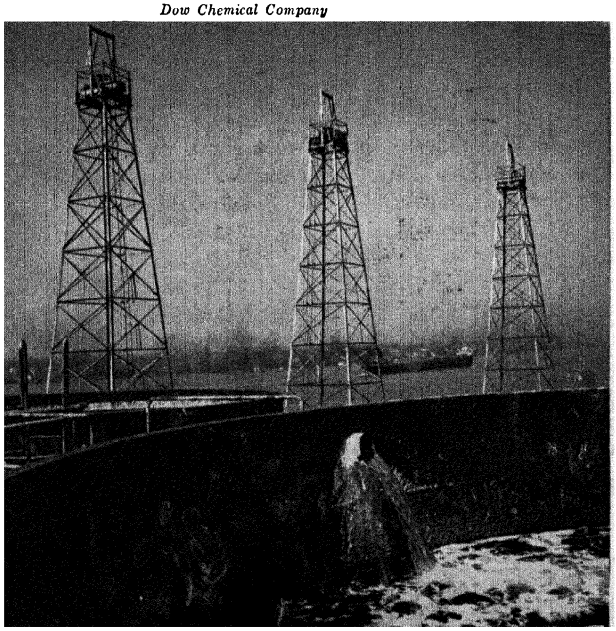
seven percent sodium chloride and 13 percent of another salt, magnesium chloride. The presence of this latter salt (because of its deliquescence) causes table salt to cake in moist weather. Prepared salt often contains 0.1 percent of tricalcium phosphate or one percent $CaCO_3$ to keep it free-flowing.

It is too costly to separate salt from sea water by boiling. Therefore sea water is usually collected in shallow basins near the shore, and the salt is concentrated by evaporation resulting from the heat of the sun, or *solar evaporation.* Early colonists in America obtained their salt by this method. During the winter in some countries, such as China and Japan, sea water is run into shallow troughs, and as the top layers of water freeze, the ice is removed until the salty sea water below becomes very concentrated. This concentrated brine is then heated to drive off the remaining water.

Salt is obtained also from salt lakes, as in India and at the Great Salt Lake in western United States, and from deposits of solid salt known as *rock salt,* or *halite.* Millions of years ago the sea covered part of what is now dry land. As the land rose, or the sea receded, or both, sea water was trapped in depressions in the land. This water gradually evaporated, leaving deposits of solid layers of salt. This explanation of the origin of the rock-salt mines near Syracuse, New York, and the famous potassium salt deposits of Carlsbad, New Mexico, is accepted generally.

Rock salt, containing as much as 95 percent sodium chloride, is either mined like coal or brought to the surface by first dissolving it

Dow Chemical Company



Brine flowing from salt wells into a storage tank. Great quantities of salt are essential in industry particularly in the manufacture of chemicals.

in water forced down through pipes, and then pumping the saturated salt solution to the surface by compressed air. Most of the salt used in this country is obtained from brine wells.

Though impure salt has many uses, for certain other uses it must be purified. To accomplish this, hydrogen chloride gas is bubbled through a concentrated solution of impure salt, causing pure sodium chloride to crystallize out (see *common-ion effect,* pages 244–245).

Fractional crystallization separates a mixture of salts. The various salts found mixed with sodium chloride have different solubilities in water. Their separation from one another depends upon both their solubility in water and their concentrations. A less soluble salt crystallizes out before a more soluble salt, provided their concentrations are the same. A salt present in a higher concentration crystallizes out before a salt present in a lower concentration, provided their solubilities are the same. Hence, that salt which is present in solution in a relatively concentrated form and whose solubility is comparatively low is the first to separate from a solution containing a number of different salts. This is the principle of *fractional crystallization,* used frequently in the preparation of pure salt crystals such as sodium bicarbonate and potassium nitrate.

How sodium chloride is used. Salt plays an important part in the bodies of all animals, because it is necessary in maintaining the water content of the tissues. Plants and animals originally developed in sea water. The blood of most animals resembles sea water. The animal maintains its cells in an internal environment resembling the ancient sea of its origin. Blood has a fixed amount of salt; to reduce this amount very much results in throwing the normal processes of the body out of balance. In fact, in cases of shock following injuries or surgical operations, salt in the form of *normal saline solution,* 0.8 percent salt in water, the concentration of salt in blood serum, is injected into a vein or under the skin.

So necessary is salt to animal life that wild herbivorous animals are known to travel great distances in order to reach "salt licks" where they can satisfy their craving for this mineral. Human beings use salt as a seasoning in almost all foods. This salt, with the salt present naturally in foods, supplies the teaspoonful of salt that an adult needs daily. From it, gastric cells produce the hydrochloric acid present in the gastric juice. In conditions of excessive perspiration, great quantities of salt are lost from the body, and should be replaced by a greater-than-normal salt intake. Salt, in the form of *salt tablets* or salt from other sources, may be used to prevent the effects of this kind of salt starvation.

In addition to its use as a food, salt is a key chemical for it serves as the foundation material for numerous industrial processes. Of 15 million tons of salt consumed annually in this country, only about one pound out of ten is used in foods. The remaining nine pounds are used in many industrial processes such as the manufacture of NaOH, $NaHCO_3$, HCl, Na, Cl_2, soap, glass, and enamel.

Rock salt is used in curing fish, meat packing, curing hides, and in making freezing mixtures, especially for the manufacture of ice cream. This use is based on the principle that a salt, as it goes into solution, absorbs heat from any material with which it is in contact. In addition, melting ice absorbs heat. Salt mixed with ice or with water near its freezing point will produce a temperature as low as −22°C. For years, salt has been used in controlling ice on city streets and on the subsurface soil of the beds of railroad tracks to prevent the tracks from heaving as a result of freezing. Sodium chloride is used also in water-softening (see page 491).

Salt on the farm. Great quantities of salt are consumed on farms. Rock salt and salt blocks are used to provide artificial salt licks for farm animals, and salt is added to commercially produced animal feeds. Farm food preparation, including the canning and preserving of vegetables, fruits, and meats, requires salt. Weed killers and insecticides often contain salt, and many commercial fertilizers require salt in their production.

The economic importance of salt is very great. Some nations keep the production and sale of salt a government monopoly or at least levy a tax on it. In times past, cakes of salt have even been used as money, as, for example, in Tibet and Abyssinia. In our own country, during the War Between the States, one of the main purposes of a Union campaign into southwestern Virginia was to capture and destroy one of the chief sources of salt of the Confederate States, located at Saltville.

The manufacture of sodium bicarbonate, chief constituent of baking powder. Sodium hydrogen carbonate, or *sodium bicarbonate,* $NaHCO_3$, is manufactured chiefly by the Solvay process, which replaced the older Le Blanc process invented in France about the time of the French Revolution. Ernest, at 23, and Alfred Solvay, Belgian chemists, perfected the new process about 1863. In this process purified brine is sprayed in at the top of an absorption tower, in which it meets ammonia gas and carbon dioxide. The following reaction takes place.

$$NaCl + H_2O + NH_3 + CO_2 \rightarrow NH_4Cl + NaHCO_3$$

The temperature must be carefully controlled, since otherwise this reaction is reversible. The sodium bicarbonate produced is separated from the ammonium chloride by fractional crystallization.

The ammonium chloride is heated with slaked lime to recover the ammonia gas, which is used again.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 \uparrow + CaCl_2 + 2H_2O$$

The carbon dioxide used in the Solvay process is obtained from limestone. One of the largest plants in which sodium bicarbonate is manufactured by this process is located at Syracuse, New York, where the raw materials are nearby and plentiful.

Sodium bicarbonate is a constituent of all baking powders and is therefore called *baking soda.* Under the name *bicarbonate of soda* it is used in medicine. A very effective, yet low-cost, dentifrice can be prepared by mixing one part by weight of sodium bicarbonate with approximately two parts of salt.

Sodium carbonate, or washing soda. Most sodium bicarbonate is converted into sodium carbonate, Na_2CO_3. When sodium bicarbonate is heated, carbon dioxide is liberated and anhydrous sodium carbonate, a white powder, is formed. The carbon dioxide formed in the reaction is used in the Solvay process.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \uparrow$$

When this sodium carbonate is dissolved in water and crystallized out, the crystals formed contain ten molecules of water of crystallization, and are called *sal soda.*

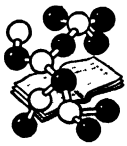
$$Na_2CO_3 + 10H_2O \rightarrow Na_2CO_3 \cdot 10H_2O \text{ (crystallized washing soda)}$$

This salt, $Na_2CO_3 \cdot 10H_2O$, is efflorescent and, on exposure to air, loses nine molecules of water, forming the stable white salt, $Na_2CO_3 \cdot H_2O$. Upon heating, this stable salt yields Na_2CO_3. *Soda ash* obtained from burning seaweed contains about 98 percent sodium carbonate.

Because sodium carbonate is the salt of a strong base and a weak acid, it hydrolyzes in part, forming sodium hydroxide (lye). For this reason, sodium carbonate is a good cleansing agent. And because sodium carbonate is a valuable water-softener (see page 489), it is used to some extent in home laundering and in laundries as *washing soda.* The recently-developed "Ammo" is a mixture of Na_2CO_3 and an ammonium salt.

Soda ash is industry's third most important chemical. More than 4.5 million tons of it are produced annually in the United States.

The manufacture of glass consumes one-third of this amount, and an equal amount goes into the manufacture of soap and other cleansers. It is used also in tanning, as a lumber dip to prevent formation of stains that are produced by fungi and molds, and in the manufacture of paper pulp.



YOU WILL ENJOY READING

Laurie, Alexander. *Soilless Culture Simplified.* McGraw-Hill Book Co., New York, 1940.

Mansfield, George R. "American Potash Reserves." *Industrial and Engineering Chemistry,* Dec., 1942, pp. 1417–1421. Deals with the potash industry in the United States and discusses also Federal and private development of our resources of potassium compounds.

Moore, F. J. *History of Chemistry* (3rd ed.). McGraw-Hill Book Co., New York, 1939. The life and work of Liebig and his friendship with Woehler.



USING WHAT YOU HAVE LEARNED

Group A

1. The ancients fertilized their fields. (a) What method did they use? (b) Is it likely that they understood the chemistry of this method? (c) Why?

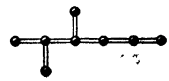
2. Copy and complete the following statements. Do not write in this book. Chemistry was first used in agriculture by .... He showed that plants could live upon ... independent of organic matter such as manure. In England a man named ... started the first agricultural experiment station at ....

3. (a) Why should most soils be fertilized? (b) What three elements must be in fertilizers? (c) Why?

4. What are three methods of preserving the topsoil?

5. How was K_2CO_3 obtained by American colonists?

6. Is America still dependent for its potassium compounds upon foreign sources? Explain.



7. What is a *complete* fertilizer?

8. (a) What mineral plentifully distributed in the earth's crust is a compound of K? (b) What problem must be solved

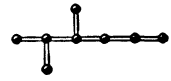
before this mineral can be used as a source of potassium fertilizers?

9. Name four sources of potassium salts in the United States.

10. What are the chief sources of (a) $NaNO_3$ and (b) KNO_3?

11. Compare the action of KNO_3 on litmus with that of Na_2CO_3. Explain.

12. (a) What element used often as an antiseptic is found with $NaNO_3$ in caliche? (b) In what compound does it occur?



13. What were niter plantations?

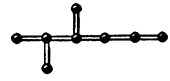
14. (a) What is the composition of gunpowder? (b) Why cannot $NaNO_3$ be used instead of KNO_3 in gunpowder? (c) On what does the explosive quality of gunpowder depend? (d) Write the reaction for the explosion.

15. A manufacturer has 200 tons of KNO_3 on hand. What is the greatest weight of gunpowder that he can prepare?

16. Which is the better fertilizer: $NaNO_3$ or KNO_3? Explain.

17. Write a balanced equation showing how KNO_3 can be made from $NaNO_3$.

18. (a) What is hydroponics? (b) How widely used may hydroponics become? (c) Why?



19. In what three ways do most sodium, potassium, lithium, and ammonium salts resemble one another?

20. (a) What are the chief sources of NaCl? (b) Why does common table salt become lumpy?

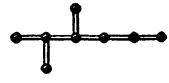
21. (a) NaCl is a necessary constituent of the food of all animals. Why? (b) In certain countries all NaCl is taxed. Why?

22. (a) What is fractional crystallization? (b) Illustrate it.

23. Describe two methods used in extracting NaCl from sea water.

24. (a) What is rock salt, and (b) how was it probably formed?

25. (a) What four important chemicals use large quantities of NaCl in their manufacture? (b) What are six other uses of NaCl?

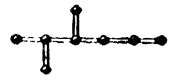


26. Write equations illustrating the preparation of NaCl by: (a) direct combination, (b) neutralization, (c) the combination of a carbonate and the proper acid. (d) The last two reactions go to completion. Why?

27. Make a table of three columns. In the first column write: (a) baking soda, (b) washing soda, (c) soda ash, and (d) bicarbonate of soda. Write the formula for each of these four substances in the second column. In the third column write the uses for each of these compounds.

28. Write a single chemical equation that gives the chief reaction involved in the Solvay process.

29. (a) Name the only substance used in the manufacture of Na_2CO_3 that is not recovered and used again. (b) Explain how each of the other substances used is recovered and used again.



30. Most of the sodium bicarbonate manufactured is converted into washing soda. (a) Write an equation to show this change. (b) Under what condition does the reaction occur? (c) How may it be reversed?

31. Explain what happens when crystals of washing soda are left exposed to the air.

32. Why is it more economical to use powdered, rather than crystalline, washing soda?

33. What are the two chief uses of Na_2CO_3?

34. Write an equation showing the reaction between baking soda and an acid.

35. Which will liberate more CO_2 gas when acted upon by H_2SO_4: 200 g. of anhydrous Na_2CO_3 or 200 g. of $NaHCO_3$?

Group B

36. Why is the Nile River valley so fertile?

37. How can the elements that are removed from the soil by certain crops be determined?

38. How was Na_2CO_3 produced before the discovery of methods of preparing it from NaCl?

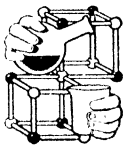
39. According to the electron theory, explain the structure of NaCl.

40. How can you tell the difference between $NaHCO_3$ and Na_2CO_3?

41. Why does 1 g. of NaOH neutralize more acid than 1 g. of KOH?

42. Describe how KNO_3 is prepared by fractional crystallization.

43. (a) How was Germany helped during World War I by the perfection of the Haber process for making synthetic nitrates? (b) In what condition is the United States with regard to nitrates?



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Write a two- or three-page report on the way in which Justus von Liebig's contributions to agriculture have affected our ways of living.

2. If you live in a farm area, make a study of the nature of the soil in that area and the types of fertilizers used. Report your findings to the class. What do you conclude from your findings?

3. In spite of all the knowledge that science has accumulated concerning the proper growing of crops, why do crops not flourish in many cases? List as many reasons as you can find, and place them in the order of their importance.

4. Make a study of all the sodium and potassium salts that are used in your home and on your farm (if you live on one). State the uses in each case. What do you conclude concerning these salts?

5. Prepare some pure KNO_3 crystals by dissolving pure $NaNO_3$ and pure KCl in a minimum volume of hot water (use about 10% more $NaNO_3$ than KCl). After the solution cools down to room temperature place it in a refrigerator for an hour. Now pour off the liquid and examine the KNO_3 crystals formed. Why did the KNO_3 rather than the NaCl crystallize out? (Examine solubility curve on page 219.)

6. Make an investigation of the relative amounts of fertilizers used in your community during the past 30 or 40 years. What do you conclude?



31 CALCIUM: ITS COMMON COMPOUNDS

. . . The water which drips from the stalactite, deposits some more calcium carbonate on the floor and, in the course of ages, there rises up to meet the descending stalactite a corresponding column from the floor. Ultimately the two meet and slowly coalesce to form those mighty snow-white pillars which hold up and support the roofs of the most stupendous caverns. Geoffrey Martin, 1911

Calcium and the other alkaline earth metals. Because calcium stands high in the replacement series of the metals, it never occurs free. Calcium compounds are very stable. Calcium lends electrons easily; combines readily with oxygen, water, and acids; and, like sodium, is prepared by the electrolysis of one of its fused salts, calcium chloride. Since the atomic weight of calcium is 40, the structure of its atom is represented as in Fig. 103.

In addition to calcium, Group II of the periodic table includes barium, beryllium, magnesium, strontium, and radium — the so-called *alkaline earth metals.* When heated in a flame, a barium or a strontium compound gives a color to the flame. The strontium flame is red; the barium flame is green. Hence, compounds of barium and strontium are used in making tracer bullets, fireworks, and signal lights, or *fusees.*

Calcium carbonate and its forms. Calcium carbonate, $CaCO_3$, occurs in four forms: *limestone, marble, chalk,* and *calcite.* Calcium carbonate is the second most widely distributed mineral on earth. It is a part of the great rocky masses of sedimentary land formations. Limestone is often found mixed with ores and in their metallurgy it must be eliminated as gangue.

Limestone is a sedimentary, or *alluvial,* deposit of calcium carbonate built up from the shells of minute aquatic animals. Thousands of tons of limestone are used each year in the manufacture of glass. The metallurgical industries consume tremendous amounts of limestone as a flux. It is also the sole source of commercial lime.

Marble is limestone that has been so heated and compressed in the ground by natural forces that its close texture permits a fine polish. Limestone and marble are used as building materials. The exteriors of the buildings in Rockefeller Center in New York contain 150,000 tons of Indiana limestone. Some of the best marble is used in sculpture.

Chalk is calcium carbonate that was deposited on the sea floor. In general, it consists of the shells of certain minute aquatic organisms. Pearls, coral, and many shells also are largely calcium carbonate. Eggshells are composed almost entirely of $CaCO_3$. Hens gets calcium in the form of oystershell or grit in their diet.

Pure crystalline calcium carbonate is colorless and transparent. It is called *calcite,* or *Iceland spar.* Some calcite crystals measure as much as three feet across and are easily split, or cleaved, in three directions.

How limestone caves are formed. Calcium carbonate is almost insoluble in pure water, but in water containing a good deal of dissolved carbon dioxide, the insoluble calcium carbonate forms soluble calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \text{ (calcium bicarbonate)}$$

Carbonic acid in running underground water, therefore, causes the gradual dissolving away of limestone deposits, producing caves.

A stream rich in dissolved calcium bicarbonate often finds its way through the roof of a limestone cave. As a drop of this water remains suspended from the roof of the cave, it may evaporate, and

Fig. 103. Structure of the calcium atom.

The atomic number of calcium is 20
Calcium is a typical metal
The valence of calcium is +2
Calcium is very active

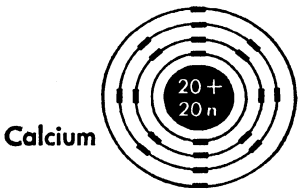
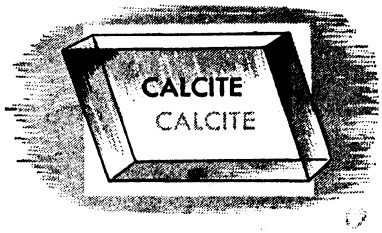


Fig. 104. A calcite crystal separates light rays so that objects appear double.



the calcium bicarbonate may decompose, liberating carbon dioxide and leaving behind a crystal of calcium carbonate.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

The gradual accumulation of millions of these crystals forms an icicle-shaped *stalactite.*

Another drop may fall to the floor of the cave. After the water evaporates, the calcium bicarbonate decomposes, leaving a crystal of calcium carbonate on the floor. This may grow into a *stalagmite.* By the joining of many stalactites and stalagmites, columns are formed and eventually the cave may be completely filled. The beauties of the Luray Caverns of Virginia, the Mammoth Cave of Kentucky, the Carlsbad Caverns in New Mexico, and many others owe their origin to this chemical action.

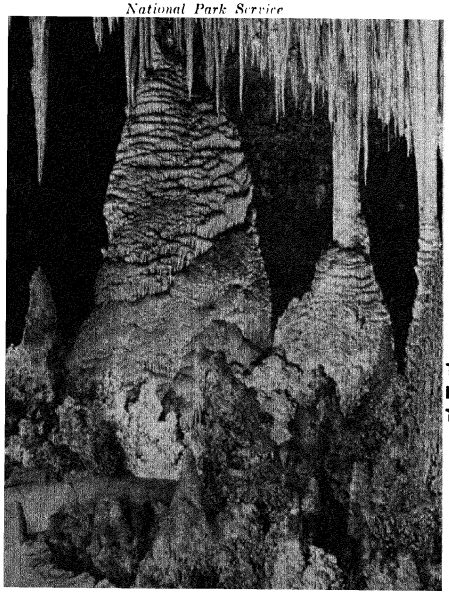
Making lime from limestone. In remote times *lime,* a white, soft solid, was thought to be an element. However, in 1808, Davy showed it to be calcium oxide, CaO. It is prepared by heating limestone, which liberates carbon dioxide and crumbles to a powder, CaO.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

This reaction is sometimes used as a source of carbon dioxide, in which case the lime produced is a byproduct.

The time-honored way of making lime was to dig a large pit in the side of a hill making a draft-hole at the bottom. The pit was then filled with material containing calcium carbonate. Fuel was added, lighted, and left to burn out.

National Park Service



This beautiful limestone formation in Carlsbad Caverns, New Mexico, is known as "The Temple of the Sun."

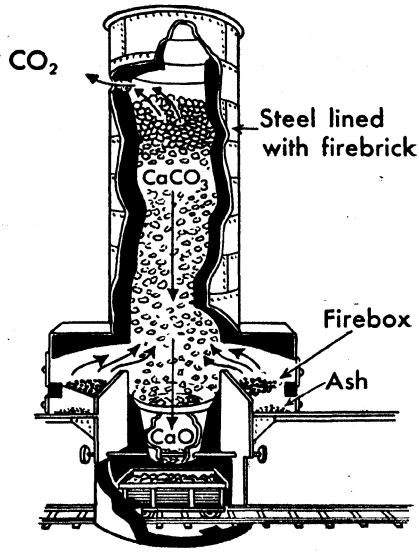


Fig. 105. Simplified cross section of a vertical lime kiln.

Today the industrial manufacture of lime is carried out in large vertical or horizontal rotary kilns. Through the upper end crushed limestone from the quarries is added, and through the other end hot gases are forced. The temperature in a lime kiln is about 1000°C. The heat decomposes the limestone, and the carbon dioxide gas is forced out of the kiln.

In the limelight. Lime, also called *quicklime,* does not burn when heated even to a high temperature, but it glows with a brilliant white light. Hence *limelights* were used at one time for stage spotlights and footlights. From this use of lime comes the expression "to be in the limelight."

Because lime has an extremely high melting point, it is used as a refractory. As you already have learned, lime is used as the basic lining in various metallurgical furnaces such as the open-hearth. It is used also in the manufacture of iron, because it combines so readily with impurities, forming a slag which can be removed. It is used for a similar purpose in other industries.

$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ (calcium silicate slag)}$$

What is slaked lime? You may have watched workmen adding cold water to white lumps of lime until the mixture seemed to come alive (hence, the name *quick* lime) ; it began to swell, crumble, boil, and give off large volumes of steam. Probably you were amazed at

the sight of cold water raising the temperature of the lime to the boiling point of water, instead of cooling off the lime, as might be expected. This evolution of heat is caused by the exothermic reaction of water and lime, a basic anhydride, forming calcium hydroxide, or *slaked lime.* Its "thirst" for water was slaked.

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat}$$

Slaked lime, or $Ca(OH)_2$, is a white solid. It is slightly soluble in water, forming *limewater.* Limewater is a fairly strong base. Even though calcium hydroxide is only slightly soluble in water, its solubility *decreases* further on *rise* of temperature. It is extensively used wherever a low-cost base is required. For example, slaked lime is used in removing hair from hides. When slaked lime is added to water in large amounts, a white suspension is formed, which we know as *whitewash,* or sometimes, as *milk of lime.*

The fertility of soil depends in part upon calcium ions. Calcium, though rarely lacking in most soils, is an essential element in plant nutrition. Scientists think that it has some connection with the formation of the cell wall. The legumes are lime-loving plants and require large amounts of it.

Some soils turn blue litmus pink, and exhibit other acid properties. Some crops including pineapples, potatoes, and cranberries grow best on such soils; others, including sugar beets, clover, alfalfa, and peanuts, do not thrive on acid soils. Such soils must be *sweetened.* Their *sourness* may be removed by the addition of finely ground limestone, slaked lime, or crushed sea shells. These substances neutralize the acids, and this procedure is called *liming* the soil.

Scientific farming involves determining the *p*H value (see page 235) of a soil before calculating the amount of calcium compounds to be added. Lime also acts mechanically, loosening clay soils and making sandy soils more firm.

Ground limestone and other calcium carbonates may be spread on the soil at any time; but it is usually not considered advisable to apply limestone, manure, and ammonia compounds at the same time. The limestone must be thoroughly mixed with the soil. An effective method of accomplishing this is by harrowing the soil shortly after spreading the limestone. Application of calcium compounds other than carbonates requires extreme care. For example, lime will possibly injure tender plants and seeds if it comes in contact with them.

Lime in building. If sand is added to freshly slaked lime, a plastic mass called *mortar* is formed. Mortar adheres to wood, bricks, and stone, and is used to hold these materials together.

Some of the chemical and physical changes that take place when mortar is setting are still not thoroughly understood, but we do know that, as the mass dries and hardens, water is given off and calcium silicate is formed:

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 + H_2O$$
Slaked lime + sand → calcium silicate

Some of the grains of sand are held in colloidal suspension (see Chapter 38), giving a definite body and hardness to the mass. The outside of the mortar comes in contact with the carbon dioxide in air, and minute crystals of calcium carbonate are formed, which help in the solidification.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

In most construction work, lime mortar has been largely displaced by the much stronger cement, but it is still widely used in home building (see Chapter 33).

If quicklime remains exposed to air for a long enough time, it reacts with water vapor in the air, forming calcium hydroxide. By uniting with the carbon dioxide in air, this calcium hydroxide forms calcium carbonate. Quicklime to which this has happened is said to be *air-slaked.* Such air-slaked lime cannot be safely used for making mortar. Why?

How slaked lime is used in preparing bleaching powder. Bleaching powder, $CaOCl_2$, already discussed in the chapter on chlorine, is prepared commercially by passing chlorine vapor through rooms containing a three-inch layer of freshly slaked lime. A grayish-yellow powder called *chloride of lime* or chlorinated lime is formed.

$$Ca(OH)_2 + Cl_2 \rightarrow H_2O + CaOCl_2$$

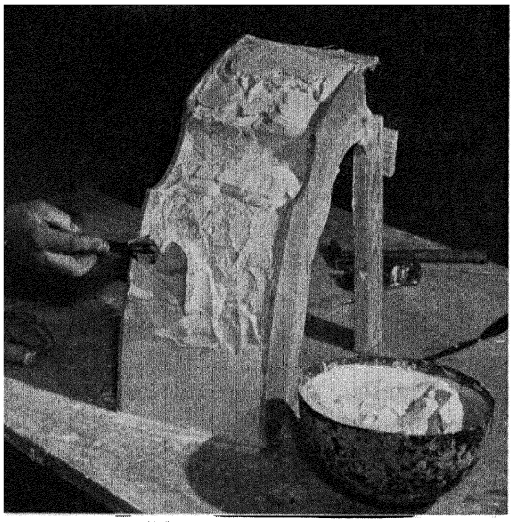
A more recent method combines free chlorine and lime directly as they mingle with each other while passing through a pipe.

$$CaO + Cl_2 \rightarrow CaOCl_2$$

Bleaching power is not as pure or stable as $Ca(ClO)_2$. It liberates its chlorine when heated or when acted upon by even weak acids, such as the carbonic acid in the air.

$$CaOCl_2 + H_2CO_3 \rightarrow CaCO_3 + H_2O + Cl_2\uparrow$$

Bleaching powder thus furnishes a simple means of obtaining free



U.S. Gypsum Company

Spreading plaster of Paris on a form. After the plaster hardens, it will be removed and used as a mold.

chlorine for bleaching and disinfecting purposes. It is used also in the manufacture of paper.

Calcium sulfate and plaster of Paris. The great blocks of the pyramids of Egypt were cemented together by a plaster made from a powder obtained by heating a white, soft rock called *gypsum*, $CaSO_4 \cdot 2H_2O$. This material, still used today, is called *plaster of Paris*.

To make plaster of Paris, gypsum is carefully heated. After losing three-fourths of its water of crystallization, the gypsum changes to plaster of Paris.

$$\underset{\text{gypsum}}{2CaSO_4 \cdot 2H_2O} \rightleftarrows 3H_2O + \underset{\text{plaster of Paris}}{(CaSO_4)_2 \cdot H_2O}$$

Plaster of Paris, on the addition of water, combines with three molecules of water and re-forms gypsum. The reaction is thus reversible. This recombining of plaster of Paris with water is called *setting*, and is accompanied by the liberation of some heat. In preparing plaster of Paris care must be taken not to heat the gypsum above 175°C., since all the water would then be driven off, and the gypsum would be said to be *dead-burnt*, and would be useless for plaster.

Plaster of Paris is used in cheap statuary, casts for broken or dislocated bones, and molds of various objects such as teeth and metals. It is used also in plastering inside walls and ceilings, and in making plasterboards and similar partition materials.

The superphosphate of calcium. In the discussion of the chief uses of chamber sulfuric acid, mention was made of the manufacture of calcium superphosphate. This compound was first prepared

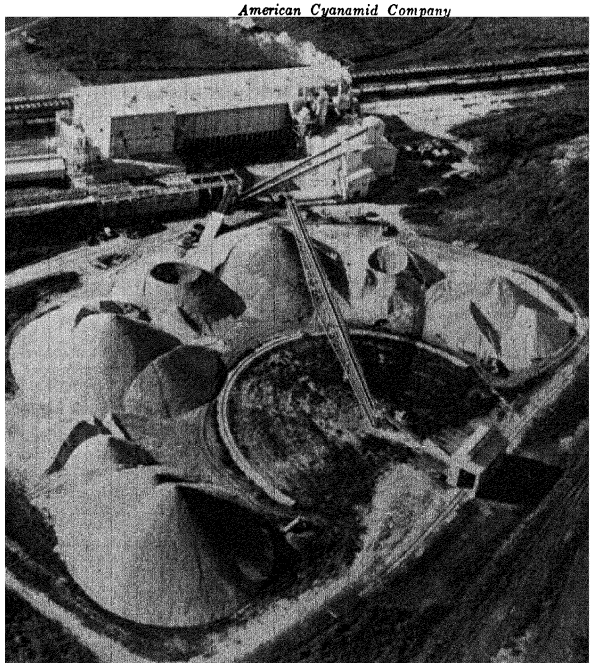
as a fertilizer from rock phosphate by John Lawes, in 1842, and his patented process is still in use today. Calcium phosphate is insoluble in water, but the superphosphate is soluble and, hence, can be utilized by plants at once.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow \underbrace{2CaSO_4 + Ca(H_2PO_4)_2}_{\text{superphosphate}}$$

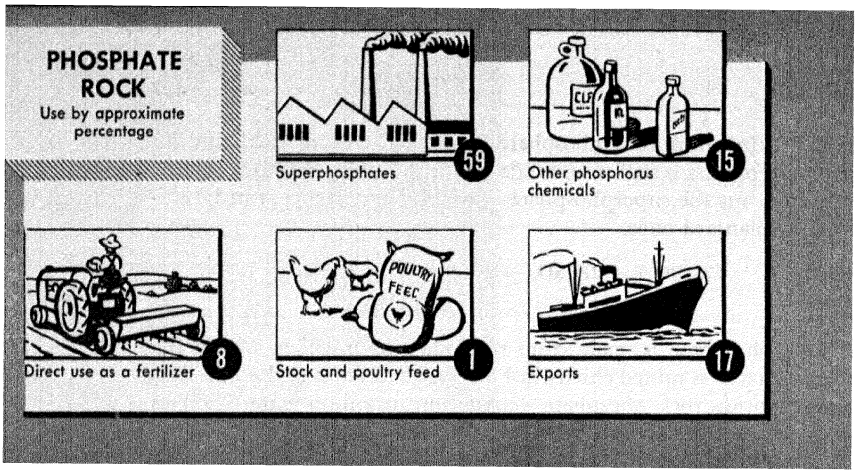
Superphosphate is made from rock phosphate which, within the United States, is mined chiefly in Florida, Tennessee, and South Carolina. Florida rock phosphate (containing uranium impurities) is composed principally of $Ca_3(PO_4)_2$, the tricalcium salt of orthophosphoric acid, H_3PO_4, a tribasic acid. Almost four million tons of rock phosphate are used in fertilizers each year in this country. Superphosphate as shown in the equation above is really a mixture of monocalcium phosphate and gypsum, and contains the equivalent of about 17 percent P_2O_5.

Triple superphosphate is a concentrated phosphate fertilizer developed by the Tennessee Valley Authority (TVA), a government agency created by the Congress in 1933. Since most soils in the Tennessee Valley are deficient in phosphorus, a plan was formulated for phosphate manufacture using the raw phosphate rock of Tennessee. Triple superphosphate is now widely used throughout the nation. It contains about three times as much available phosphate as ordinary

American Cyanamid Company



Aerial view of a Florida phosphate rock plant. Under each of the storage piles are doors which, when opened, permit the rock to fall onto underground conveyor belts. The belts carry the rock into the plant for processing.



superphosphate because the manufactured product contains no gypsum. It is made by the action of phosphoric acid on phosphate rock.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

With this low-cost and highly-concentrated phosphate American farmers are winning the battle against an impoverished soil.

Calcium phosphate as the source of pure phosphorus. Calcium phosphate is also a source of the *pure phosphorus* used in the manufacture of phosphoric acid, P_2O_5, PCl_5, and matches. The phosphorus is prepared by heating a mixture of calcium phosphate, sand, and carbon in a totally enclosed electric furnace. The calcium phosphate decomposes into calcium oxide, CaO, and phosphorus pentoxide, P_2O_5. The sand, SiO_2, unites with the calcium oxide, forming calcium silicate slag, $CaSiO_3$, which is drawn off from the bottom of the furnace. The carbon reduces the phosphorus pentoxide, forming phosphorus vapor and carbon monoxide. The phosphorus vapor is condensed under water and cast into sticks. The entire reaction may be represented as follows:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + 2P$$

Most of this phosphorus is burned in dry air to P_2O_5 which is used to make phosphates including phosphoric acid.

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

This weak acid is used in soft drinks, jellies, and preserves.

Hard water and calcium ions. Water containing dissolved calcium salts will not form a lather with soap until the calcium ions are removed. We call water containing such dissolved salts *hard water*. When the soluble calcium salts are precipitated as calcium soaps, the

water will then form a lather with soap, and we say that we have *softened the water*. In other words, to soften hard water, the free calcium ions must be removed.

There are two kinds of hard water: (1) *temporary hard water;* (2) *permanent hard water*. Temporary hard water is water that contains *calcium bicarbonate*. Such water may be softened in two ways: (1) by boiling, and (2) by adding washing soda. When temporary hard water is boiled, the soluble calcium bicarbonate changes to insoluble calcium carbonate, which precipitates out. Thus the free calcium ions are removed. The ionic equation is:

$$Ca^{++} + 2(HCO_3)^- \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

Washing soda softens temporary hard water in the following way:

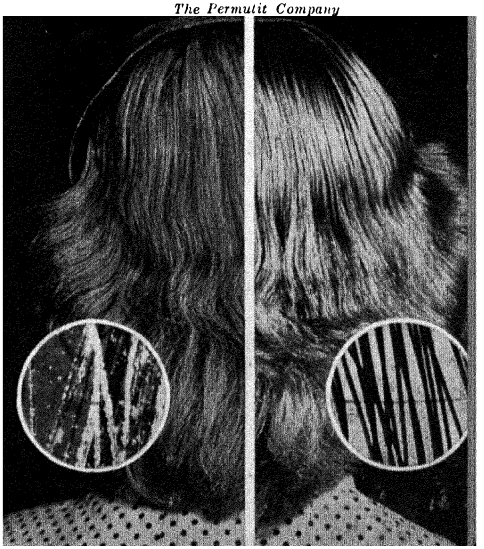
$$Ca^{++} + 2(HCO_3)^- + 2Na^+ + CO_3^{--} \rightarrow CaCO_3 \downarrow + 2Na^+ + 2(HCO_3)^-$$

Permanent hard water is water that contains *calcium sulfate*. Such water cannot be softened by boiling, but may be softened by the addition of washing soda, as the following ionic equation shows.

$$Ca^{++} + SO_4^{--} + 2Na^+ + CO_3^{--} \rightarrow CaCO_3 \downarrow + 2Na^+ + SO_4^{--}$$

Another water-softener is Na_3PO_4 (trisodium phosphate or TSP), which forms insoluble calcium and magnesium phosphates, which are easily rinsed away. Glassy sodium metaphosphate, $NaPO_3$, which prevents the precipitation of calcium and magnesium soap, is found in dishwashing mixtures and is also used in municipal water supplies. The hexametaphosphate, $(NaPO_3)_6$, is marketed under the trade name, "Calgon."

The Permutit Company



This composite photograph shows the difference between hair when washed in hard water (left) and washed in soft water (right). Note the soap scum deposits in the photomicrograph (left).

For many purposes, hardness of water need not be removed. For example, in drinking water the calcium ions are actually beneficial, since they supply an element necessary for bone-building. But in many industries using large quantities of water, the presence of calcium salts becomes a source of waste, and raises serious plant problems. Calcium salts in boilers form deposits, or *scales,* which gradually get thicker until they clog the pipes of the boiler. The efficiency of a boiler lined with a scale of calcium salts is greatly reduced and much heat is lost because the heat does not pass readily through the scale to heat the water. This may lead to explosions.

If hard water is used in the home for laundering, bathing, washing dishes, and so forth, the amount of soap required is much greater than if the water is soft.

Although calcium salts are the most common cause of hard water, the salts of magnesium, iron, or barium also make water hard. What has been said about calcium salts holds true for the salts of these three elements also. Hardness in water is measured either in *parts per million* (ppm) or in *degrees.* One degree is equal to one grain of calcium salt per gallon of water.

Ion-exchange method of softening water. One of the most efficient methods of softening water is by the use of "Permutit." This is the trade name for either a natural or synthetic compound composed of a complex sodium silico-aluminate called *zeolite,* which looks like a greenish-gray sand. Hard water is passed through a filter containing "Permutit"; the calcium ions replace the sodium ions, forming a calcium compound, calcium zeolite, which remains behind in the filter. There is no radical change in the structure of the solid zeolite during this interchange.

$$Na_2 \text{ zeolite} + CaSO_4 \rightarrow Ca \text{ zeolite} + Na_2SO_4$$

Adapted from a drawing by The Permutit Company

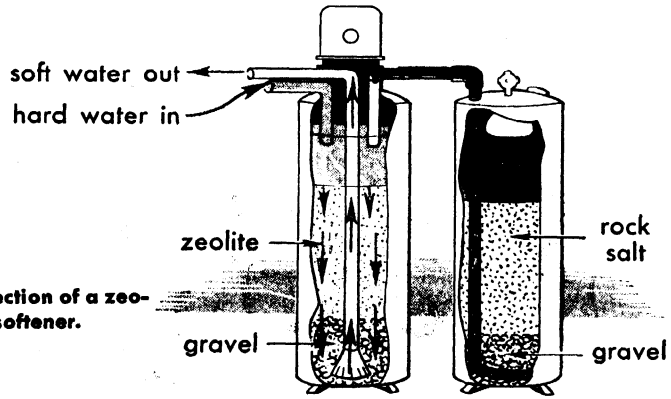


Fig. 106. Cross section of a zeolite home water-softener.

When all the sodium in the "Permutit" has been replaced by calcium, the zeolite is covered with a ten percent solution of sodium chloride; the sodium of the sodium chloride replaces the calcium of the zeolite, which is now ready to soften more water. Again there is an ion exchange.

$$\text{Ca zeolite} + 2NaCl \rightarrow CaCl_2 + \text{Na}_2\text{ zeolite}$$

This interchangeability of Na and Ca ions enables "Permutit" to act as a water-softener for years without losing its effectiveness to any great extent.

Demineralized water. Ion-exchange is also used in purifying water. Sodium zeolite removes calcium and magnesium ions but not the sodium or chloride ions of salt or other ions such as sulfate and bicarbonate that may be present. We now have other synthetic resin ion-exchangers that can rid water of these ions by a two-step process. Water is passed through alternate layers of two different exchangers and stripped of all its ionized salts. The first is a cation exchanger which removes the metallic ions and changes all salts present to their corresponding acids. In the following formula, the synthetic resin is represented by the symbol R.

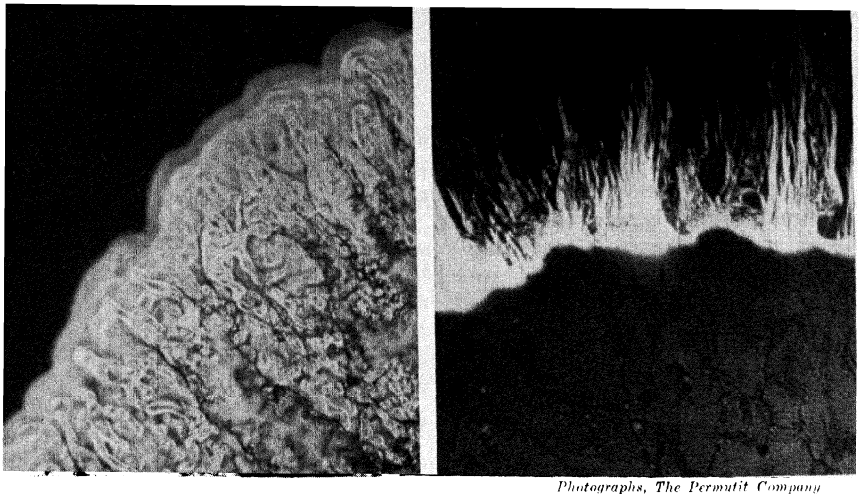
$$(1)\quad HR + NaCl \rightarrow NaR\downarrow + HCl$$

The second is an anion exchanger that removes the free acids formed. In the following formula, the synthetic resin is represented by the symbol R′.

$$(2)\quad R' + HCl \rightarrow R'\cdot HCl\downarrow$$

The water thus purified is called *demineralized* water and is almost as pure as distilled water. For household and many other uses it is just as good as distilled water. Ordinary tap water can be converted by means of a commercial demineralizer to almost pure water much more cheaply than by distillation. Even brackish water containing as much as 0.3 percent NaCl can be converted to water fit for irrigation. Some day even sea water may be so treated economically.

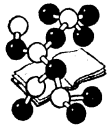
Synthetic resins are organic compounds that resemble natural resins such as amber. "Amberlites" is the trade name of one such group of resins. After use, they are regenerated and used over again. Ion-exchange is also used in the refining of sugar, and in the separation and purification of vitamins, enzymes, and antibiotics such as streptomycin and penicillin. It can even separate extremely minute amounts of amino acids in mixtures of these complex compounds



Photographs, The Permutit Company

Photomicrographs of soap dissolving in soft water (right) and trying to dissolve in hard water (left). Since soap is ineffective until dissolved, these photographs clearly illustrate why washing in hard water is unsatisfactory.

by the recently developed technique called *chromatography*. For example, such a mixture which had hitherto defied separation is sent through a long glass column, well-packed with some adsorbent material such as Al_2O_3, SiO_2, or C. All ions are not held with equal strength by an ion-exchanger. The more strongly adsorbed amino acids are held at or near the top of the column, and the more weakly adsorbed, below in bands. Substances not adsorbed run through in the filtrate. Chromatography also has been used to separate some of the products of uranium fission, as well as the constituents of cell nuclei.



YOU WILL ENJOY READING

Huxley, Julian, and Andrade, E. N. daC. *More Simple Science*, pp. 154–222. Harper & Bros., New York, 1936. The chapters on "Soil" and "Agriculture" contain interesting and valuable information on the general problem of soil enrichment as seen by two English scientists.

Walton, Harold F. "Ion-Exchange." *Scientific American*, November, 1950, pp. 48–51. Explains the technique of replacing electrically charged atoms or groups of atoms with others of the same charge.

U.S. Department of Agriculture. *Liming Soils for Better Farming*. Farmers' Bulletin No. 2032 (1951). Supt. of Documents, U.S. Govt. Printing Office, Washington 25, D.C. 15¢. A valuable illustrated pamphlet for the farmer.



USING WHAT YOU HAVE LEARNED

Group A

1. Name the alkaline earth metals.

2. Using diagrams showing the distribution of the electrons of Na and Ca, compare their chemical properties.

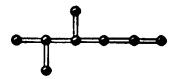
3. (a) List the four forms of $CaCO_3$. (b) Opposite each form write its chief use.

4. (a) Under what conditions does insoluble $CaCO_3$ go into solution? (b) What salt is it that dissolves? Write the equation that shows how it forms. (c) When will the reaction begin to reverse?

5. (a) Explain the formation of limestone caves. (b) How could a limestone cave be entirely filled with limestone by a natural process?

6. (a) Describe a commercial method of preparing lime. (b) Write the equation.

7. In the industrial preparation of quicklime, how is the reaction $CaCO_3 \rightarrow CaO + CO_2$ made to go to completion?



8. On what properties of lime was the use of limelight based?

9. (a) On what physical properties does the use of quicklime as the basic lining of various furnaces depend? (b) on what chemical property? (c) Write an equation that illustrates this chemical property.

10. (a) What type of reaction is the slaking of lime? (b) Write the equation for it.

11. (a) How is limewater made? (b) What are its properties and uses? (c) What is whitewash? (d) What is milk of lime?

12. (a) Using an equation, explain how limewater is used as a test for CO_2. (b) What happens if you continue to pass CO_2 into limewater? (c) Write an equation explaining what happens. (d) How can this reaction be reversed?

13. Ca appears below Na in the replacement series of the metals. (a) How would you expect Ca to react with water? (b) Compare its action on water with the action of Na on water.

14. (a) If you left a barrel of lime outdoors on a rainy day, what would happen? (b) If the lime were then exposed to the air, what compound would be formed, at least in small quantities? (c) Write equations showing the reaction in each case.



15. Explain the old rhyme:

"Lime and sand and water
Make a very good mortar."

16. Write two equations illustrating two changes that take place during the setting of mortar.

17. Ca is an element essential in plant nutrition. Explain.

18. How are calcium compounds used to "sweeten" soils?

19. Explain the formation of the thin hard film on the surface of limewater in an open jar.

20. What weight of lime can be produced from 200 tons of limestone containing 90 percent $CaCO_3$?

21. CO_2 was passed through limewater and 150 g. of $CaCO_3$ were precipitated. What volume of CO_2 was used?



22. (a) How is bleaching powder made? (b) Write the equation.

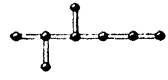
23. Write an equation that shows both the manufacture of plaster of Paris and the setting of plaster of Paris.

24. How would you tell crystals of gypsum from crystals of calcite?

25. (a) What property of rock phosphate keeps it from being used as a fertilizer? (b) How is it changed into a fertilizer? (c) Write the equation.

26. Using equations, describe the manufacture of (a) P, and (b) H_3PO_4.

27. The smell of Cl_2 is detected when a fresh can of $CaOCl_2$ is opened. Explain.



28. Explain the "Permutit" process for softening water.

29. (a) What do hard waters contain that makes them hard? (b) By what simple test can housewives tell whether water is hard?

30. From the point of view of the dissociation theory, distinguish between temporary and permanent hard water.

31. Explain the two-step, ion-exchange process for demineralizing water.

32. (a) How is temporary hard water softened in the home? Write the equation. (b) Which costs less: the softening of hard water or using large quantities of soap?

33. (a) How is temporary hard water softened for industrial use? (b) Write the equation.

Group B

34. State three recent industrial applications of the ion-exchange process for removing undesirable ions.

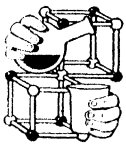
35. Write formulas of: (a) a calcium compound used as a dehydrating agent, and (b) a calcium compound used in the fixation of N_2. (c) What combustible gas is made from this latter calcium compound?

36. For the commercial bleaching of cotton cloth, a weak solution of sulfuric acid and bleaching powder is used. Chlorine is released. Write the equation for this reaction.

37. (a) Describe fully a method you would use in the laboratory to prepare pure chalk. (b) What forces the reaction during which the chalk is formed to go to completion?

38. Why do the walls of freshly-plastered houses "sweat"?

39. What volume of CO_2 can be obtained from ten pounds of oyster shells containing 78% $CaCO_3$?



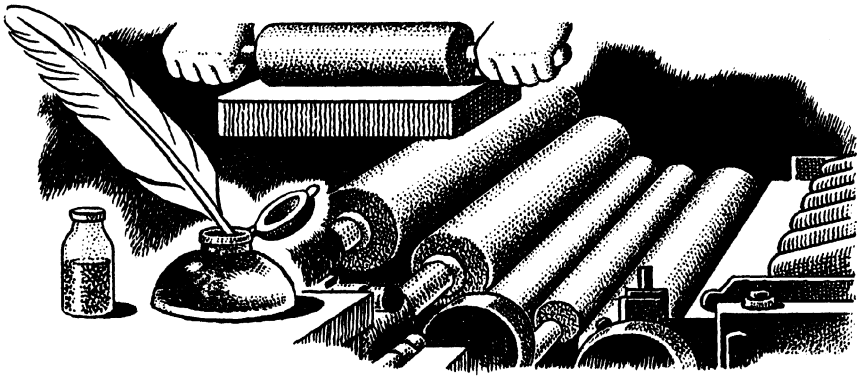
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make an investigation of the method or methods used in your home or community to soften the water. Report to your class on your findings. If your community water supply is hard, make a survey of the cost of softening it. How would you justify such an expenditure?

2. Bring a sample of water used for washing purposes in your home. Show the class whether it is hard or soft water, and, if hard, then soften it as a demonstration. Your teacher will supply you with the necessary material if you cannot obtain it yourself.

3. Write a report on the present state and future possibilities of using sea water for irrigation and industrial purposes. (Read past issues of *Chemistry* published by Science Service.)

4. Sprinkle some water over a few lumps of quicklime in a pan. Report your observations to the class.



32 IRON: SOME SPECIAL COMPOUNDS

. . . In the "secretas" of the twelfth century mention is made of sour galls, green vitriol (iron sulfate), and a host of unimportant materials as being employed in the admixture of black inks. The first two (tannogallate of iron), when used alone, form the sole base of all unadulterated gall inks. D. N. Carvalho, 1904

Iron forms two series of compounds. As we have already learned, copper has two valences and forms both cuprous and cupric salts. Iron also has two valences. *Ferrous* ions carry two positive charges and *ferric* ions carry three positive charges. Chemists explain the existence of the ferrous and ferric ions in the same way that they explain the existence of cuprous and cupric ions. Because the distribution of the electrons differs in ferrous and ferric ions, iron forms two series of salts. Because the ferrous ion is less stable than the ferric ion, a ferrous salt tends to change into the corresponding ferric salt.

How ferrous and ferric chlorides are related. A solution of ferrous chloride and also a solution of ferric chloride both contain chlorine ions. But the solutions differ in properties because of the presence of two different iron ions. A solution of ferrous chloride is almost colorless, while a solution of ferric chloride is brownish-yellow. Therefore, we may conclude that ferrous ions are almost colorless, while ferric ions are brownish-yellow. Ferrous chloride, $FeCl_2$, is prepared by the action of iron on HCl away from air.

$$Fe^0 + 2H^+ + 2Cl^- \rightarrow Fe^{++} + 2Cl^- + H_2\uparrow$$

Ferric chloride, used as an astringent in medicine, may be prepared by dissolving iron in hydrochloric acid and then passing chlorine through the resulting ferrous chloride solution.

$$2Fe^{++} + 4Cl^- + Cl_2 \rightarrow 2Fe^{+++} + 6Cl^-$$

From this equation we see that this reaction is an oxidation-reduction reaction. The iron in ferrous chloride has been oxidized to the ferric condition, since there has been an increase in valence from two to three (Fe^{++} to Fe^{+++}). At the same time free chlorine with a valence of zero was changed to a valence of minus one. Therefore, chlorine has been reduced since it has gained an electron.

Conversely, ferric chloride may be changed to ferrous chloride by the action of hydrogen, as shown by the following equation.

$$Fe^{+++} + 3Cl^- + H \rightarrow Fe^{++} + 2Cl^- + HCl$$

Here the ferric ion has gained an electron and its valence has changed from three to two. Therefore, the iron in the ferric chloride has been reduced.

Ferrous chloride, on exposure to the oxygen in air, changes gradually into ferric chloride, the change being easily noted because of the change in color that accompanies the chemical reaction.

How to identify ferrous and ferric ions. Further evidence that the ferrous ion differs chemically from the ferric ion is found in the different tests that are used to identify each ion. A solution of *potassium ferrocyanide,* $K_4Fe(CN)_6$, added to a solution of a ferric salt forms ferric ferrocyanide, a deep blue precipitate called *Prussian blue.*

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN)_6]_3 \downarrow + 12KCl$$

A solution of *potassium ferricyanide,* $K_3Fe(CN)_6$, added to a ferrous solution forms ferrous ferricyanide, a deep blue precipitate

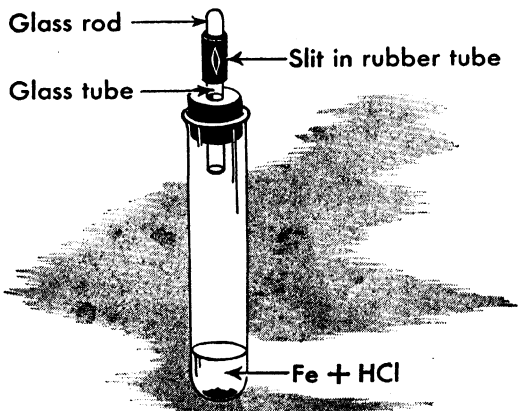


Fig. 107. Laboratory preparation of ferrous chloride. The narrow slit in the rubber tube allows the escape of hydrogen from the test tube and prevents air from entering.

whose composition and color, however, differ from prussian blue. This precipitate is called *Turnbull's blue.*

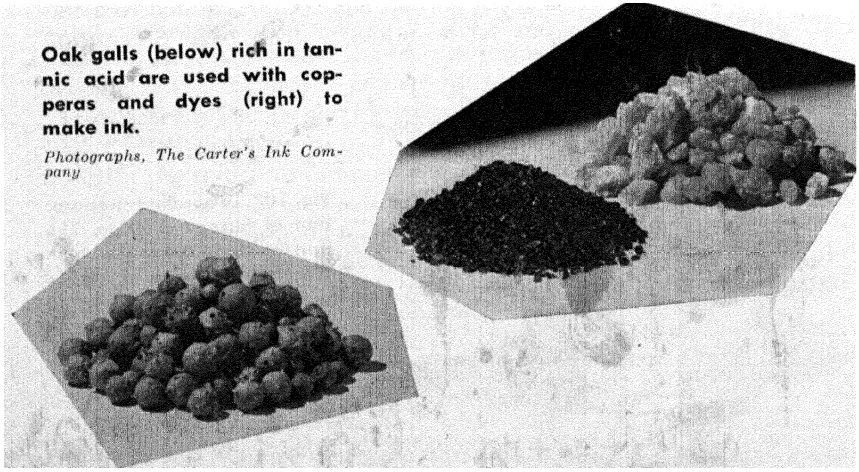
$$3FeCl_2 + 2K_3Fe(CN)_6 \rightarrow Fe_3[Fe(CN)_6]_2 \downarrow + 6KCl$$

These differing deep blue precipitates are specific tests for ferric and ferrous ions. The test for a ferric salt will not work with a ferrous salt, and vice versa.

The reduction of ferric to ferrous salts is used in blueprints. The reversible change of ferrous to ferric compounds is made use of in the manufacture of blueprint paper and ink. Architects and engineers use blueprints instead of the original plans. The process of making blueprints was invented by Sir John Herschel, the eminent English astronomer. White paper is coated with a thin film of (1) ferric ammonium citrate, and (2) potassium ferricyanide. This sensitized paper is then covered with tracing paper containing the design to be reproduced. In darkness, reaction does not occur because a ferric salt does not react with potassium ferricyanide in the absence of light.

When exposed to light, the ferric ammonium citrate is *reduced* to a ferrous salt, which then reacts with the potassium ferricyanide, $K_3Fe(CN)_6$, forming deep Turnbull's blue. In places where the sensitized paper has been exposed to light, that is, wherever the design on the tracing paper has not protected it, the paper will be blue. In places where light has not reached it, the paper remains white. After exposure, the excess chemicals are washed off in running water, leaving the blue precipitate clinging to the paper.

The oxidation of ferrous to ferric salts is used in making writing ink. The commonly used blue-black writing ink is a water solution



Oak galls (below) rich in tannic acid are used with copperas and dyes (right) to make ink.

Photographs, The Carter's Ink Company

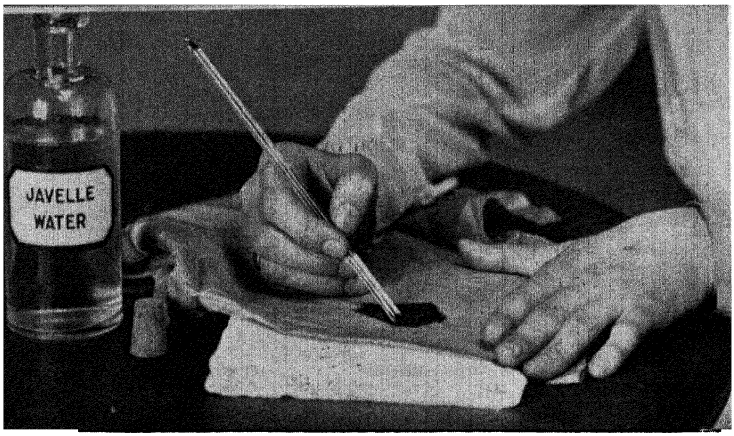
of an iron salt of tannic acid held in suspension by a gummy substance, or *colloid,* called *gum arabic.* A small amount of carbolic acid is added to prevent the growth of molds. Such an ink is prepared by adding green ferrous sulfate called *copperas,* $FeSO_4 \cdot 7H_2O$, to tannic acid obtained from *nutgalls,* a kind of abnormal growth on trees caused by the sting of certain insects such as wasps. The ferrous tannate that is formed is almost colorless. On exposure to air, however, the ferrous tannate changes to ferric tannate, which is a black insoluble substance. Since the black ferric tannate is not formed until the ink has had a chance to oxidize on the paper, a temporary blue coloring matter, such as indigo, is added to the ink. The color change, therefore, is from blue to black. The chemical equation may be represented thus:

$$\underset{\text{colorless}}{\text{Ferrous tannate}} + \text{oxygen (from air)} \rightarrow \underset{\text{black}}{\text{ferric tannate}}$$

Removing stains made by ferro-tannate inks. Ferro-tannate inks are *permanent* inks, that is, they are not affected by oxygen or water. To remove stains made with this kind of ink, it is necessary to reduce the black ferric tannate with some suitable reducing agent, such as oxalic acid (oxalates are present in rhubarb), lemon juice (citric acid), or sour milk (lactic acid). The soluble ferrous tannate and the other ingredients of the ink may then be washed away.

In using oxalic acid to remove a stain made by a permanent ink, soak the stain for a few seconds in a solution of three tablespoonfuls of oxalic acid crystals dissolved in one pint of water. Rinse by dipping first in hot water and then in water to which a few drops of household ammonia have been added. This method of stain removal should not be used on weighted silk fabrics, since oxalic acid attacks silk fibers. Solutions of bleaching powder or of sodium hypochlorite also are used effectively in removing the stains made by permanent inks.

Some inks do not contain iron salts. Not all inks contain iron salts. For example, *laundry ink* used for marking linen consists of an ammoniacal solution of silver nitrate mixed with a small amount of *provisional,* or temporary, color and a gum for thickening the ink. On exposure to light, the silver nitrate eventually changes to a very finely divided *colloidal silver,* which is black and is unaffected by ordinary reagents. *India ink, indelible ink,* and *printing ink* all consist of carbon (lampblack) held in colloidal suspension by gum arabic or some other colloid. They are permanent, since neither acids nor bases dissolve carbon.



U.S.D.A. Bureau of Home, Nutrition and Home Economics

Javelle water is used to remove certain kinds of stains.

Removing stains made by printing ink. To remove a stain made by printing ink, rub the stain with lard or Vaseline and work it well into the stain. This softens the medium in which the carbon pigment is held and, to some extent, disperses the carbon. If the stained material is washable, wash well with soap and water. Otherwise, sponge with carbon tetrachloride, ethylene trichloride, or gasoline.

Kerosene alone will frequently remove printing ink stains. Soak the stained material in kerosene for several hours, wash thoroughly with soap and hot water, rinse, and dry. Since this method of stain removal is rather vigorous, it is recommended for rugged fabrics only.

Washable inks. Some inks are solutions of certain aniline dyes, such as *eosine* (red) or *nigrosine* (black) crystals. As such inks are usually temporary, or *washable,* inks, they are not suitable for making permanent records. They fade after long exposure to air and stains made by them may be washed away with water.

Sympathetic inks. A concentrated water solution of cobalt chloride is pink (color of the cobalt ion), yet the anhydrous salt is blue. Therefore, paper on which a dilute solution of this salt has been used for writing will show a very pale pink, practically colorless writing when damp, and a clear blue writing when the paper is dried by being warmed. Hence it can be used as a *sympathetic ink;* that is, it may be changed from invisible to visible by proper treatment.

Pellets of alumina impregnated with $CoCl_2$ are used in some salt shaker caps. The $CoCl_2$ changes from blue to pale pink as it absorbs moisture. It can be heated in an oven to drive out the water, and used over again.

Another kind of sympathetic ink was used during the Indian Mutiny in 1857. The besieged English soldiers sent out secret messages through the Indian lines by writing with colorless rice water. The

receiver of the message dipped the paper in weak iodine solution and writing appeared. This effect was caused by the precipitation of a bluish-black substance by the reaction of the rice starch and iodine.

Laundry bluing. Most white fabrics have a slightly yellowish tint. The use of bluing does not remove this tint but in combination with the yellow already present, merely masks it by producing a faint gray that appears white. One of the many kinds of soluble bluings in use consists of Prussian blue. Others are blue dyes.

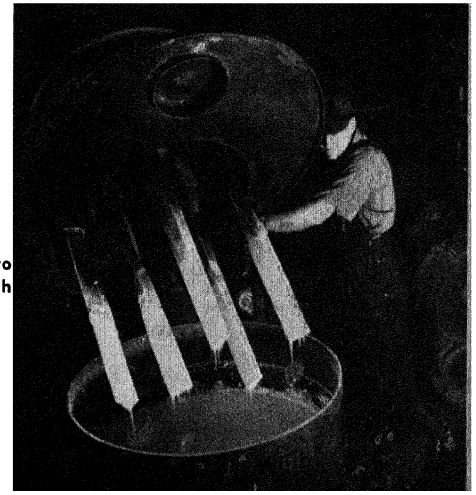
Life too, depends on this reversible change of Fe^{+++} and Fe^{++}. In almost all living cells respiration is controlled by a change of Fe^{+++} to Fe^{++} — containing catalysts called *cytochromes*. The Fe^{+++} picks up an electron from, let us say, sugar and changes to the Fe^{++} condition. The Fe^{++} cytochrome transfers this electron to oxygen thus returning to the Fe^{+++} state.

Lodestone, and two other oxides of iron. A most interesting ore is *lodestone*, an oxide of iron whose formula is Fe_3O_4. The ancients knew about the valuable magnetic property of this iron compound, and among their writings we find: "It not only attracts iron rings but also imparts to them a similar power of attracting other rings, and sometimes you may see a number of pieces of iron suspended from one another so as to form a long chain." The magnetic property of lodestone was first used by mariners in the magnetic compass, which enabled them to venture far out to sea. It may be made by passing steam over hot iron.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$$

Ferric oxide, Fe_2O_3, occurs abundantly as hematite. It may also be prepared by roasting a ferrous compound. Ferric oxide is used

International Printing Ink



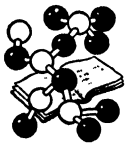
The first step in making printing ink is to mix a chemical pigment with a vehicle such as linseed oil.

as a red pigment in paints, and as *jeweler's rouge* for polishing metals. It is frequently the red pigment in rouge, lipstick, and other cosmetics. *Iron rust* is the hydrated form of hematite. Its formula may be written $(Fe_2O_3)_2 \cdot 3H_2O$.

The brown or red color of certain soils, particularly in Georgia and certain sections of Minnesota, is caused by iron compounds. Most of the iron made in America before and during the Revolutionary War was produced by the reduction of the relatively low grade hematite ores on the Atlantic seaboard.

Ferrous oxide, FeO, a black powder which readily oxidizes to ferric oxide, may be obtained by reducing ferric oxide with hydrogen. The equation is:

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$$



YOU WILL ENJOY READING

National Bureau of Standards. *Inks.* Circular No. 95. Washington, D.C.

U.S. Department of Agriculture. *Stain Removal from Fabrics: Home Methods.* Catalogue No. A1.9:1474/3. Supt. of Documents, Washington, D.C. 10¢. Discusses the removal not only of ink stains but of many other common stains.



USING WHAT YOU HAVE LEARNED

Group A

1. In what ways does the ferrous ion differ from the ferric ion, physically and chemically?

2. Using equations, tell how ferrous chloride can be prepared (a) from iron, (b) from ferric chloride.

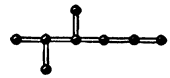
3. Using an equation, show how ferric chloride may be prepared from ferrous chloride.

4. What is the relation between change of valence and oxidation?

5. What is the relation between change of valence and reduction?

6. According to the electron theory, define and illustrate oxidation.

7. According to the electron theory, define and illustrate reduction.



8. When Zn dissolves in H_2SO_4, is the Zn oxidized or reduced? Explain.

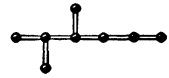
9. A solution contains an iron salt. How would you determine whether the salt is a ferrous or a ferric compound?

10. What is the valence of the first iron in Prussian blue, $Fe_4[Fe(CN)_6]_3$?

11. What is the valence of the ferricyanide ion in Turnbull's blue, $Fe_3[Fe(CN)_6]_2$?

12. A solution contains both ferrous salts and ferric salts. How would you test for the ferrous salt?

13. What uses are made of the reduction and oxidation of iron salts?



14. (a) What is the light-sensitive chemical with which blueprint paper is covered? (b) Light changes it into what other compound?

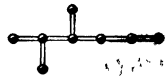
15. Explain how blueprinting is done.

16. Why is it necessary to wash blueprint paper after exposure?

17. What is the chief chemical change that takes place in blue-black writing inks?

18. Name the functions of gum arabic and carbolic acid in writing ink.

19. (a) How would you remove fresh ink stains from cotton cloth? (b) What type of reaction is involved?



20. What are black ink crystals?

21. Describe one kind of sympathetic ink.

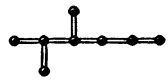
22. (a) What is the composition of laundry ink? (b) What chemical change does it undergo during drying?

23. What three inks contain lampblack as a base?

24. (a) Can lampblack ink stains be removed by reducing agents? (b) Why?

25. What are the formulas and names of three iron oxides?

26. Name two washable inks.



27. What is the relation between the change of Fe^{++} to Fe^{+++} and respiration?

28. Write the equation for the reaction between hot iron and steam.

29. What is the composition of (a) jeweler's rouge, (b) lodestone, (c) rust?

30. Why are ferric compounds more stable than ferrous compounds?

31. What two oxidizing agents can be used to change a ferrous salt to a ferric salt?

32. Determine the percentage of Fe in $Fe_4[Fe(CN)_6]_3$.

33. Assume the formula of limonite to be $(Fe_2O_3)_2 \cdot 3H_2O$. What weight of Fe could be made from 25 tons of this ore?

34. What volume of Cl_2 must be passed over hot Fe to form 150 g. of $FeCl_3$?

Group B

35. Find the percentage of water present in crystals of copperas obtained as a byproduct in manufacture of sheet iron.

36. Why do writing ink stains gradually turn brown?

37. Account for the formation of rust stains on clothes.

38. According to the electron concept of matter, explain the difference between the ferrous atom and the ferric atom.

39. Commercial copperas ($FeSO_4 \cdot 7H_2O$) always contains a small number of ferric ions. Explain.

40. Using an equation, show how oxidation may take place without either oxygen or an oxide entering into the reaction.

41. Study each equation below and state what element or compound is oxidized and what element or compound is reduced. Compare the number of electrons lost or gained by each of the substances affected.

a) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

b) $8KI + 5H_2SO_4 \rightarrow 4I_2 + 4K_2SO_4 + H_2S + 4H_2O$



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Prepare a message in a sympathetic ink similar to the kind used by the besieged English soldiers during the Indian Mutiny in 1857. Show how the message is brought out by reaction with a weak iodine solution.

2. Write a two- or three-page report on the discovery and uses of the magnetism of lodestone. Consult an encyclopedia.

3. Demonstrate to your class the use of blueprint paper. Prepare the blueprint paper for your demonstration.



33 GLASS AND SOME SILICON COMPOUNDS

. . . I have seen the time when glass makers were in great demand because they made the faces for the windows in the churches. Those who painted such faces did not dare eat garlic nor onions, for if they had done so the paint would not have adhered to the glass. . . . The profession of glass making is honorable and the men who pursue it of good repute.

Bernard Palissy, 1510–1589

Silicon, the second most abundant element on earth. Silicon is a member of the carbon family with a valence of four. This lustrous, brittle nonmetal may act as a metal. Its atomic weight is 28.06. The structure of its atom is represented in Fig. 108. Silicon is never found free, but in its compounds, it comprises more than 25 percent by weight of the crust of the earth. Three of the four most important rock-forming minerals — quartz, feldspar, and mica — contain this element.

Silica, most abundant mineral on earth. Silicon dioxide, SiO_2, called *silica,* is the most common mineral on our planet. *Sand* is chiefly SiO_2 with varying amounts of other substances. *Quartz* is pure crystalline silicon dioxide. It is an extremely hard, difficultly fusible mineral which occurs in various gems (jasper, amethyst, opal, onyx, and carnelian), some of which are shown in color following page 382. The hard glassy crystals that form a large part of granite are quartz. Thin sheets of natural and synthetic quartz crystals are used to control radio frequency.

Prolonged inhalation of quartz (silicic) dust from mining or cutting operations often results in a lung disease called *silicosis.* Medical scientists believe this dust poisons the scavenger cells (*phagocytes*)



Fig. 108. Structure of the silicon atom.

of the blood. Quartz miners and stonecutters, who are subject to this serious disease, are protected by mechanical filters that prevent the dust from entering their lungs. Aluminum dust inhalation also is believed by some researchers to act as preventive and remedy for silicosis.

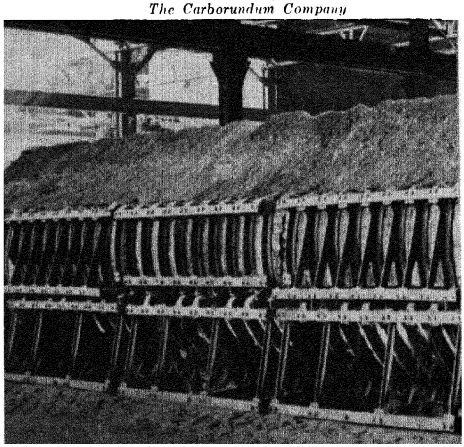
Diatomaceous, or *infusorial, earth* is another form of quartz. This earth is a fine deposit of the microscopic skeletons of countless millions of one-celled aquatic plants called *diatoms* laid down in both fresh water and salt water, probably millions of years ago. It is found in beds hundreds of feet thick and thousands of acres in area, as in California. It is used in making filters; as an insulating material against heat, cold, and sound; in making concrete and mortar; as an extender in paints, and as an abrasive, or polishing, powder.

Silicon carbide and its discovery. At very high temperatures carbon unites with silicon, forming silicon carbide, SiC (see Chapter 22). In this reaction silicon acts as a metal, uniting atom for atom with carbon, whose valence is four also.

The story of silicon carbide begins with an idea in the mind of Edward Acheson, the inventor of artificial graphite (page 324), for making an inexpensive abrasive that would take the place of natural emery and sandstone. He knew that carbon gives steel its hardness, so he decided to try impregnating clay with carbon at high temperatures.

To obtain a very high temperature, he constructed a crude, resistance type electric furnace from an iron bowl with carbon rods as electrodes. He packed coke and clay around the carbon rods and passed a current through the mixture. On examination, he did not find what he expected, but he did notice some tiny, sparkling, bluish,

The Carborundum Company



In this furnace, silicon carbide is produced by passing an electric current through a mixture of coke, sand, sawdust, and salt.

diamond-like crystals which he collected on the moistened end of his lead pencil. He drew the crystals across a piece of glass and found that the glass was scratched very easily. He had discovered a new abrasive, almost as hard as diamond. He called this new abrasive "Carborundum." It is closely related to the diamond in structure — every other carbon atom in the giant diamond lattice is replaced by a silicon atom.

Today "Carborundum" is made at Niagara Falls in electric furnaces about 50 feet long. A charge of coke, sand, sawdust, and salt is subjected to a high temperature until large crystals of silicon carbide collect around the core of the furnace. The sawdust keeps the mass porous, so that gases may pass out freely. The equation for this reaction is:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

An even harder artificial abrasive is *boron carbide,* B_4C, which is manufactured by a method very similar to that used in making silicon carbide. Next to diamond, it is the hardest substance known.

Silicon carbide abrasive devices. Silicon carbide crystals or dust are used in making many kinds of abrasive wheels employed in cutting, polishing, and grinding metals, glass, and teeth.

Cloth and paper coated with silicon carbide crystals embedded in synthetic resins are used widely in industry and compete with emery cloth and sandpaper. Nonskid and nonslip walking surfaces are often composed of silicon carbide crystals.

How is water glass, Na_2SiO_3, made? When sand and soda ash (Na_2CO_3) are heated in a furnace, carbon dioxide is liberated and anhydrous sodium silicate solidifies as a glassy mass.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 \text{ (sodium silicate)} + CO_2 \uparrow$$
$$\text{Soda ash} + \text{sand} \rightarrow \text{water glass}$$

Commercial water glass, in glassy platelike form, is not a pure compound and contains a large percentage of silica.

The thick, colloidal water solution of water glass is used to a limited extent in preserving eggs. It fills the pores of the eggshell, thereby excluding bacteria and air which cause the egg to decay. Water glass is used as a binder in cements, as a low-cost adhesive in paper box and corrugated paper manufacture, and as a filler in inferior soaps. It is also used in sizing paper, in "weighting" silk, in fireproofing curtains and wood, in certain ore-flotation processes.

Sodium silicate is a salt of silicic acid, H_2SiO_3, a very weak acid. Because it is the salt of a strong base and a weak acid, sodium silicate

exhibits a basic reaction. When silicic acid is heated, it loses water and changes to silicon dioxide.

$$H_2SiO_3 \rightarrow H_2O + SiO_2$$

All silicates, except those of sodium and potassium, are insoluble in water. Calcium silicate was mentioned before as the slag formed during the metallurgy of steel. It is used as a heat insulator.

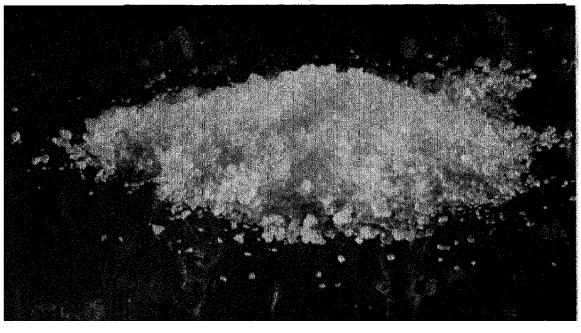
Silica gel, the great adsorber. One of the most useful of the adsorbing substances is *silica gel,* made by treating sodium silicate with hydrochloric acid or by dehydrating silicic acid. The dried substance looks very much like grains of crushed quartz and is riddled with almost invisible pores so numerous that one cubic inch of the substance has a surface area of more than 50,000 square feet.

Silica gel adsorbs both gases and vapors and is very useful in the recovery of organic solvents that would normally be lost by evaporation in many industrial processes. Perhaps its greatest use is in removing water from air. On heating, this water is driven off and the silica gel is *reactivated,* or restored to use.

Great quantities of silica gel are used in air-conditioning, particularly in conditioning rooms in which metal equipment is stored and containers in which metal equipment is shipped. For example, in shipping airplane engines, the engines are first carefully dried and wrapped in a watertight plastic covering, silica gel is added, and the covering is sealed. The engines thus are assured a very dry atmosphere and arrive at their destination without rusting. If a pink coloration occurs when a small amount of cobalt chloride is added to the silica gel, it indicates that the humidity is 30 percent, the danger point for the rusting of most metals. Platinized silica gel, that is, silica gel to which platinum has been added, is used as a catalyst in the cracking of petroleum, and in the manufacture of synthetic rubber.

The development of modern glass. Glassmaking has been carried on since earliest times. Ever since some observant and inquisitive man noticed the formation of a hard, smooth glassy mass around a roaring fire, which fused sand and an alkali such as lime, glass has

Davison Chemical Corporation



Silica gel, a widely used drying agent, or dessicant.

been an article of commerce. From Egyptian tombs, dating back to 4000 B.C., glass beads have been unearthed. Glassworking reached its greatest artistic development in Venice during the sixteenth century. Wandering Venetian glassblowers spread the art throughout Europe.

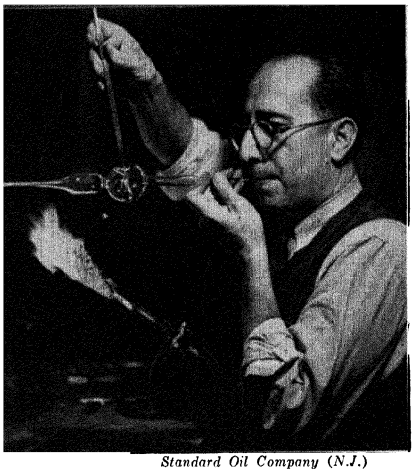
America was almost without glassmakers until the beginning of the eighteenth century. Stringent European emigration laws made it very difficult for glassblowers and other skilled craftsmen to come to the New World. In 1609 some Dutch and Polish glassworkers were sent over by a London company, and a glass factory that made beads and bottles was started in the Jamestown settlement in Virginia. This factory was the first chemical manufacturing plant in America. The industry did not thrive very well until 1859 when the discovery of petroleum opened up a large field for the sale of glass lamps and lamp chimneys. Our best glass, however, was imported from abroad until about 1917, when American initiative and technical skill developed and improved glassware for all uses.

An event of great interest in the development of glass manufacture took place in 1934 when the Corning Glass Works poured the largest single piece of glass in the world. It was a special low-expansion, borosilicate glass disk, 200 inches in diameter, which is now the huge "eye" of the largest telescope in any observatory in the world. It is situated on Mount Palomar in southern California. With this telescope, astronomers can penetrate 500 million to one billion light years into space — distances never attained by any other telescope.

Importance of glassblowing to chemists. Molten glass is converted into glass articles by handworking, blowing, and pressing in molds, or drawing and rolling. The chief contribution of the United States to glassmaking was the invention of automatic glassmaking machinery. For example, the Owens bottle-making machine turns out 5000 bottles per minute.

The chemist counts glassware among his most important tools. In research especially, a knowledge of glassblowing is indispensable. The glassblower and the blowing iron are still essential for turning out delicate glassware and laboratory glass apparatus. Many a difficult problem has been solved by using glass apparatus that was designed and constructed by chemists. After the glass rod and the test tube have given up a secret to the research chemist, the chemical engineer is enabled to carry out the process on a factory scale.

What is the composition of glass? Glass is a hard, transparent or translucent solid formed by cooling a molten mass of silicates with sufficient rapidity to prevent the formation of crystals. Glass is not a true compound, for its composition varies.



Standard Oil Company (N.J.)

Glass is blown in the laboratory to meet the special needs of the research chemist.

During the making of glass, carbon dioxide is liberated and the resulting mass has a fairly uniform composition, which may be represented by $Na_2O \cdot CaO \cdot 6SiO_2$. We may represent the making of glass by the following equation:

$$Na_2CO_3 + CaCO_3 + 6SiO_2 \rightarrow 2CO_2\uparrow + \underset{\text{(soda-lime, or plate, glass)}}{Na_2O \cdot CaO \cdot 6SiO_2}$$

Soda-lime, or plate, glass is used in making bottles and windowpanes.

Making special glasses. Although silicon dioxide and sodium carbonate are used in the manufacture of all glass, other compounds are added to make different glasses with special properties. Thus, lead oxide, PbO, is used instead of calcium oxide in making glass for electric-light bulbs and the heavy, sparkling cut-glass for vases and dishes. Potassium carbonate and arsenic trioxide, As_2O_3, are used with sodium carbonate in optical glass.

Aluminum oxide, Al_2O_3, and boric oxide, B_2O_3, are ingredients of glass that is to be used in cooking ware and in the chemical laboratory. Such glassware can withstand great changes of temperature without cracking because of its low uniform expansion even when heated until it is red. It is used for top-of-stove glass cooking utensils — the so-called "flameware." It is also very resistant to the action of chemicals. "Pyrex," developed in this country, is such a glass. It is a sodium-aluminum-borosilicate glass containing a little arsenic oxide.

Glass of almost any color may be made by adding small amounts of chemicals (usually oxides) to the molten glass. Cobalt oxide makes a blue glass; tin oxide, a white glass; and chromium oxide, a yellow-green glass. Colloidal gold makes a ruby-red glass. Red selenium glass is used in automobile tail-lights and in danger signals. Greenish glass used for windshields absorbs the sun's heat and reduces eyestrain.

A new type of glass has been made, using P_2O_5 instead of SiO_2. This new glass resists even HF and UF_6 (used in making the atomic bomb).

How is plate glass made? In the manufacturing of plate glass, a mixture, or *batch,* of white sand, SiO_2; limestone, $CaCO_3$; and soda ash, Na_2CO_3, is melted in a tank furnace of fire clay by slow heating for about ten days. Waste glass, or *cullet,* may comprise as much as 75 percent of the batch. The heating is done by flames of oil or producer gas. During the melting, carbon dioxide is liberated, and the molten glass must be *refined* until all gas bubbles have been removed.

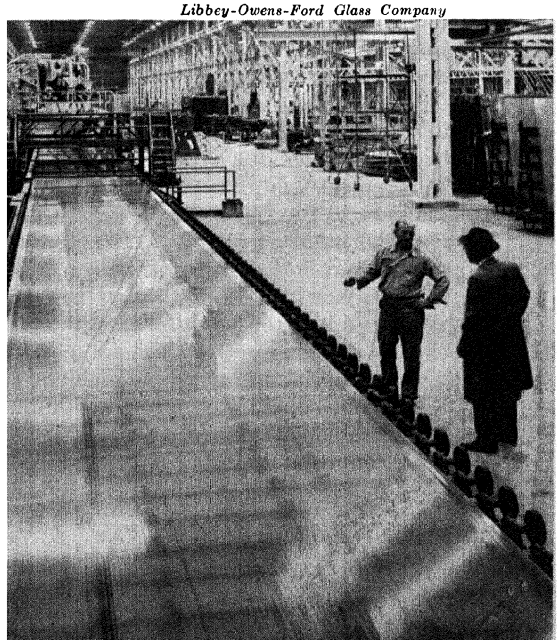
$$CaCO_3 \rightarrow CaO + CO_2\uparrow\ ;\quad Na_2CO_3 \rightarrow Na_2O + CO_2\uparrow$$

The molten glass is now poured on an iron table over which it is spread by means of a huge iron roller until it makes a sheet about half an inch thick. This sheet then passes through an *annealing furnace,* in which the glass cools very slowly, making it less brittle than if it were cooled rapidly.

This glass plate is cut into sheets, ground with a mixture of sand and water, and finally polished with felt and rouge. New equipment now permits grinding simultaneously both sides of a continuously flowing ribbon of glass ten feet wide and one-sixth of a mile long.

Nonreflecting, or "invisible," glasses. Glass can be made almost perfectly transparent. A low degree of reflection may be produced by treating the surface of the glass with an extremely thin film of

Libbey-Owens-Ford Glass Company



This ribbon of plate glass has just come out of the annealing oven and is on its way to be ground on both sides simultaneously.

a metallic fluoride. This thin film, applied to the glass at high temperature as a vapor, causes the light reflected from the glass surface to cancel itself out by interference. Show windows that appear almost invisible are made by this method; but greatest use of nonreflecting glass at present is in the manufacture of "treated" lenses for binoculars, rangefinders, telescopes, and other optical instruments. "Invisible" glass, used in making certain show windows, reflects but little light because of the way in which the glass is curved.

How shatterproof glass is made. To reduce the dangers of flying glass, a *triplex shatterproof glass* is universally used in automobiles. Two pieces of plate glass are covered on one side each with a very thin layer of a special adhesive. Then between the two pieces of glass is inserted a layer of cellulose acetate, or some other transparent synthetic plastic. Heat and pressure are applied and the three layers are thus fused together into what appears to be a single sheet resembling clear glass. Finally, the edges are sealed to prevent the entrance of air or moisture. When such glass breaks, the crack radiates, but the glass splinters remain firmly adhered to the plastic layer. Hence the name *shatterproof.*

Another type of safety glass, called "Securite," does not break into sharp splinters but into small rounded particles, which are not likely to cause serious injury. It is made by sudden quenching, which leaves the surface layer in a state of compression. Glass thus "case-hardened" is very strong.

Glass is widely used in construction. Architectural glass is being used in rapidly increasing amounts as a structural and ornamental material. Glass bricks are widely used in construction. Plate glass doors and walls have become a common sight in modern buildings. Glass pipes, glass tanks, and glass-lined equipment are widely used in the food-processing and chemical industries. There are even glass ovens to enable one to see what's cooking.

"Foamglas," a glass construction material, is a "blown-up" glass that weighs about the same as cork (ten pounds per cubic foot) and has similar insulating properties. It consists of glass in which air is imprisoned, and is made by feeding crushed glass mixed with carbon into furnaces at a temperature of about 2000°F. The glass softens and the heat of the furnace causes the carbon to produce gases, which expand the glass and produce air cells. The resulting product can be sawed easily and cut into convenient shapes. It is not affected by water and, hence, is used to provide buoyancy for life rafts, buoys, and other flotation equipment. It is an excellent insulator against heat, sound, and electricity and, like other glass products, is both

rodentproof and verminproof. It is noncombustible. "Foamglas" is used widely in building ships and in construction of buildings.

"Fiberglas" is made by applying steam under terrific pressure to molten glass fibers as they emerge from tiny holes. These glass fibers can be spun into yarn or woven into cloth used for drapes and curtains which are sunproof, fireproof, and waterproof. Fibrous glass in fluffy masses is used for heat, sound, and electric insulation. It is verminproof, weatherproof, tough, and resilient. Another good insulating material is *rock wool* made by passing live steam through molten feldspar.

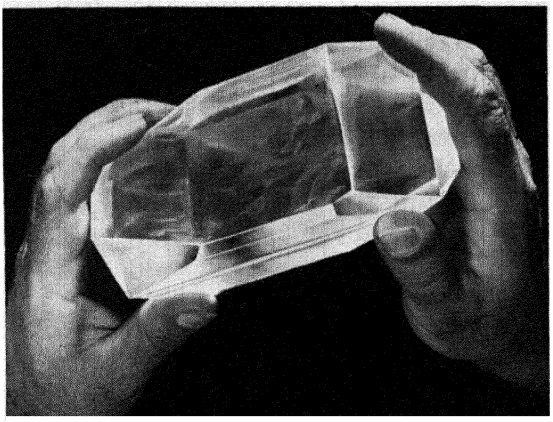
How mirrors are made. A *mirror* consists of a glass plate with a backing of silver, gold, lead sulfide, or some other light-reflecting substance. Fine mirrors are made of heavy plate glass, while inexpensive mirrors are made of thin sheet glass, often window glass.

Before silvering, the glass is polished, cleaned, and rinsed with distilled water. Then the glass is flushed with a solution of either stannous chloride ($SnCl_2$), formaldehyde, Rochelle salt, or some other reducing compound. Immediately, a solution of silver nitrate and ammonia is poured over the glass and left undisturbed for approximately one hour. Reduction of the silver nitrate produces a film, or coating, of silver on the glass. After drying, the coating is protected by being lacquered or painted.

Mirrors are also made by a spraying process in which the chemicals are mixed and sprayed onto the glass. Another method of producing mirrors is by depositing the reflecting coating at low pressure directly from the vapor state.

How enamelware is made. *Enamelware* is steel covered with a layer of glass or glaze. This fused layer is made by melting or spraying a paste of ground glass or glazing materials on the sandblasted surface of the metal and placing the ware in a furnace where the enamel is fused onto the steel. This covering protects the steel against rust and other chemical changes. Enamelware is used in kitchen utensils, refrigerators, bathtubs, sinks, and signs.

Quartz glass is used in research. *Quartz glass,* made by melting pure sand at very high temperatures, has important advantages over ordinary glass. It can be heated to redness and plunged into cold water without cracking. Quartz glass can withstand sudden changes of temperature because it has a low coefficient of expansion — that is, it expands and contracts very little during great changes in temperature. It is much harder than ordinary glass and is only slightly attacked by alkalies. Unlike ordinary glass, it transmits short-wave ultraviolet light, which is beneficial to health.



This is the largest man-made quartz crystal. It was grown on natural quartz seed plate in a period of 28 days.

Brush Laboratories Company

Chemists use beakers, test tubes, ignition tubes, and many other pieces of apparatus made of quartz glass. "Vitreosil" is the trade name of one kind of quartz glass. "Vycor" used for beakers and other laboratory ware is composed of 96 percent silica and four percent B_2O_3. It is comparable to fused quartz. Quartz fibers are used in electric instruments, and quartz is used also in making ornaments, vases, and lenses.

Natural quartz crystals have been cut into lenses. The low expansion of quartz when heated makes it more desirable than glass in many optical instruments. Quartz lenses for telescopes were at one time limited to very small instruments. Today quartz lenses for large telescopes are made by a process developed by the research staff of the General Electric Company at West Lynn, Massachusetts. Finely divided quartz is fed into an oxyhydrogen torch, melted by the flame, and then sprayed on a plate in a specially built furnace until the desired quartz disk is built up.

What is clay? Another important rock-forming mineral is *feldspar.* This is potassium aluminum silicate, $KAlSi_3O_8$. It is decomposed by the action of CO_2 of the air and water (*weathering*), forming clay, a mixture of substances the most important of which is hydrogen aluminum silicate, $HAlSiO_4$. When pure, hydrogen aluminum silicate is a white soft substance called *china clay,* or *kaolin,* a corruption of the Chinese word *Kau-ling*, the name of the hill from which were taken the earliest samples of this clay that reached Europe. Clay is one of the most abundant compounds on earth. Like graphite, clay structure consists of sheets loosely bound to each other, making it slippery and plastic.

How clay is used in making pottery. *Pottery* includes objects fashioned from clay and hardened by fire. The potter's art has been practiced for thousands of years. The simplest form of pottery is made by crushing clay to a powder, adding water until a pasty mass is formed, and then shaping this mass either on the potter's wheel or in molds. After being heated, or *fired,* the clay becomes hard and porous. *Earthenware* is the term applied to the coarser, porous kinds of pottery.

To make earthenware nonporous, various methods are used. The simplest consists of throwing salt on the fuel bed. The salt vapor permeates the fire-clay boxes, or *saggers,* while the clay is being fired, and a layer of a sodium aluminum silicate forms over the surface of the earthenware. This is the simplest form of *salt glaze.* It is dense, smooth, hard, and nonporous, and resists most kinds of chemical action. Whiteware, such as dinnerware, floor and wall tile, as well as glazed bricks, drain pipes, sewer pipes, and terra cotta are treated in this way.

Different and varying chemical substances in the clay produce objects of various colors. Red brick, for example, owes its color to iron compounds in the clay used.

Porcelain and *chinaware* are made from pure clay (kaolin) mixed with powdered quartz and feldspar. Before firing, the molded object is sprayed, brushed, or dipped into a fine suspension of kaolin richly mixed with powdered quartz, feldspar, and certain metallic oxides such as lead oxide. During the heating fusion takes place and the glaze that forms is thicker and more resistant to chemical action than salt glaze. Decorations are painted on the object either before the first glazing or between the first and second glazings. (The Chinese were the oldest and greatest of potters, but in more recent times the western nations have developed *ceramics,* the art of making objects from clay, to a high state of perfection.)

How Portland cement is made. For centuries cement in one form or another has been used as a binding material in roads and various structures. The most common form used today is *Portland cement.*

Portland cement is made in slightly inclined rotating cylindrical kilns of steel lined with firebrick. These kilns are the largest pieces of rotating machinery in industry. Some of them are as long as three pullman cars, and 14 feet in diameter. A mixture of clay and limestone is crushed and dumped in at the top of the slightly inclined kiln. As this mixture gradually works its way down the kiln, it meets long tongues of flame produced by burning powdered coal, oil, or natural gas at the bottom of the kiln. These hot flames raise the

temperature of the mixture to about 1600°C. At this point, complicated chemical reactions take place, and water (steam) and carbon dioxide are liberated. The product, called *clinker,* consists of glass-hard masses varying in size from birdshot to large marbles.

When cool, the clinker passes through a series of grinding machines in which it is ground to a powder so fine that it will pass through a screen that contains 40,000 openings per square inch. Such a screen is so fine that it actually holds water. During the grinding, a very small percentage of gypsum is added. The gypsum regulates the early hardening period of cement when it is mixed with water and prevents cracking. The finely ground product is Portland cement.

How cement hardens. Although the composition of cement is not fixed, it may be considered to be a mixture of calcium aluminate and calcium silicate together with some calcium hydroxide, all in varying amounts. The following reaction gives some idea of the chemical change that takes place during the manufacture of cement.

$$5CaCO_3 + 2HAlSiO_4 \rightarrow \underbrace{2CaSiO_3 + Ca_3(AlO_3)_2}_{\text{cement}} + 5CO_2\uparrow + H_2O\uparrow$$

Limestone + clay →

The hardening of cement, which takes place even under water, is caused both by chemical changes which produce hard crystals and by the colloidal nature of the finely powdered cement. The nature of the hardening process is not thoroughly understood, but the following reaction describes one of the changes that takes place:

$$Ca_3(AlO_3)_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2H_3AlO_3$$

Portland cement takes a number of days to harden, or *set,* completely. Quick-setting cements, capable of hardening within 24 hours, have been developed and are in use. *Asbestos cement* is made by mixing the two. It is used for sewer pipes, wallboard, and house shingles. *Stucco* is made from a mixture of cement, CaO, and SiO_2.

Concrete is made by adding sand, screened gravel, or stone to cement. When wire mesh or steel rods are embedded in the concrete, the product is called *reinforced concrete.*

Another silicate and cosmetics. Hydrated magnesium silicate, or *talc,* is used in making nearly all bath powders and is present in smaller amounts in most face powders. In very finely ground form called *talcum,* it is the substance that causes powders to spread on easily and smoothly. Kaolin is added to face powders for adhesion, and to precipitated chalk for absorbing perspiration. Titanium

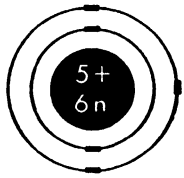


Fig. 109. Structure of the boron atom.

dioxide, TiO_2, and zinc oxide, ZnO, are used as white pigments for covering. Perfumes of various kinds are added also.

Under the Federal Food, Drug, and Cosmetic Act of 1938 supervision of cosmetics is a responsibility of the Food and Drug Administration. Hence, face powders made by reputable manufacturing cosmeticians do not contain substances that are harmful to the skin. However, certain persons may find that one brand of face powder irritates the skin, while another brand does not. Such a discovery means only that these persons are allergic to components of the first brand, and that none of these substances is present in the second. Nothing more serious than a change of powders is indicated, in most cases. Frequently, an inexpensive powder is just as satisfactory as a much more expensive one.

Structure of the boron atom. The element boron is fifth in the table of atomic numbers. It has, therefore, three electrons in its outermost ring and is trivalent. Like silicon, it shows distinct nonmetallic properties in its chemical behavior. Its electron structure is represented in Fig. 109. Like silicon, boron does not occur free, and it does not have important uses as a free element.

Death Valley supplies us with borax, sodium tetraborate. Borax, $Na_2B_4O_7 \cdot 10H_2O$, is the most common compound of boron and, like the sodium salt of silicic acid, it is soluble in water. Most of the borax used today is obtained from saline lakes, such as Searles Lake in the Mojave Desert of California, or from the beds of dried-up lakes, such as Death Valley in southeastern California. The discovery of the region of these important deposits was a dramatic event. A party of gold-seekers bound for California in 1850 parted from the main caravan to take a shortcut. The country became more rugged and as they reached the summit of what is now known as Funeral Range, they looked down upon a deep and narrow valley whose walls were steeper than any they had yet seen. With ropes and chains they lowered their wagons down from the mesa and, finding no water, made what proved to be their last camp. Only a few survived, and to commemorate the fate of those who perished for lack of water, the region was named Death Valley.

Thirty years later, rich borax deposits were discovered in this desolate country. The famous 20-mule-team caravans hauled this

salt across almost 200 miles of desert to a railroad which carried it to glassworks, soap factories, plants making glazes and enamels, and to millions of homes where it was and still is used as a mild alkali for cleaning purposes. It is also used for softening water.

Since borax is the salt of a strong base (sodium hydroxide) and a very weak acid (boric acid), it undergoes hydrolysis readily, giving an alkaline reaction.

Today, borax is a factory-made product. In Inyo County, California, not far from Death Valley, calcium borate occurs in large deposits. When this compound is treated with sodium carbonate, a double replacement occurs and the sodium tetraborate formed is separated by crystallization.

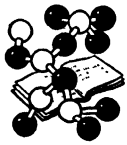
Boric (boracic) acid, H_3BO_3. This white, soapy powder is found mixed with borax. In Tuscany and in Nevada it occurs alone, issuing with steam from the ground. It is condensed from this foamy steam solution, or is prepared by treating calcium borate with sulfuric acid. It may be used, with care, as an antiseptic in eyewashes. Its water solution is an extremely weak acid, scarcely affecting litmus paper. When powdered boric acid is heated, it changes to boric oxide, B_2O_3, a clear, glassy solid resembling quartz.

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

How borax is used in the so-called bead tests. While borax is being heated, it first loses its ten molecules of water of crystallization as steam and then decomposes further, forming a complex double compound containing B_2O_3. This oxide of boron has the property of combining with traces of metallic oxides which impart color to the glassy bead. This property furnishes chemists with a convenient laboratory test for a number of metallic elements. Cobalt oxide, for example, gives a blue bead, and manganese oxide a violet bead.

Borax is used as a flux in welding, soldering, and brazing. The oxides found on the surface of the metals dissolve in it.

Borates in fireproofing. Manganese and zinc borates are used in fireproofing textiles. They are fusible at low temperatures and cover the fibers of the textiles on exposure to flame to prevent the fire from creeping. Zinc borate also prevents the growth of mildew.



YOU WILL ENJOY READING

Clow, A. and N. *The Chemical Revolution,* pp. 269–292. Batchworth Press, London, 1952. Chapter XIV deals with glass.

Harrison, George R. *Atoms in Action: The World of Creative Physics,* pp. 65–81. William Morrow & Co., New York, 1941. Deals with "Glass More Precious Than Rubies."

Wall, Florence E. "Cosmetics." *Journal of Chemical Education,* Sept., 1942, pp. 435–440. An excellent article on cosmetics for skin, hair, hands, and personal hygiene.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) What part of the crust of the earth is composed of silicon compounds? (b) What are the names of some of these compounds?

2. Make a diagram of the atom of Si.

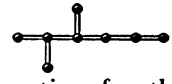
3. (a) In what ways do sand, quartz, and amethyst differ from one another? (b) In what ways do they resemble one another?

4. Describe the (a) formation, (b) composition, and (c) uses of diatomaceous earth.

5. (a) Write the equation for the manufacture of SiC. (b) What is its chief use and (c) on what two physical properties does this depend?

6. Copy and complete the following statements. Do not write in this book. SiC is manufactured in an .... It was first made by .... The two chief substances used in the manufacture of this compound are ... and .... As an abrasive, SiC is harder than ... but softer than .... Another widely used abrasive first prepared by a chemist is ....

7. (a) How is silica gel made? (b) Name some of its uses.



8. (a) Write the equation for the preparation of water glass. (b) What is its chemical name? (c) What are three important uses of water glass?

9. (a) Name a soluble silicate other than water glass. (b) What is the formula of a silicate made during the metallurgy of Fe?

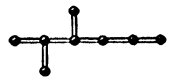
10. Theoretically what weight of sand is needed in making 250 tons of SiC, assuming that the sand is 99 percent SiO_2?

11. (a) From what is plate glass made? (b) Write the equation.

12. Describe the process of changing molten glass into plate glass.

13. (a) How is shatterproof glass made? (b) Is it shatterproof? (c) Why?

14. How many cubic feet of CO_2 are liberated during the making of 2500 lb. of plate glass whose composition is assumed to be $Na_2O \cdot CaO \cdot 6SiO_2$? (The ounce-molecular volume is 22.4 cu. ft.)



15. (a) What are three kinds of glass other than plate glass? (b) Tell the way in which the composition of each differs from that of plate glass.

16. (a) Describe the annealing of glass. (b) Why is annealing necessary?

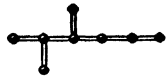
17. (a) What substance is used in making red glass? (b) white glass? (c) yellow-green glass?

18. What is (a) "Foamglas"? (b) "Fiberglas"? and (c) rock wool?

19. Describe how a mirror is made.

20. (a) Of what substance are most sinks and bathtubs composed? (b) Describe the manufacturing process involved.

21. What are three advantages of quartz glass over ordinary glass?



22. (a) In what ways are Si and C similar in properties? (b) In what ways do they differ? (c) Compare the oxides of these two elements.

23. Describe the manufacture of chinaware.

24. Describe briefly how cement is made.

25. On the basis of structure explain why quartz is so hard and clay so plastic.

26. What changes take place during the hardening of cement?

27. What are the chief ingredients present in a face powder?

28. Make a diagram of the atom of boron.

29. (a) What is borax? (b) How is it obtained for use in industry?

30. How would you expect a borax solution to react with litmus?

31. Using an equation, show what happens when H_3BO_3 is heated to a high temperature.

32. (a) Describe the borax bead test. (b) Give two examples.

33. Compare SiO_2 and Al_2O_3 in physical and chemical properties.

34. Explain the presence of substances of diamond-like appearance in the steps of much-used stairways made of certain minerals.

35. Describe briefly the method used in making large glass disks for telescopes.

Group B

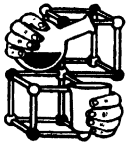
36. Does exposure to the action of the weather affect glass? Explain.

37. How would you distinguish between crystals of quartz, calcite, and washing soda by physical tests?

38. NH_4OH should not be stored in bottles closed with ground glass stoppers. Why?

39. We are told not to heat washing soda in silica dishes. Why?

40. What are the chief differences between Portland cement, hydraulic cement, and natural cement?



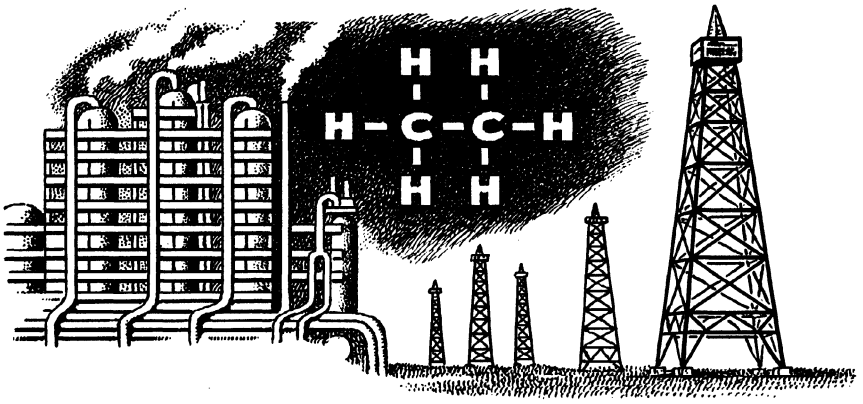
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. On the basis of a conversation with a stone mason or cement contractor and what you can get from books, write a report on the uses of mortar and cement. What do you conclude from your study?

2. Make a so-called *silica garden* as follows and describe it to your class. Mix a 40 percent water glass solution with about seven times its volume of water in a tall jar. Drop tiny crystals of cobalt chloride, nickel sulfate, or a manganese salt into this solution and watch them "grow."

3. Investigate the types of insulating material used in: (a) the walls of your house, (b) your refrigerator, (c) your furnace, and (d) around the pipes. Report your findings to the class.

4. Make a study of various face powders in common use and compare prices and ingredients present if possible. Discuss your conclusion.



34 HYDROCARBONS AND THEIR DERIVATIVES

. . . Let us learn to dream, then perhaps we shall find the truth . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding. Kekulé, 1829–1896

The tremendous scope of organic chemistry. As you will remember, Woehler's synthesis of urea, in 1828, changed chemists' definition of *organic chemistry* from the *chemistry of the products of living things* to the *chemistry of the compounds of carbon,* regardless of whether they are *natural* or *synthetic.*

We have already learned about the two oxides of carbon as well as a few other carbon compounds. But what we have learned is only an infinitely small part of organic chemistry. Woehler himself recognized this, for he forsook his first love almost in its infancy, complaining that, "Organic chemistry nowadays almost drives me mad. To me it appears like a primeval tropical forest full of the most remarkable things, a dreadful endless jungle into which one does not dare enter, for there seems no way out." At that time, Woehler's feelings were justified. Most of the theories that have helped make organic chemistry more clearly understood were then unknown.

Why is there such a tremendous number of compounds of carbon? One reason lies in the unique property of carbon atoms which can unite with one another, forming compounds containing many carbon atoms. A second reason is that it is possible to make two or more carbon compounds having the same percentage composition

and the same simple formula, but differing fundamentally in both physical and chemical properties. These differences are caused by the fact that the atoms within the molecule of each compound are arranged in different ways. This phenomenon, known as *isomerism,* is characteristic of carbon compounds. One such compound is an *isomer* of another such compound. Cellulose and starch, for example, have the same percentage composition but are entirely different compounds both chemically and physically.

In general, organic compounds are non-polar, do not dissociate and hence do not react quickly with each other as do inorganic compounds. Heat decomposes them more easily than inorganic compounds. Organic compounds usually dissolve in organic solvents and are usually insoluble in water.

What are hydrocarbons? Of all the organic compounds, the simplest are those compounds of two elements only — carbon and hydrogen. These compounds are hydrocarbons.

Among the important and less complex hydrocarbons are methane, CH_4; acetylene, C_2H_2; ethylene, C_2H_4; benzene, C_6H_6; naphthalene $C_{10}H_8$; and turpentine, $C_{10}H_{16}$. From such compounds, an almost infinite variety of substances is built up by substituting, for certain of the hydrogen atoms of their molecules, other atoms or groups of atoms.

Methane, and its substitution products. In Chapter 24, we learned that natural gas contains as much as 95 percent methane, CH_4, and coal gas as much as 40 percent. We may write the formula for methane by placing the symbol C in the center and the symbols for hydrogen outside, as shown in Fig. 110. Each of the hydrogen atoms represented is joined to the carbon atom by a dash, or *bond.* Such a formula is the *structural formula* generally used by organic chemists. Each single bond represents a valence of one; thus the formula shows the tetravalence (valence of four) of carbon and the univalence of hydrogen. Fig. 110 also shows a second method of representing a molecule of methane in which two dots stand for each pair of shared electrons.

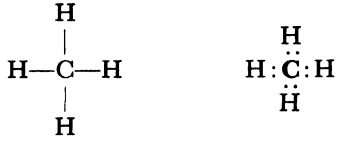


Fig. 110. Two methods of representing the structural formula of a molecule of methane.

The hydrogen atoms of methane may be replaced by some other univalent element or radical, thus forming new compounds, which we call *substitution products* of methane. Thus, when one atom of hydrogen from methane is replaced by a chlorine atom, we get *monochloromethane,* or methyl chloride, used as a local anesthetic. When two of the hydrogen atoms are replaced by chlorine, we get *dichloromethane;* when three are replaced, *trichloromethane;* and, finally, when four are replaced by chlorine, *tetrachloromethane.* The formulas, common names, and structural formulas of these substitution products are:

CH_3Cl methyl chloride	CH_2Cl_2 methylene chloride	$CHCl_3$ chloroform	CCl_4 carbon tetrachloride
H H:C:H Cl	H H:C:Cl Cl	Cl H:C:Cl Cl	Cl Cl:C:Cl Cl

The methane series of compounds. To facilitate the study of the thousands of organic compounds, chemists have arranged many of them that have similar structure into groups. The methane group of hydrocarbons, usually called the *paraffin series,* consists of a number of compounds which differ in composition from methane by one or more CH_2 groups. For example, ethane, C_2H_6, differs from methane, CH_4, by one CH_2 group.

Propane, C_3H_8, the third member of the paraffin series, differs from ethane, C_2H_6, by another CH_2 group. "Pyrofax," a gaseous fuel, used chiefly for cooking and heating in rural areas, is essentially propane, with some butane (C_4H_{10}), the next member of this series. Other members of the series may be seen in Table 16. Note that the formulas of the paraffin hydrocarbons may be represented by the formula C_nH_{2n+2} in which n represents any number.

Methane	Ethane	Propane
H | H—C—H | H	H H | | H—C—C—H | | H H	H H H | | | H—C—C—C—H | | | H H H

Each member of such a series differs from the member that precedes it in both physical and chemical properties; the physical properties, as a rule, differ from one another gradually and in the same direction (see Table 16). Such a series of compounds, each of which

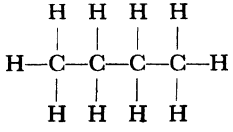
TABLE 16.
MEMBERS OF METHANE, OR PARAFFIN, SERIES

NAME	FORMULA	BOILING POINT	NORMAL STATE
Methane	CH_4	−161.4° C.	Gas
Ethane	C_2H_6	− 88.3	Gas
Propane	C_3H_8	− 44.5	Gas
Butane	C_4H_{10}	+ 0.6	Gas
Pentane	C_5H_{12}	36.2	Liquid
Hexane	C_6H_{14}	69.0	Liquid
Heptane	C_7H_{16}	98.4	Liquid
Octane	C_8H_{18}	124.6	Liquid
Hexadecane	$C_{16}H_{34}$	Melts at 18° C.	Solid
Hexacontane	$C_{60}H_{122}$	Melts at 102° C.	Solid

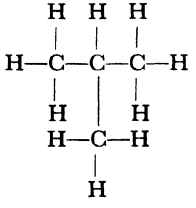
differs by a common group from the compound immediately before it or following it in the series, is called a *homologous series.* For example, if the members of the paraffin series are listed according to molecular weights, the boiling point of each member is higher than that of the members that precede it.

Each member of a homologous series can be used in making substitution products. This property of building more and more complex compounds from simpler ones by the addition of carbon groups is one chief reason for the wide scope of organic chemistry.

How the structure of the butane molecule explains isomers. We may write the structural formula of butane in two ways:



and



Normal butane, or *n*-butane

Isobutane

You can see that the same number of carbon and hydrogen atoms is present in each molecule represented by the two structural formulas, but that the way the atoms are connected, or grouped, is different. This difference in grouping of atoms is accompanied by a difference in physical and chemical properties of the compounds represented. The two substances are thus isomers. Very many such isomers

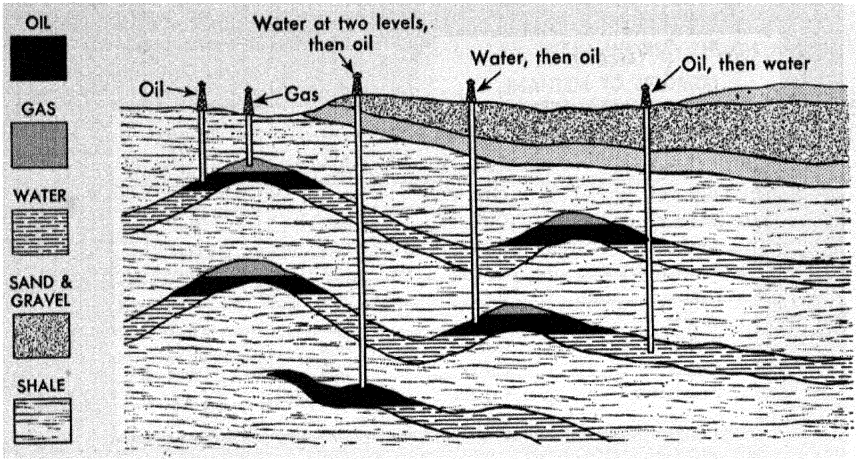


Fig. 111. Cross section of oil-bearing strata.

exist; indeed, certain organic compounds may have hundreds of isomeric modifications. All this is further explanation for the great number of carbon compounds.

How petroleum was discovered in the United States. Petroleum, or *crude oil,* is the chief source of hydrocarbons.

It is generally a dark-colored and unpleasant-smelling liquid found underground either in certain shale rocks or held in natural reservoirs under great pressure by nonporous (*impervious*) rock layers. During the boring of salt wells in certain sections of the United States it was found that some petroleum, or "rock oil," was generally present. This oil was first used in small amounts as a medicine, but when the possibilities of using it in lighting homes were realized, definite attempts were made to obtain it by drilling.

In 1859, Edwin L. Drake was placed in charge of a company which was to attempt to extract oil from the earth in the region around Titusville, Pennsylvania. Mr. Smith, a well-driller, was employed to drill the well. Late one sultry Saturday afternoon, Smith drew out an iron bit from a well-hole and started to measure the depth, which previously was 69 feet. Within a few feet of the top gurgled a black, oily liquid. Using a tin pitcher-pump, he raised several barrels of oil. Then, with a sample of "rock oil," Smith climbed on a mule and set out posthaste to spread the news that "Drake's Folly" was, after all, a "dream come true." This dramatic incident was the beginning of a new era.

After the War Between the States, men from the disbanded armies literally rushed to the oil fields. From then on, the oil industry grew by leaps and bounds. With the increasingly widespread use of farm

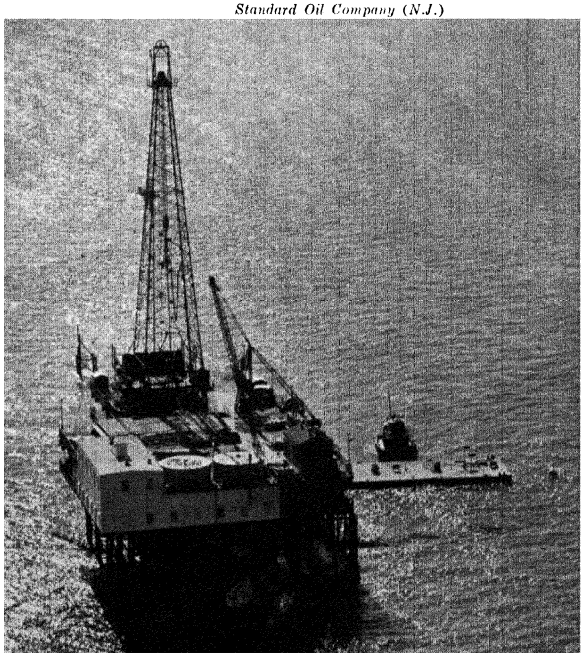
tractors, airplanes, oil burners, automobiles, and other machinery, the demand for oil has grown, until in a recent year the United States produced more than 2.3 billion barrels of oil (about 50 percent of the world's production). The oil business is the biggest business in the United States.

Crude oil is sent from well to refiner. Crude oil is pumped from the wells through underground pipelines to storage tanks, and then shipped to the refineries by rail in tank cars, by sea in tankers, or is pumped continuously through underground pipelines.

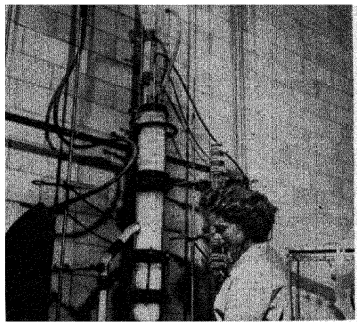
This type of unseen "railroad," more than 170,000 miles of which are now in operation, delivers approximately 75 percent of the crude oil to the refineries. The fields in Texas, Oklahoma, and California supply almost two-thirds of our oil production.

How petroleum is refined. Crude oil is a mixture of hydrocarbons containing varying amounts of such impurities as free sulfur, compounds of sulfur, wax, clay, and other substances. The work of the refiner consists first of removing these impurities. Then his major job is to separate this mixture of hydrocarbons into groups of compounds, or *fractions,* each of which has different uses. He makes use of the fact that the boiling points of different hydrocarbons are not the same. The process of separation is called *fractional distillation.* The oil is heated in a pipe still furnace. The resulting mixture of liquids and vapors is discharged into a *fractionating* or "bubble"

Standard Oil Company (N.J.)



A Diesel-operated oil rig located seven miles from shore in the Gulf of Mexico. The rig contains living quarters, storage tanks, and all other facilities for maintaining the operation of the oil well. The crude oil is carried to the mainland in barges.

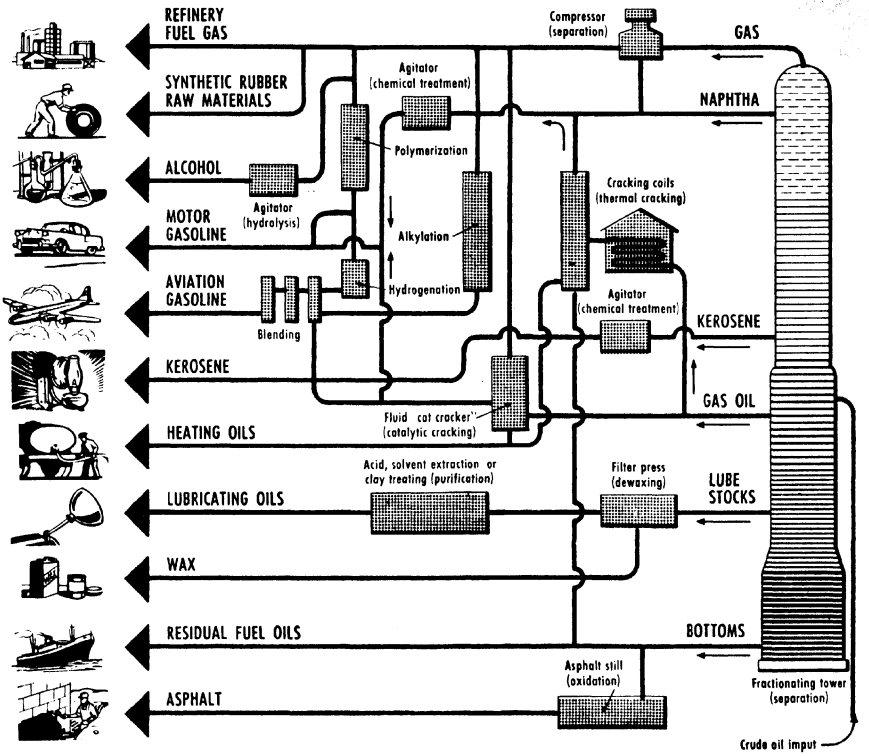


Standard Oil Company (N.J.)

A chemical research engineer demonstrates a catalyst flow operation. The catalyst, which is used in the giant "cat" crackers, is composed of silica and alumina so finely divided that it may be circulated through pipes and otherwise treated much like a liquid.

tower in which the vapors rise. Here fractions of the hydrocarbons are sorted out according to their boiling points in *one continuous operation.* Liquid products condense and are drawn off at various levels of the tower (see illustration below). The heavier fractions (with the higher boiling points) condense on the lower trays. The lighter fractions condense on the higher and cooler trays. Several gases from methane through butane are collected at the top of the tower. Then come, in descending order, naphtha, gasoline, kerosene,

PETROLEUM REFINING FROM CRUDE OIL TO END PRODUCT



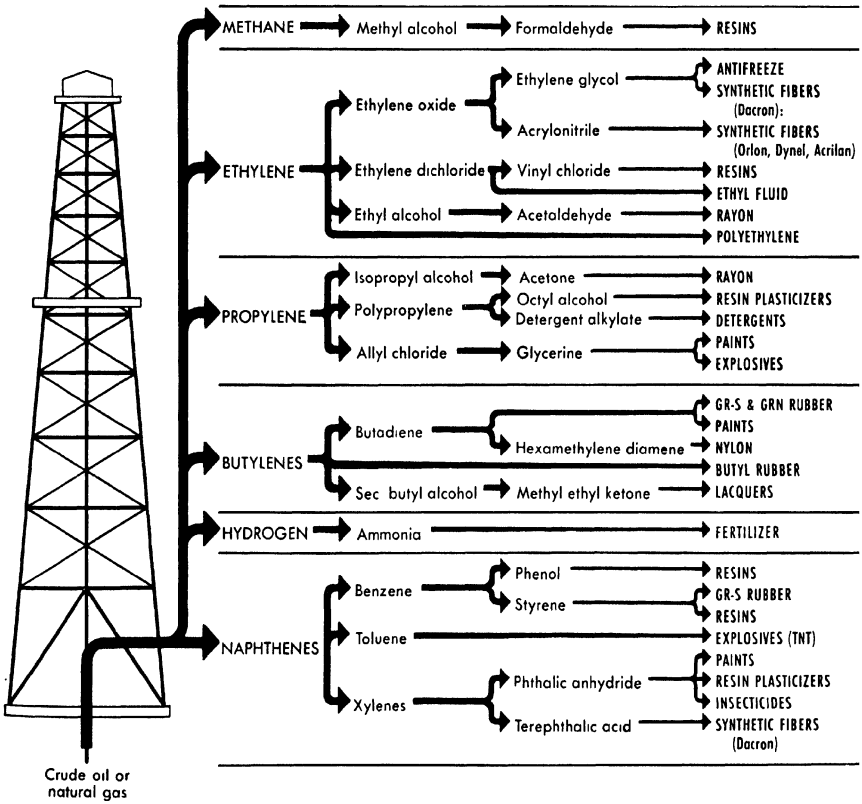
gas oils, heating oils, lubricating oils, waxes, tars, and asphalts.

The final residue is petroleum coke used as fuel and for electrodes. From a 42-gallon barrel of crude oil, it is possible to obtain 19 gallons of gasoline, 16 gallons of gas and fuel oil, 2 gallons of kerosene, 1.5 gallons of lubricating oils, and 3.5 gallons of other products.

The composition and treatment of gasoline. Gasoline itself is not a single hydrocarbon. On the contrary, it is a mixture of hydrocarbons, chiefly C_6H_{14}, C_7H_{16}, and C_8H_{18} (octane). As these individual hydrocarbons differ only slightly from one another in boiling points, they are not separated in refining because of the high cost.

Gasoline is a colorless liquid with a characteristic odor, and is not *miscible,* or mixable, with water. It boils, on the average, at about 80°C. and is highly combustible. Today it is the most widely used and most important single distillate obtained from the refining of petroleum. With the advent of the automobile, the demand began to shift from kerosene to gasoline, and numerous processes have been

PETROCHEMICALS: MORE THAN 650,000 POSSIBLE COMPOUNDS



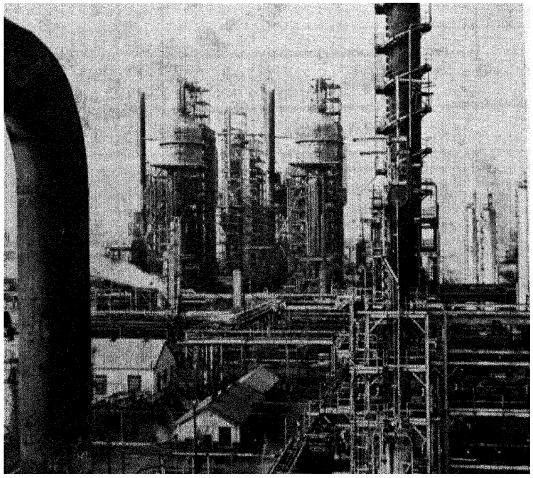
devised to increase the amount of gasoline obtained from a barrel of crude oil. However, kerosene is still widely used in rural areas for lighting and heating and is a primary fuel for jet aircraft.

"Cat cracking," second major branch of refining. Kerosene, gas oil, and fuel oil differ from gasoline in that they are composed of hydrocarbons containing a large number of carbon and hydrogen atoms in their molecules. By subjecting these heavier fractions of petroleum to carefully regulated higher temperatures and pressures in specially designed stills, these more complex hydrocarbons, such as $C_{12}H_{26}$, are broken down, or *cracked,* into simpler molecules, such as C_8H_{18}, that is, into the hydrocarbons found in gasoline. This process is called *thermal cracking,* first successfully introduced in 1913 by William M. Burton.

In the early days, *thermal* cracking of petroleum, involving high heat and pressure alone were used. Today most petroleum is cracked *catalytically* and at a lower temperature. One of the catalysts used in catalytic cracking is a claylike powder, which must be brought in contact with the vaporized oil. The powder catalyst flows like a fluid into an incoming stream of vaporized oil, every molecule of which comes in contact with a particle of the catalyst. The bubbling, boiling mass resembles a dust storm. Most of the high-octane aviation gasoline is produced by catalytic cracking. This fluid "cat cracking" process was introduced in 1936.

Polymer gasoline. The volume of gasoline obtainable from crude oil has been increased not only by cracking but also by *polymerization.* In a sense, this process is the reverse of cracking. We start with the lighter hydrocarbons whose small molecules of the *same* architecture are joined together to form larger molecules or *polymers.* These molecules after hydrogenation become gasoline hydrocarbons.

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A general view of an oil refinery. In the left background are three catalytic crackers; in the center is an alkylation unit.

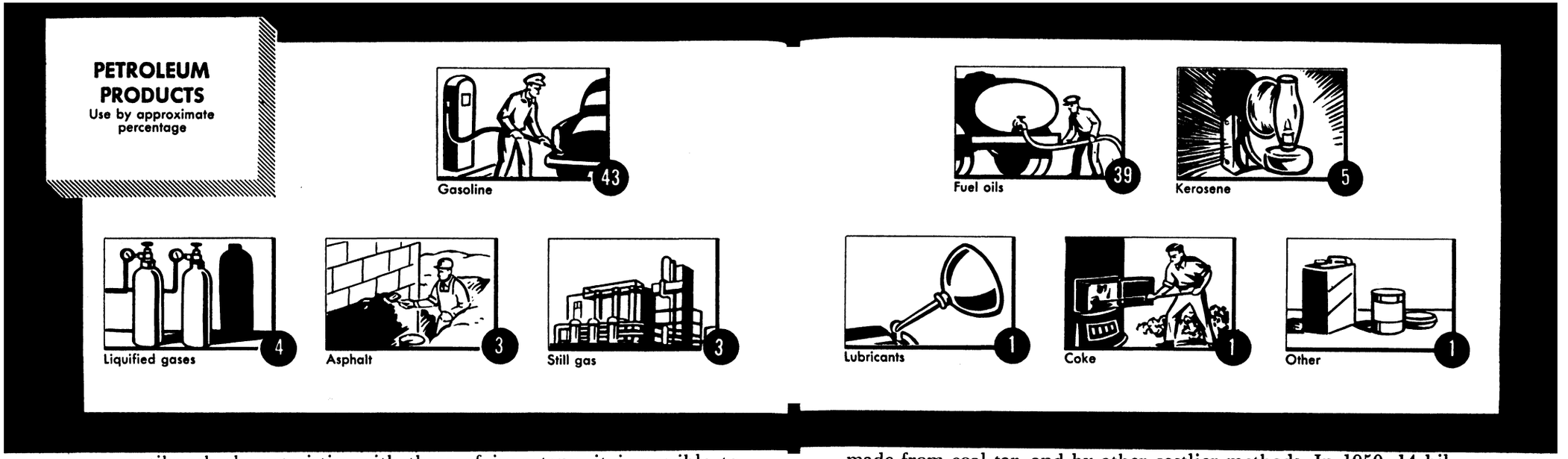
In *alkylation,* the small hydrocarbon molecules of *unlike* composition are hooked together, with the help of concentrated sulfuric acid or anhydrous HF as catalysts, to form additional gasoline. In 1899 only five gallons of gasoline were obtained in the *straight-run* (simple fractional distillation) from a barrel of petroleum. Today 19 gallons may be obtained.

Casing-head gasoline is obtained by cooling and compressing the "wet" natural gas liberated from oil wells. This supplies about ten percent of our gasoline.

What makes a gasoline engine knock? The gasoline vapor-air mixture must be properly compressed before ignition. If the mixture burns too rapidly the gases expand faster than the piston of the engine can move, and the motor knocks. *Severe* knocking results in loss of power and damage to the engine. In 1921 Thomas Midgely, Jr. prepared *tetraethyl lead,* $(C_2H_5)_4Pb$, which, when added to gasoline (three milliliters per gallon of gasoline), retards the speed of combustion of the gasoline-air mixture and, thus, prevents knocking. "Ethyl fluid" is an anti-knock preparation containing tetraethyl lead (TEL), a clear, heavy, oily, poisonous liquid, and ethylene dibromide, $C_2H_4Br_2$. The ethylene dibromide helps to remove the lead products through the tailpipe thus preventing injury to valves and ignition points.

What the octane number of a gasoline means. The term *octane number* is applied to gasolines to measure their tendency to knock in engines. A high octane number designates a gasoline with less knocking tendency than a gasoline with a low octane number. The standard of comparison for arriving at octane numbers is the hydrocarbon known as *iso-octane.* This compound has high antiknock characteristics. Another hydrocarbon, *n-heptane,* has very poor antiknock qualities. By mixing these two substances and using the resulting mixture as fuel in an engine, it is possible to compare the antiknock characteristics of gasolines under the same conditions. For example, if under the same conditions a gasoline knocks the same amount as a mixture of 84 percent iso-octane and 16 percent *n*-heptane, the gasoline is given an octane number of 84. This was the average octane number of regular gasolines in 1950, that of premium gasolines was 91.

A 100-octane gasoline, such as is used widely in aviation, has as good antiknock characteristics as pure iso-octane. Such high-octane gasolines are produced by blending carefully selected ingredients. The octane number of gasoline is increased by adding synthetic blending agents, such as iso-octane or isopentane, and "Ethyl fluid." Since the octane number of a gasoline is merely a comparison of its



antiknock characteristics with those of iso-octane, it is possible to produce gasolines that are even more knockless than iso-octane itself. Gasolines surpassing 100 octane in performance are in use.

Solving the problem of scarce motor fuels. The specter of the greatly depleted petroleum resources of the world has been seen by the chemist. Already definite strides have been made not only in cutting down waste of our irreplaceable natural gas and petroleum reserves but also in (1) the synthesis of gasoline by the hydrogenation of coal (by the Bergius process, described on pages 333–335), (2) the synthesis of gasoline by treating coal or natural gas with steam and oxygen (by the Fischer-Tropsch process), and (3) the economical extraction of gasoline from our huge deposits of oil shale.

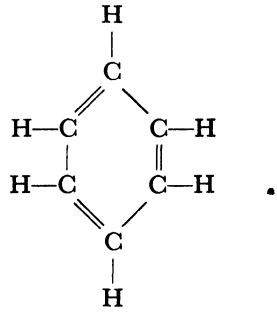
Countries such as England, France, Germany, and Italy depend for their needs upon petroleum sources outside their borders. In an effort to make themselves self-sufficient in motor fuel, they have undertaken to increase their potential fuel supplies. Their substitute motor fuels consist of compressed gases and liquids from coal and wood, and the addition of wood and grain alcohol to the gasoline that is used in their motorcars, buses, trucks, and other motor conveyances. (More explanation about the mixture of alcohol and gasoline that is used as a motor fuel is given in Chapter 35.) At present these substitute fuels can compete with natural gasoline only with the aid of special legislation and government subsidies.

Petrochemistry. This is the science of converting petroleum and natural gas into hundreds of important organic chemicals formerly made from coal tar, and by other costlier methods. In 1950, 14 billion pounds of such chemicals were manufactured — a 2000-fold increase in a generation. Among them are synthetic ethyl alcohol and butanol formerly obtained exclusively by fermentation; glycerine formerly a byproduct in the manufacture of soap; benzene and toluene which used to be obtained chiefly from coal tar; acetic acid formerly obtained from alcohol; as well as acetone, isopropyl alcohol, ethylene glycol and ethylene dibromide, synthetic rubber, synthetic fibers such as "Orlon," "Dacron," and nylon, some plastics, insecticides, and detergents.

Benzene, another hydrocarbon. This was first obtained in 1825 by Michael Faraday, who separated some fish oil by fractional distillation into various compounds. One of these compounds was *benzene,* a colorless, highly combustible liquid. It is lighter than water, in which it is slightly soluble. It has a pleasing, characteristic odor and boils at 80.5°C. It is composed of molecules containing six atoms of carbon and six atoms of hydrogen. Thus, its formula is C_6H_6.

For many years after the discovery of benzene, the structural formula of this compound was unknown. In 1865 Kekulé (kā'kŏŏ-lā), an eminent German chemist, who had been baffled by this problem and had pondered over it for years, solved it in a curious way. When, after a strenuous day in his laboratory, he had fallen asleep in a chair before his fireplace in Ghent, suddenly, he began to dream of snakes and atoms whirling round and round before him. The old benzene problem was haunting him. "All at once," he reported, "I

saw one of the snakes seize hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke and spent the rest of the night in working out the consequences of the hypothesis." He had solved this knotty problem. He gave the benzene molecule a ring or hexagon structure.



Structural formula of benzene, C_6H_6.

Note that alternate carbon atoms are joined by *double bonds*. The *ring structure* of benzene was the key to the composition of many other compounds. Its discovery ushered in a renewed advance of organic chemistry. Years later in talking of this unusual discovery Kekulé remarked, "We must learn to dream."

Ring hydrocarbons such as benzene differ from others in that they readily react with other chemicals such as nitric and sulfuric acids to form hundreds of other organic compounds, known as *benzene derivatives*. It thus is the starting point in the manufacture of many compounds essential to the dye, explosive, plastic, rubber, and perfume industries. Benzene is also an excellent solvent for gums, fats, and resins. (*Benzine,* a mixture of hydrocarbons from petroleum should not be confused with *benzene,* the pure chemical compound described here.)

Chloroform, an early anesthetic. Chloroform, $CHCl_3$, is formed by the replacement of three of the hydrogen atoms of methane by three chlorine atoms. It is a heavy, colorless liquid with a characteristic, agreeable odor and pleasant taste, and boils at 61°C. It is a good solvent for fats and many other complex organic compounds. Its most generally known use is as an *anesthetic,* a substance that produces temporary local or general insensibility.

The first use of this chloroform as an anesthetic was made toward the close of 1847 by James Simpson, an Edinburgh surgeon. A year earlier, Dr. John C. Warren performed the first major surgical operation in which an anesthetic was employed. This was in the Massachusetts General Hospital, where the patient was put under the

influence of *ether,* another anesthetic. This incident ushered in a new era in medicine, for it banished overnight the dreadful pains of surgery without anesthesia. Thus chemistry and medicine, hand in hand, were responsible for one of the greatest advances in the progress of civilization. Incidentally, Oliver Wendell Holmes, American poet and physician, suggested the name *anesthetic.*

Iodoform, an antiseptic. *Iodoform,* CHI_3, another halogen derivative of methane, is a yellow, crystalline solid with a characteristic odor. It is used as an antiseptic, especially on surgical bandages.

Carbon tetrachloride fights fires and removes stains. *Carbon tetrachloride,* CCl_4, is a derivative of methane, all of whose hydrogen atoms have been replaced by chlorine atoms. It is a colorless, heavy, nonflammable liquid with a low boiling point. Under the name "Pyrene," it is used in fire extinguishers, and since it is a nonconductor, is especially useful in fighting fires around electric equipment.

Carbon tetrachloride is also an excellent solvent for fats, oils, waxes, and other organic compounds. It is used in the degreasing of bones, garbage, hides, and raw wool. When mixed with naphtha, it makes an excellent dry-cleaning fluid. The fumes of carbon tetrachloride are poisonous and it should therefore be used in a well-ventilated room, and kept away from children. Dry cleaning is now done with trichlorethylene (C_2HCl_3) and perchlorethylene (C_2Cl_4) which are less toxic.

Aniline, foundation of the coal-tar dye industry. When benzene is treated with nitric acid, one of its hydrogen atoms may be replaced by an NO_2 group, forming *nitrobenzene,* $C_6H_5NO_2$. This NO_2 group may be reduced with hydrogen, forming $C_6H_5NH_2$, *aniline,* a colorless liquid which is the basis of many *coal-tar dyes,* or *aniline dyes.*

Coal → benzene → nitrobenzene → aniline → aniline dye

A mistaken notion exists among many people that coal tar is a magic mixture that contains all the dyes, drugs, and perfumes used by man, and that the chemist has only to wave a magic wand over it to obtain them. In reality, only a thorough knowledge of the composition and chemical properties of the various substances obtained by the fractional distillation of coal tar enables the chemist to build up the thousands of synthetic compounds used today. A discussion of these chemical reactions is beyond the scope of this book, but it may be found in textbooks on organic chemistry.

Sources of rubber, another hydrocarbon. During his second visit to America, Columbus saw some boys in Santo Domingo playing with black balls made from a liquid obtained from certain trees.

Later some of the *natural rubber* from which these balls were made was taken back to England, and Priestley found a use for it in erasing pencil marks, and so gave it its name. Years later, in Scotland, a man named MacIntosh spread rubber, dissolved in a suitable solvent, over fabric and marketed the first rubberized raincoats. Today its thousands of uses make rubber an essential of our highly industrialized age.

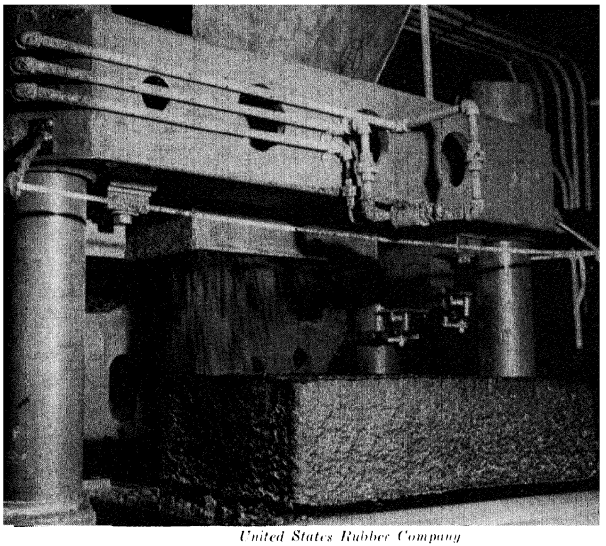
Raw rubber is an elastic solid obtained from a milky liquid sap, *latex,* which occurs in several tropical plants. The purest and best raw rubber is *Pará rubber,* originally collected from trees in the Amazon Valley. The largest rubber plantations today are found in Indonesia, Malaya, Ceylon, Indochina, and India, where more than 80 percent of all the world's rubber is grown.

Each molecule of rubber is actually a giant polymer, composed of thousands of molecules of the colorless liquid *isoprene,* C_5H_8, so hooked together as to form a very long molecule of high molecular weight. Such linkage of atoms in chains (polymerization) is an essential characteristic of the formation of all rubber-like materials and is very closely related to such qualities as elasticity, insolubility, and flexibility (see pages 292, 592, and 602–603).

How rubber is processed. When raw rubber is heated, it becomes soft. Such a substance is called a *thermoplastic.* In addition, raw rubber has relatively little strength and very slight durability. Obviously, raw rubber is not well suited to the manufacture of long-wearing commodities. However, when sulfur is mixed with rubber and the resulting mixture is heated, the rubber is vulcanized and is no longer thermoplastic. In vulcanization, it is believed that the molecules of the long polymers are cross-connected and linked up at frequent intervals throughout their length by combining with atoms of sulfur.

Actually, before rubber is vulcanized, other substances in addition to sulfur are added. Among these are carbon black, lead oxide, zinc oxide, and carbonates of calcium and magnesium. The amount and kinds of substances to be added are determined by the characteristics desired in the finished rubber. After thorough mixing has been completed by the kneading action of large rollers, the rubber is molded and vulcanized by heat.

Raw latex is used on an extensive scale in the production of thin rubber products. The raw rubber is precipitated by electricity from a latex solution, to which ammonia has been added to prevent coagulation of the rubber. The rubber is precipitated directly onto forms of the desired shape. Rubber-asphalt mixtures are being used on



United States Rubber Company

A 75-pound loaf of synthetic rubber emerges from the drier, the final step in its manufacture. It will be weighed, baled, and shipped to another plant for conversion into tires or other useful products.

concrete roads for longer life and more riding comfort. Latex solutions whipped with air form a spongy, cushiony rubber used in making foam rubber articles such as mattresses and gaskets.

The organic chemist gives the world synthetic rubber. Partly as the result of emergency needs, and also to build up new domestic industries, the governments of several nations have called upon their chemists to produce rubber-like substances to take the place of natural rubber. The triumph of these attempts is another example of a profound chemical revolution. It also demonstrates the tremendous value and social force of synthetic chemistry, for today our whole industrial machine literally rolls on rubber.

In 1892, Sir William Tilden, an English chemist, observed that isoprene changed into a rubber-like substance, especially in the presence of pure sodium, which acted as a catalyst. During World War I, German chemists produced a rubber substitute called *buna*. It was inferior to natural rubber and also was too expensive to manufacture for peacetime needs. However, they were able to use an improved product during World War II.

In our own country various experimental synthetic rubbers were made, but not until 1931 did the first successful American man-made rubber appear. In that year du Pont announced the beginning of the commercial manufacture of a synthetic rubber called *neoprene*. Neoprene is not identical in composition with natural rubber. It is an *elastomer* which includes rubber, and other plastics with rubber-like properties. Credit for the fundamental experiments which led to this great achievement belongs to the late Dr. J. A. Nieuwland (nū'lănd), of the University of Notre Dame. The Du Pont chemists

discovered that *monovinylacetylene,* which Nieuwland had prepared in the course of researches on acetylene, could be converted to *chloroprene,* C_4H_5Cl, by treating it with hydrogen chloride in the presence of a suitable catalyst. But more important, they found that chloroprene polymerized readily to neoprene, the first general-purpose man-made rubber.

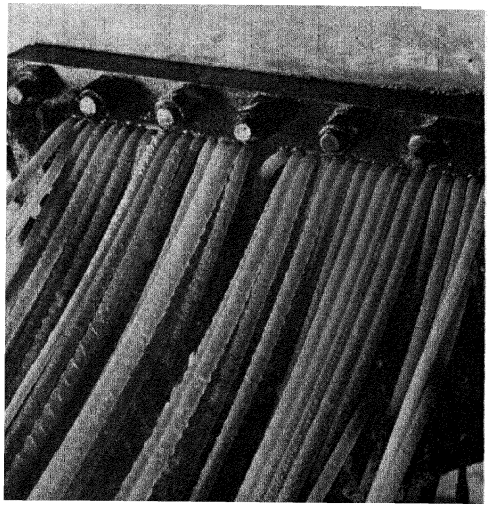
In 1942 the Japanese cut the United States off from practically all sources of natural rubber. Our manufacture of neoprene was immediately increased and, in addition, the United States government undertook to make buna-S rubber on a tremendous scale. Now annual production of synthetic rubber approximates 800,000 tons.

Synthetic rubbers are here to stay. For certain specialized uses natural rubber is superior to most synthetic rubbers. But synthetic rubbers are more resistant to deterioration than natural rubber and are superior for many uses.

It may be that the rubber tree will remain one of the sources of rubber for many years to come, but its synthetic rivals will help to keep the price of rubber in check. The bloodshed and warfare caused by the struggle for sources of natural rubber might well have been prevented by the successful synthesis of low-cost man-made rubber a century ago.

Buna-S, chief synthetic rubber. Mainstay of the government's synthetic rubber war program, buna-S rubber, now called *GR–S* (Government Rubber-Styrene), is most like natural rubber in its processing and performance qualities. It is manufactured from two hydrocarbons, *butadiene* (bū-tə-dī'ēn), a gas, and styrene, a clear liquid. Butadiene is obtained from both petroleum and ethyl alcohol. Styrene is obtained from benzene and petroleum. Thousands,

Standard Oil Company (N.J.)



Extrusion of butyl rubber in a synthetic rubber plant.

of molecules of butadiene and styrene are polymerized in the presence of a catalyst to build a single molecule of buna-S. The process for making buna-S may be represented as follows:

1) **Butane → butene → butadiene (C_4H_6)**
2) **Ethylene + benzene → ethylbenzene → styrene (C_8H_8)**
3) **Butadiene + styrene → polymerization → buna-S**

Other synthetic rubbers include *buna-N* (GR–N), a copolymer of butadiene and acrylonitrile, suitable for low-temperature use; *butyl rubber,* a polymer of isobutylene used to make inner tubes; and *thiokol.*

Naphthalene and its many uses. A small portion of certain fractions obtained during the destructive distillation of coal consists of white, shiny crystals having a tarry odor. These crystals are *naphthalene,* insoluble in water, but soluble in benzene, alcohol, and ether. It burns with a smoky flame. Its formula is $C_{10}H_8$. This compound is the starting point in the manufacture of many valuable chemicals such as dyes, plastics, and paints, and it is also generally used in the home under the name *moth balls* or *camphor balls.* Naphthalene sublimes at ordinary temperatures, and thus gradually disappears.

Control of clothes moths. In addition to naphthalene, *paradichlorobenzene,* a benzene derivative, is useful in the control of clothes moths. It is the larvae of these moths that cause damage to textile fibers of animal origin. Methods of control are to stop the larvae from eating, or to kill them. Paradichlorobenzene or naphthalene crystals will do both, if used in sufficient quantities, and if the fabrics are placed in relatively airtight containers so that the vapors given off do not become too diluted with air. One pound of paradichlorobenzene or naphthalene crystals to 100 cubic feet of relatively airtight space is recommended.

Sprays consisting of *pyrethrum* or *derris* extracts in light oils are fairly effective in moth control. Pyrethrum is a flower that is cultivated in Peru, Japan, and Africa. A pyrethrum-like chemical is now made synthetically. Such sprays are contact insecticides and kill only the insects or larvae with which they come in contact. Mothproofing solutions, consisting chiefly of water solutions of fluorides, are effective if applied in the manufacture of the fabric to be protected or when the fabric is wet and thorough impregnation is possible.

Turpentine, the thinner for paints. Another hydrocarbon that is used extensively in industry is *turpentine,* $C_{10}H_{16}$. It is a colorless, oily liquid having a strong characteristic odor. It is obtained by distillation from the pitch of certain kinds of pines. Turpentine boils

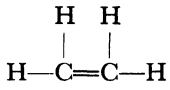
at 155°C., is combustible, and is an excellent solvent for rubber, resins, and other organic compounds. It is insoluble in water, but mixes with ether and absolute alcohol. From it, *synthetic camphor,* another enemy of clothes moths, has been prepared.

The manufacture of *synthetic camphor,* $C_{10}H_{16}O$, much cheaper than the natural product, is another of the triumphs of synthetic chemistry. Previously, the wood of camphor trees in Japan and Formosa was the sole source of this white, crystalline substance.

The chief use of turpentine is as a *thinner* in the manufacture of paints and varnishes. A *varnish* is a liquid containing a resin and linseed, or tung, oil mixed with turpentine. Upon drying by evaporation and oxidation, varnish leaves a thin, lustrous, generally transparent film over the surface to which it has been applied. Enamel paint is a varnish containing some pigment.

Ethylene, C_2H_4, a very versatile and fruitful gas. Ethylene is a flammable, colorless gas obtained from cracked oils and natural gases.

Structural formula of ethylene.



Such a compound is said to be *unsaturated,* because its two carbon atoms are joined not by a single bond but by a *double bond.*

Atoms of chlorine and other elements, and radicals, such as the hydroxyl, can be united with unsaturated compounds, forming *addition products.* Among these are ethylene dibromide, and ethylene glycol, or *glycol.* This colorless, practically odorless compound, $C_2H_4(OH)_2$, has a boiling point of about 197°C. and is used as an antifreeze in radiators under the names "Prestone," and "Zerex." Another of these ethylene addition products is glycol ether, an excellent solvent for organic compounds.

Ethylene gas is used in the manufacture of synthetic ethyl alcohol, fibers, and plastics, and in the artificial ripening, coloring, and bleaching of some fruits and vegetables. Ethylene mixed with oxygen is used as an anesthetic.

DDT, most effective insecticide. Insecticides protect millions of people, their crops, and their livestock. They include: (1) repellents such as sulfur; (2) stomach poisons such as arsenic compounds which are used against beetles and other chewing insects; and (3) body contact poisons which attack sucking insects such as plant and body lice. The world's most effective contact insecticide, *dichlorodiphenyltrichloroethane,* or DDT, is a white crystalline substance. It was first synthesized in 1874, but its remarkable insect-killing powers were

unrecognized until several years ago when it saved the Swiss potato crop, which was severely threatened by the Colorado potato beetle.

DDT's first important uses were during World War II, for it was promptly adopted as the active ingredient of the most effective louse powder ever made. Before its advent, it was said that soldiers engaged in campaigns were never without lice, and while lice in themselves are not pleasant, the fact that they carry typhus fever makes them triply dangerous. DDT's effectiveness as a killer of lice is unparalleled. It is so effective that after one application, underclothing can be considered louseproof for as many as eight weeks.

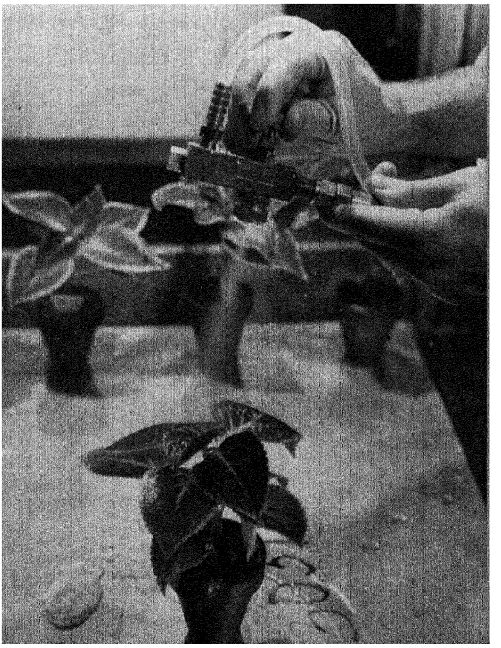
In peacetime, DDT protects people all over the world against insect-borne diseases such as malaria, typhus, and bubonic plague. It also protects their livestock against lice, ticks, and horn flies.

So far, DDT is known to be effective against flies, fleas, mosquitoes, bedbugs, lice, moths, silverfish, codling moths, and most agricultural pests. Unfortunately DDT apparently kills useful insects along with the insect pests. It is applied in powder form, as a spray, and in *aerosol bombs*, (see page 149).

Other effective insecticides are benzene hexachloride, methoxychlor, and the toxaphenes which are made from turpentine and used against the boll weevil and livestock pests.

2,4–D, a selective weed-killer. A weed-killer that is effective against broad-leaved plants, such as poison ivy and ragweed, but not against

Standard Oil Company (N.J.)



Testing a new plant fungicide in an organic chemistry research laboratory.

grasses or other narrow-leaved plants is known as *2,4–D*. It is a plant hormone which kills by stimulating very rapid growth. (It has also been used to control the flowering of the pineapple plant.) A water solution of the sodium salt of dichloro-phenoxy acetic acid, 2,4—D, is applied as a spray. Millions of acres of the cereal belt of this country are treated with this herbicide. Another weed-killer is ammonium sulfamate (*ammate*) which kills any plant which it touches including poison ivy.



YOU WILL ENJOY READING

"DDT: Deals Death to Disease." *Chemistry,* Feb., 1945, pp. 1–10.

Haynes, Williams. *This Chemical Age.* Alfred A. Knopf, New York, 1942. A very interesting discussion of various methods of manufacturing rubber-like substances.

Peterson, J. M. "History of the Naval Stores Industry in America." *Journal of Chemical Education,* May, 1939, pp. 203–212; June, 1939, pp. 317–322. Gives the history of the discovery of benzene.

Raper, Howard R. *Man against Pain: The Epic of Anesthesia.* Prentice-Hall, New York, 1945. Good for popular reading.



USEFUL IDEAS DEVELOPED

1. Organic chemistry is the chemistry of the compounds of carbon.

2. The tremendous number of organic compounds may be explained by: (1) the unique property of carbon which enables its atoms to unite with one another, forming compounds containing many carbon atoms; (2) isomerism, the existence of compounds having the same percentage composition but different properties as a result of different arrangements of their atoms.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) Why is organic chemistry no longer defined as the chemistry of compounds derived from living organisms?

(b) Who was the first man to make a compound hitherto formed only in living organisms? (c) What compound did he synthesize?

2. Today what does the study of organic chemistry include?

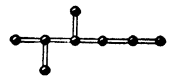
3. What are two reasons for the existence of a larger number of compounds of C than of compounds of any other element?

4. (a) What are isomers? (b) Give examples using structural formulas.

5. (a) What is a hydrocarbon? (b) Give the names and formulas of four hydrocarbons.

6. What is "pyrofax"?

7. Write the chemical names and structural formulas of the four chlorine substitution products of CH_4.



8. (a) What is a homologous series of compounds? (b) Write the structural formulas of the first four members of the methane series.

9. (a) When and (b) by whom was the first successful oil well dug in the United States?

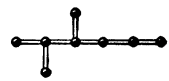
10. What are two chemicals usually found present in or near petroleum deposits?

11. What is the chemical composition of petroleum?

12. (a) What is the principle underlying the refining of petroleum? (b) Name five important products obtained in the refining of petroleum in the order of their liberation from the crude oil.

13. What is the composition of the most important single distillate produced in the refining of petroleum?

14. (a) What important chemical change takes place during cracking? (b) What is the difference between thermal and catalytic cracking?



15. (a) In what way does casing-head gasoline differ from straight-run gasoline? (b) What is polymer gasoline?

16. Assuming the composition of gasoline to be C_8H_{18}, find the volume of air necessary for the complete combustion of 172 g. of this gasoline.

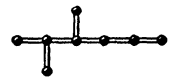
17. What volume of air is needed for the complete combustion of the CH_4 contained in 1500 l. of natural gas, assuming that the natural gas is 95 percent CH_4?

18. (a) What is octane number? (b) How may the octane number of a gasoline be changed?

19. What are three different methods of increasing our nation's gasoline supply from our own natural resources?

20. What substitutes for gasoline are being used today?

21. What is petrochemistry?



22. Give two examples of the science of petrochemistry.

23. Why is an open vessel of gasoline more dangerous than an open vessel of kerosene?

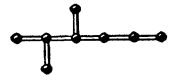
24. What is the difference between fractional distillation and destructive distillation?

25. When and by whom was C_6H_6 discovered?

26. What industries depend upon C_6H_6 for use in the manufacture of their products?

27. Compare (a) the properties, (b) chief source, and (c) uses of benzene with those of benzine.

28. (a) Describe how Kekulé discovered a method of representing the structural formula of C_6H_6 in which he was able to uphold the theory that carbon has a valence of four. (b) Of what value was his discovery?



29. What is the principal difference between the structure of the molecule of $CHCl_3$ and that of C_6H_6?

30. What chemical relationship exists between CH_4 and CHI_3?

31. Match correctly the words in the two columns.

1) trichlorethylene	a) turpentine
2) anesthetic	b) ethylene
3) aniline	c) Warren
4) Tilden	d) coal-tar dyes
5) camphor balls	e) cleaning fluid
6) paint	f) rubber
7) fruit ripening	g) naphthalene
	h) synthetic camphor

32. Each molecule of one of the members of the CH_4 series contains 12 atoms of carbon. What is the formula of this compound?

33. (a) From what is natural rubber prepared? (b) What is the reason for the desire among chemists to make rubber substitutes?

34. What are some advantages of synthetic rubber over natural rubber?

35. (a) What is meant by the statement that C_2H_4 is an unsaturated compound? Illustrate by a structural formula. (b) For what is C_2H_4 used?

36. (a) Name three types of insecticides. (b) How does 2,4-D work?

Group B

37. A ton of coal gave 5000 cu. ft. of illuminating gas containing 40 percent CH_4, 50 percent H_2, five percent CO, and five percent nitrogen by volume. (a) What weight of CO_2 would be produced by the complete combustion of this volume of gas? (b) What volume of CO_2 and of water vapor would be formed?

38. (a) What is a polymer? (b) a copolymer?

39. (a) How is rubber processed? (b) What is vulcanization?

40. Explain the manufacture of neoprene.

41. In what ways do synthetic rubbers differ from natural rubber?

42. Discuss the manufacture of buna-S rubber.

43. How may clothes moths be controlled effectively?

44. Name two problems that may arise from the use of DDT.

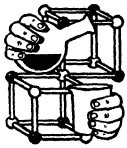
45. What dangers from gasoline are present when the carburetor of an automobile is not properly adjusted?

46. (a) Why is kerosene unsuited for use in the engine of a standard motorcar? (b) Why is gasoline unsuited for use in kerosene lamps?

47. It has been said that artificial rubber will eventually displace natural rubber. What factors tend to interfere with such an economic transition?

48. (a) What causes knocking in a gasoline engine? (b) How is it reduced or prevented?

49. Why was buna-S rubber selected for the chief role in the government's synthetic rubber war program?



PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. If you live in an oil-producing region, visit an oil well and write a report on how oil is brought to the surface. Do you find any oil being wasted? Is natural gas present? Is it being wasted or used?

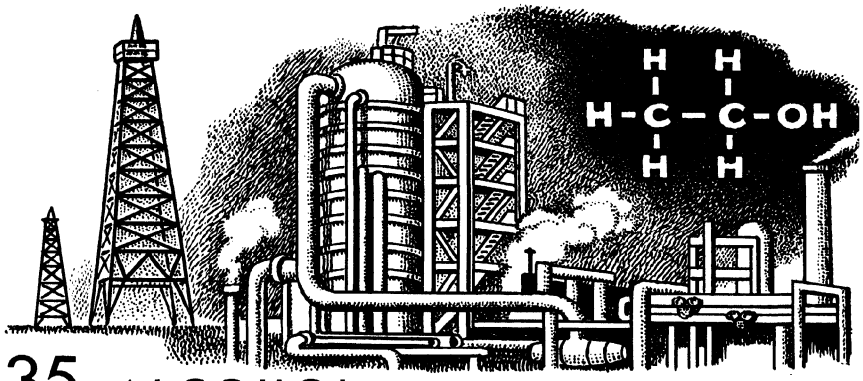
2. Have a talk with some intelligent automobile mechanic on the functions of the automatic "choke" and the carburetor. Explain to your class how improper adjustment of the "choke" and carburetor waste gasoline.

3. What should be the important factors to be considered in the selection of a gasoline for your car? Investigate the question of quality, grade, and price of various gasolines sold within your vicinity. What do you conclude from your investigation?

4. Using two different types of paper clips to represent carbon and hydrogen atoms, arrange them to show the different structures of n-butane and isobutane. See if you can determine the number of isomers of C_5H_{12} (pentane) by means of these clips.

5. Organize a class discussion on the topic "What Will Happen to the Machine Age When and If Petroleum Reserves Run Out."

6. The speed at which an automobile is driven bears an interesting relation to the amount of fuel consumed per mile. Make an investigation of this subject using reference books and talking with mechanics and drivers. Report your findings to the class. What do you conclude?



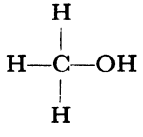
35 ALCOHOL AND OTHER ORGANIC COMPOUNDS

. . . The chemist is revolutionizing industry. He is developing new products and new ideas every hour of every day. As a result of his work, flourishing industries are being scrapped overnight. There is no industry — not one — that is not in danger of waking up tomorrow and finding that the chemist has made a discovery that might revolutionize it.
Hugh Farrell, 1926

What is an alcohol? Chemists have learned how to substitute one or more of the hydrogen atoms of any hydrocarbon with an OH group. These organic compounds, called *alcohols,* are named from the hydrocarbon from which they are formed. Thus, *methanol* is the alcohol formed by substituting an OH group for a hydrogen atom in methane. *Ethanol* is the alcohol formed similarly from ethane.

Methyl alcohol, wood alcohol, or methanol. Methanol, CH_3OH, is formed from methane by the substitution of an OH group for an H atom. Methyl alcohol is a colorless liquid, miscible with water in all proportions. It has a characteristic odor, and both the liquid and its vapors are poisonous, often causing blindness and even death.

Structural formula of methanol.



Methanol is combustible and burns with an almost colorless flame; it is used as a fuel, for example, in alcohol lamps. Its most

important uses, however, are as the starting point in the manufacture of many very important organic compounds, and as a solvent in making lacquers, varnishes, and polishes. Because of its poisonous nature, it is used in *denaturing* grain alcohol. As a result of its low freezing point, it is used as an antifreeze in automobile radiators.

Synthesis replaces the destructive distillation of wood. The old process for making wood alcohol was the destructive distillation of hard woods, such as beech. Among the products formed are charcoal, wood tar, and a brownish liquid called *pyroligneous acid.* Upon fractional distillation of this liquid, various products are obtained, including acetic acid, acetone, and wood alcohol.

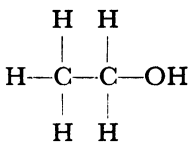
In 1925, a highly successful method of synthesizing wood alcohol from carbon monoxide and hydrogen was introduced, and almost completely replaced the older process:

$$CO + 2H_2 \rightarrow CH_3OH \text{ (methanol)}$$

The application of the law of mass action and the principles of catalysis have been used in preparing synthetic wood alcohol. Because this reaction is exothermic, a larger yield is obtained by using low temperatures and high pressures. The catalyst used is chiefly zinc oxide with ten percent chromium oxide.

Ethyl alcohol, grain alcohol, or ethanol. Ethanol, C_2H_5OH, is formed from ethane by the substitution of one of its hydrogen atoms by an OH group. It is called *ethyl alcohol, grain alcohol,* or *ethanol.* Like methyl alcohol, ethyl alcohol is a colorless liquid with a characteristic odor. It is lighter than water, with which it mixes in all proportions. Pure ethyl alcohol boils at 78.5°C. It burns with an almost colorless, smokeless flame, giving off large quantities of heat. It is an excellent fuel.

Structural formula of ethanol.



How grain alcohol is prepared. Ethyl, or grain, alcohol is prepared today, as it was thousands of years ago, by *fermentation.* Fermentation is a chemical action brought about by bacteria, yeasts, or molds. The bacteria, yeasts, or molds produce complex organic compounds called *enzymes,* that act as catalysts. When yeast cells, for example, are placed in a sugar solution and kept warm, the enzyme, *zymase,* produced by the living yeast plant, acts catalytically, helping to split

the sugar molecule into alcohol and carbon dioxide. The equation for this change is:

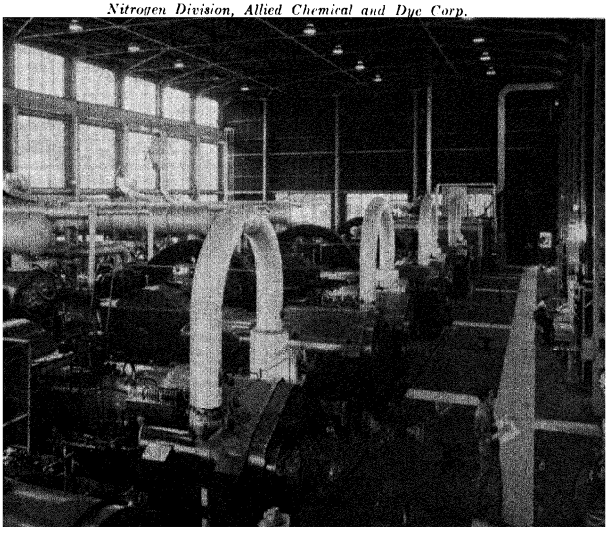
$$\underset{\text{glucose}}{C_6H_{12}O_6} \rightarrow 2\underset{\text{alcohol}}{C_2H_5OH} + 2CO_2\uparrow$$

Lavoisier used this reaction as evidence upholding the law of the conservation of matter. The carbon dioxide bubbles off as a gas, and the alcohol remains in solution. When the concentration of the alcoholic solution reaches between eight and 12 percent, the action of the yeast ceases. The concentration of the alcoholic solution may be increased to 95 percent (190 proof) by distillation, since water has a higher boiling point than pure ethyl alcohol.

Much of the industrial alcohol made in the United States in normal times is prepared by the fermentation of the sugar present in *black strap molasses,* obtained as a byproduct in the refining of cane sugar and beet sugar. Industrial alcohol is also produced from the starch of corn, barley, potatoes, rice, and wheat. The starch must first be made soluble by a process called *malting.* For example, barley is steeped in water long enough for rootlets to appear. Germination is then stopped by the removal of water and the application of heat, and *malt* results. During this partial germination of barley, *diastase,* an enzyme, is formed. This diastase changes the starch in the barley into a sugar called *maltose,* $C_{12}H_{22}O_{11}$. Yeast acts on this maltose just as it does on the sugar present in molasses.

Immense quantities of synthetic ethyl alcohol are being manufactured today from petroleum and natural gas. Synthetic ethyl alcohol from these sources now accounts for more than half the industrial alcohol produced.

Nitrogen Division, Allied Chemical and Dye Corp.



The compression section of a methanol processing plant in which methanol is synthesized from hydrogen and carbon monoxide.

The ways in which alcohol affects the human body are not yet completely understood. Alcohol is readily absorbed into the blood stream from the stomach and intestines. It is distributed by the blood to all parts of the body. More detailed discussions may be found in most high-school biology or physiology textbooks.

How ethyl alcohol is used in industry. Next to water, ethyl alcohol is the world's most useful solvent. It dissolves resins, hydrocarbons, and fatty acids, and is used in preparing hundreds of perfumes, flavoring extracts, medicines, varnishes, lacquers, and antifreeze mixtures. It is used in the manufacture of buna-S synthetic rubber and in the preparation of ether, vinegar, and chloroform. It also enters into the manufacture of an immense variety of widely used products, such as pyroxylin, plastics, and dyes.

The danger of illicit use of ethyl alcohol, coupled with its tremendous industrial importance, makes it necessary so to change, or *denature,* alcohol as to make it unfit for drinking and, at the same time, not make it unfit for use in the arts and industries. There are dozens of ways of preparing denatured alcohol. Some *denaturants* used are *alcotate* (from petroleum), wood alcohol, and benzine. The closer the boiling point of the denaturant is to the boiling point of ethyl alcohol, the greater the difficulty of separating the ethyl alcohol from the denaturant. Hence the most effective denaturant is one which has a boiling point close to that of ethyl alcohol.

What is power alcohol? The blending of ethyl alcohol with gasoline as a fuel for internal-combustion engines has been practiced in several European countries for many years. In 1943, 40 percent of the German potato crop was used in this way. Shortage of gasoline compelled this action.

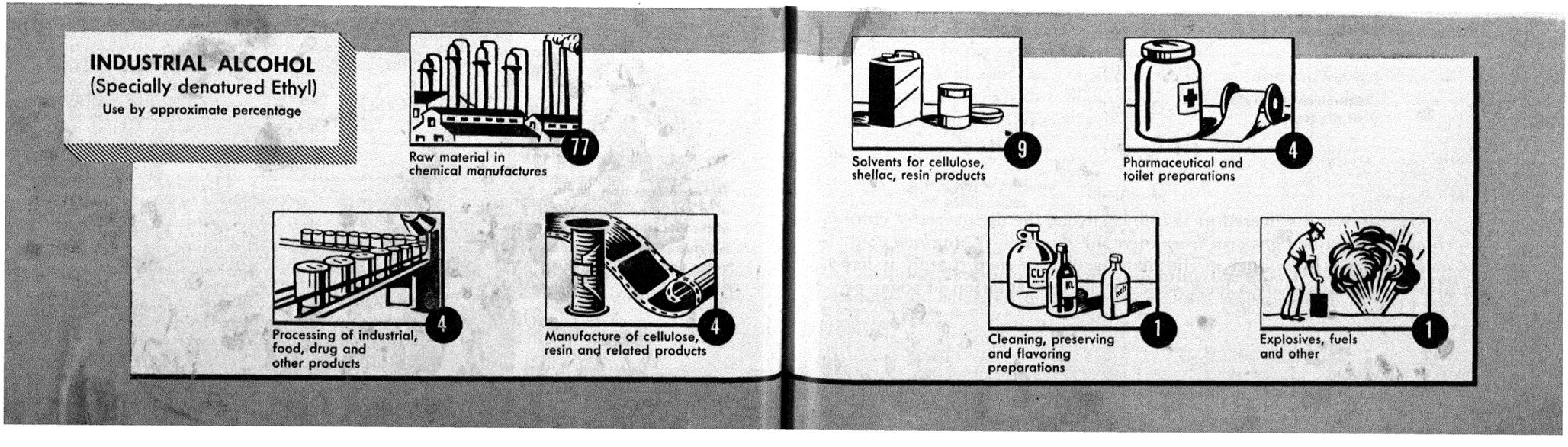
The blend of alcohol and gasoline used as a fuel is called *power alcohol.* The usual blend is about ten to 30 percent ethyl alcohol added to gasoline. The addition of ethyl alcohol to gasoline increases the octane number of the fuel.

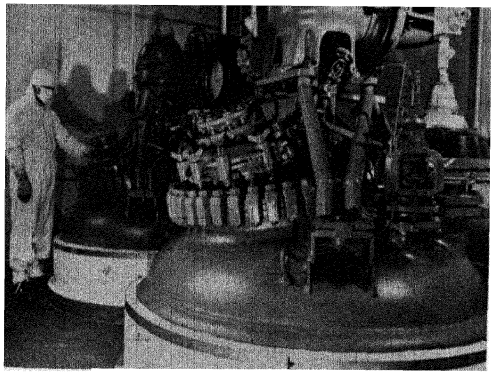
The farm as a source of raw materials for industry. The National Farm Chemurgic Council, organized in 1935 in Dearborn, Michigan, has urged the use of power alcohol in this country on the ground that it will open up a new market for farm products, help the farmer, conserve our petroleum resources, and benefit all industry. This is only one example of the significant development called *chemurgy,* whose objective is to advance the industrial use of farm products.

Enormous quantities of corn are being used to supply starch for the making of solvents, such as butyl alcohol and acetone, and other industrially important chemicals. Tung trees, grown on the Gulf coast, supply tung oil for the manufacture of paints. The use of wood pulp from quick-growing southern pines and the development of paint, oil, and plastic material from the soybean are other examples of this new development. To aid in the development of chemurgy, the United States government has set up four Regional Research Laboratories.

Butyl alcohol, or butanol. Although in quantity used the importance of butanol, C_4H_9OH, does not compare with that of ethanol, it is a most important organic compound. It was the first new solvent greatly to advance the growth of the chemical industry. Butanol is a colorless liquid with a winelike odor. Only slightly soluble in water, it is miscible in all proportions with ethanol and ether.

For many years, butanol was produced chiefly by a fermentation process. In this process, a strain of bacteria rather than ordinary yeast





A concentrating unit used in the manufacture of antibiotics. Alcohols and their esters are used in the manufacture of these and many other pharmaceuticals.

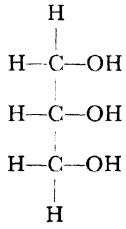
Carbide and Carbon Chemicals Company

is used. Corn and molasses are among the raw materials used. Two parts of butanol are produced to one part of acetone, another highly important industrial solvent. Chaim Weizmann (vīs'män), an eminent English chemist, was responsible for this discovery during World War I.

Today, a minor part of the butanol used in this country is produced by the fermentation process. About 90 percent is made synthetically today from both petroleum and natural gas. Butanol is used in great quantities in the production of many organic compounds and as a solvent in the plastics, lacquer, and enamel industries. It is used also in the production of butyl acetate (another important solvent), in making hydraulic brake fluid, and in the manufacture of resins and dyes.

Glycerin, another of the alcohols. During the fermentation of sugar into alcohol, a small amount of another alcohol is produced. This is called *glycerin,* or *glycerol,* from a Greek word meaning *sweet.* Glycerin may be considered a derivative of propane, three of whose hydrogen atoms have been replaced by three hydroxyl groups. Its formula is $C_3H_5(OH)_3$.

Structural formula of glycerin.



Glycerin was discovered in 1779 by Scheele, the discoverer of chlorine, who obtained glycerin from olive oil. Today it is obtained commercially as a byproduct in the manufacture of soap. Lately it has also been prepared on a large scale by the fermentation of sugar or

molasses rendered alkaline by the addition of several sodium salts. A commercial method of synthesizing glycerin from natural gas has also been developed.

Glycerin is an oily, colorless liquid, heavier than water, with which it mixes in all proportions. It is hygroscopic. It is used to some extent in preparing ointments, medicines, cosmetics, dentifrices, rayon, as a solvent for certain drugs, as a humectant (water absorber) in the control of the moisture content of tobacco, candy, adhesives, and leather, and as an antifreeze; but its chief use is in the manufacture of nitroglycerin and dynamite.

Acetic acid, the most commonly used organic acid. When ethyl alcohol remains exposed to the air, it slowly oxidizes and changes into *vinegar,* a sour liquid which is a dilute solution of *acetic acid.* The reaction may be represented as follows:

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + O_2 \rightarrow \underset{\text{acetic acid}}{CH_3COOH} + H_2O$$

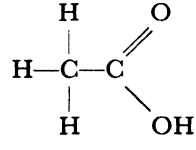
An examination of this change discloses the fact that a species of bacteria, called *bacillus aceti,* present in air falls into the alcohol solution and produces an enzyme which brings about the oxidation. This explains the souring of wine and of cider, both of which contain small amounts of ethyl alcohol.

Some acetic acid is obtained from the fractional distillation of pyroligneous acid. However, much of our industrial acetic acid is obtained by fermenting a sugar solution and subsequently allowing the alcohol in the solution formed to oxidize in the air in large generators. More than half of all the acetic acid used today in this country is made from natural gas and petroleum.

Pure acetic acid is an oily liquid which solidifies at about room temperature to icelike crystals. This is also called *glacial acetic acid.* It has the pungent odor of vinegar.

Acetic acid may be considered to be a substitution product of methane in which one of methane's hydrogen atoms has been replaced by the COOH, or *carboxyl group.*

Structural formula of acetic acid.



An organic acid is an acid containing the COOH group. Like the inorganic acids, all organic acids contain replaceable hydrogen, but

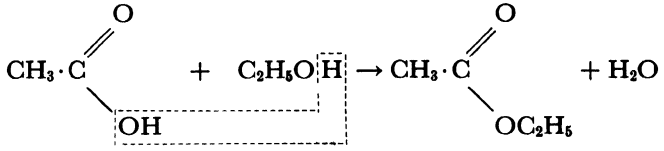
they are only slightly dissociated, producing a small percentage of hydrogen ions in solution. Acetic acid is also written $H \cdot C_2H_3O_2$, where the $C_2H_3O_2$ is the *acetate radical,* having a valence of minus one. Only one hydrogen atom in acetic acid is replaceable by a metal. Acetates are salts of acetic acid.

Other common organic acids. Oxalic, citric, and tartaric acids are all white, crystalline solids, which in water solution produce few hydrogen ions. *Tartaric acid,* $H_2C_4H_4O_6$, was first obtained by Scheele in 1769 from fermented grape juice, which contains $KHC_4H_4O_6$, the potassium acid salt of tartaric acid.

Citric acid was isolated a few years later, by the same superb experimenter, from the juice of lemons. Citric acid, present also in oranges and other fruits, was first synthesized more than half a century ago. A commercial method of making pure citric acid by the fermentation of sugar by means of a bacillus has been introduced. Citric acid is used extensively in the preparation of foods and beverages to supply a "real fruit" flavor. It is used also in making pharmaceutical preparations, among which is magnesium citrate, a laxative.

Oxalic acid, $(COOH)_2$, is a highly poisonous substance present in small amounts in rhubarb and obtained from sawdust. It is used in the bleaching of fabrics, cork, and straws, in tanning, and in the making of certain metal polishes. It is also useful in removing ink and rust stains from fabrics.

Esters include fragrant oil of cloves and explosive nitroglycerin. When an acid reacts with a base, the products formed are water and a salt. This chemical change is *neutralization.* A superficially similar chemical change takes place when either an inorganic or an organic acid reacts with an alcohol. This process is called *esterification,* and the products formed are water and an *ester,* or *ethereal salt. An ester is the product formed by the elimination of water from an acid and a hydroxyl compound or alcohol.*



acetic acid + ethyl alcohol → ethyl acetate + water

Most esters are colorless liquids, soluble in alcohol, with fragrant, fruity odors. Examples are *pear oil, oil of cloves, oil of wintergreen,* and *banana oil. Pineapple flavoring* is ethyl butyrate. But not all

esters can be used for flavoring foods. For example, *nitroglycerin* is an ester formed by the action of nitric acid on glycerin, thus:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O$$

Since the water formed would tend to reverse this reaction, concentrated sulfuric acid is added to absorb the water as fast as it is formed.

Nitroglycerin, an oily, slightly yellowish liquid, is highly explosive because of its rapid liberation of tremendous volumes of gases when it decomposes. To render nitroglycerin somewhat less sensitive to shock and safe to transport, it is made into *dynamite,* a solid substance made by soaking up nitroglycerin in wood pulp mixed with sodium nitrate. Tons of dynamite are used each year in blasting, mining, tunneling, road-building, and wrecking operations.

Synthetic perfumes and cosmetics. Originally, nearly all perfumes were produced by extracting the aromatic substances of flowers and imprisoning these aromas by means of suitable retaining substances, or *fixatives,* in either alcohol or water. Synthetic chemistry has, however, made possible satisfactory synthetic perfumes that rival the natural products and are much less expensive. Synthetic perfumes are not necessarily inferior to perfumes compounded in the original manner. The difference lies in the skill of the *blender,* the skilled craftsman who blends the ingredients to produce the final product.

In blending synthetic perfumes, synthetic compounds called *essential oils,* are used. These essential oils are closely akin to the aromatic substances produced from flowers. Some of the interesting compounds used in the blending of synthetic perfumes and flavors include: *benzyl acetate,* a colorless liquid with a typical jasmine odor, used in making jasmine-, hyacinth-, and gardenia-type perfumes; *citral,* a light yellow liquid with a penetrating lemon odor, used in the preparation of soaps, perfumes, and flavors; and *citronellol,* a colorless liquid with a definite roselike odor, used in the compounding of rose- and geranium-type perfumes and in soaps.

Animal and vegetable oils and fats are mixtures of esters. Animal or vegetable oils or fats consisting of a single compound are not found in nature. All are mixtures of esters formed by the union of alcohols (generally glycerin) and *fatty acids,* such as stearic acid, $C_{17}H_{35}COOH$. A common ester found in beef fat is *glyceryl stearate,* or *stearin,* which may be made by the action of glycerin and stearic acid:

$$C_3H_5(OH)_3 + 3C_{17}H_{35}COOH \rightarrow C_3H_5(C_{17}H_{35}COO)_3 + 3H_2O$$
$$\text{Glycerin} + \text{stearic acid} \rightarrow \text{glyceryl stearate (fat)}$$

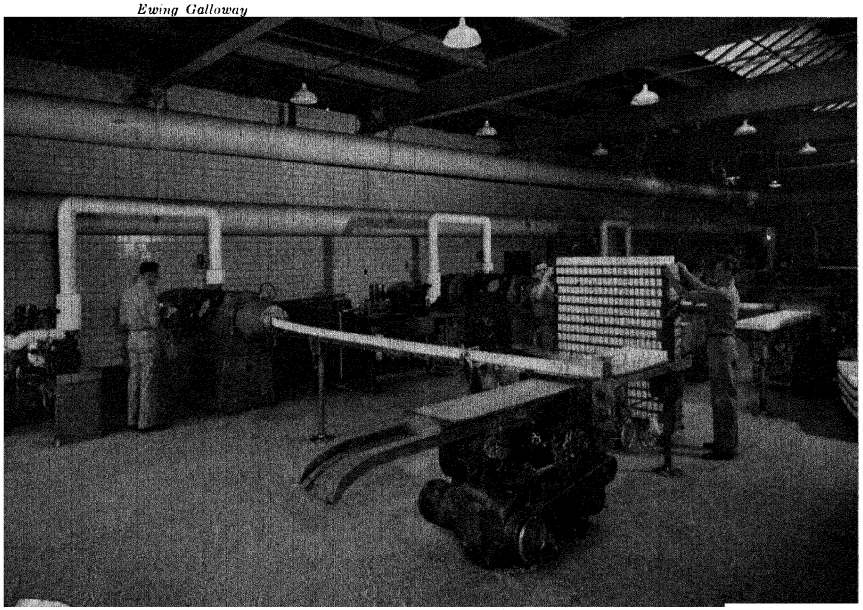
Some common vegetable oils are *cottonseed oil, corn oil, peanut oil,* and *olive oil,* and some commonly used animal fats and oils are *lard, butter, fish oil, whale oil, haliver oil,* and *cod-liver oil. Linseed oil,* obtained from flaxseed, and *tung oil* are vegetable oils used in preparing paints and varnishes. These *drying oils* harden as a result of both polymerization and oxidation. *Waxes* are the fatty acid esters of some of the higher alcohols. *Mineral oils,* of course, are not esters, but are mixtures of hydrocarbons.

What is soap? Animal and vegetable fats and oils react chemically with bases, forming soaps and glycerin. This process is called *saponification.* It is the chief source of glycerin. Thus *a soap is the metallic salt of a fatty acid.* The following reaction represents the chemical change that takes place when one of the esters of beef fat reacts with the base, sodium hydroxide. The soap formed is *sodium stearate,* the sodium (metallic) salt of stearic (a fatty) acid.

$$\underset{\text{Fat}}{C_3H_5(C_{17}H_{35}COO)_3} + \underset{\text{base}}{3NaOH} \rightarrow \underset{\text{glycerin}}{C_3H_5(OH)_3} + \underset{\text{soap}}{3NaC_{17}H_{35}COO}$$

How soap is made. Crude soap was known in antiquity. Ever since someone noticed that the fat which boiled over during the cooking of meat fused with the ashes of the wood fire and produced a pasty mass which had cleansing properties, soap has been prepared in the household by a similar but much more refined process. Today, factories turn out huge quantities of this commodity, using beef and

Extrusion and cutting of soap in a modern soap plant.
Ewing Galloway



mutton tallow, cottonseed oil, coconut oil, palm oil, castor oil, olive oil, corn oil, soybean oil, and even fish oils. Distilled fatty acids are sometimes used in place of fats and oils. Instead of wood ashes, which contain potassium carbonate, these factories use industrial bases.

Though many processes are used in making soap, production on the largest scale consists essentially of the following steps:

1) *Saponification.* About 100 tons of the melted fat or oil are poured into a *soap pan,* a ten percent sodium hydroxide solution is added, and the mixture is boiled with steam from perforated coils. More lye is added from time to time and the boiling continues until saponification is complete.

2) *Salting out.* This consists of breaking up the emulsion of soap and glycerin, and separating any excess lye and glycerin. While the boiling continues, salt is added and the soap, since it is insoluble in brine, comes to the surface. The salt and glycerin collect in the bottom layer. The glycerin is separated from the spent lye, which is drawn off from the bottom.

3) *Soap treatment.* The soap is treated with steam and water to remove impurities, which settle out. The warm liquid soap is run into *crutching pans* for the addition of such substances as rosin, coloring matter, perfumes, medicine, and, sometimes, a filler such as talc. It is then poured into frames with removable sides, cooled, and cut into slabs and bars. Most common soaps contain about 30 percent water.

A *built soap* contains one or more other chemicals such as tetrasodium pyrophosphate or trisodium phosphate (TSP). As TSP is a good water-softener, it is used (one teaspoonful to a gallon of water) in the cleaning of windows, floors, and painted surfaces.

Hard, soft, and insoluble soaps. Soap made from sodium hydroxide is *hard* soap; that made from potassium hydroxide is *soft* soap, used in liquid soaps and shaving creams. Shaving creams contain either free stearic acid or glycerin to make the lather lasting.

All soaps made from bases other than sodium, potassium, or ammonium hydroxide are insoluble in water and are useless for cleaning purposes. However, some of these insoluble soaps find other uses. Thus, when zinc hydroxide is made to react with stearic acid, *zinc stearate* (a soap), which is insoluble in water, is obtained. It is a white powder that has antiseptic properties which make it suitable for use in certain kinds of face and body powders. Lime and aluminum soaps are used as ingredients in lubricating greases; and aluminum oleate, another insoluble soap, is used as an oil thickener in making paints and in the waterproofing of textiles. Much soap is also

used as an emulsifying agent in the manufacture of synthetic rubber from butadiene and styrene.

What happens when soap is added to hard water? When a soluble soap is added to hard water (water containing Ca, Mg, or Fe ions), the sodium or potassium ions of the soap are replaced by the calcium, magnesium, or iron ions, forming insoluble calcium, magnesium, or iron soaps, which precipitate out and collect.

$$\underset{\text{soap}}{2\text{Na stearate}} + \underset{\text{hard water}}{\text{CaSO}_4} \rightarrow \text{Ca stearate} \downarrow + \text{Na}_2\text{SO}_4$$

Suds are not formed until all the calcium, magnesium, and iron ions in the water have been precipitated. The water is thus softened, and the addition of more soap produces a lather. It is less expensive, of course, to soften hard water by the addition of washing soda or ammonia water than to use enough soap to soften the water sufficiently for cleansing purposes.

Select soaps carefully. The value of a soap depends upon (1) the kinds of fats used in its manufacture, (2) the builders added, (3) the proper control of the amounts of fat and base used so that the resulting soap does not have an excess of either, and (4) the amount of water in the soap.

Toilet soaps are ordinarily made by shredding a soap, drying it, mixing it with various essential oils, milling it, pressing it into bars, and cutting it into cakes. Such soaps are called *milled soaps,* and are long lasting if used carefully and after use are so placed on a soap dish or soap rack that they can dry properly. Most widely used commercial toilet soaps are excellent soaps and are sold at a fair price. However, it is extremely doubtful that exposing a soap to ultraviolet rays improves it, and it is even more unlikely that any soap actually contains a "skin food."

Laundry soaps frequently contain rosin instead of part of the fat used in the manufacture of other soaps. However, rosin should not be used in quantities greater than one-third of the fat, for larger quantities produce a disagreeable odor and may impart a yellow color to the materials to be laundered. *Naphtha laundry soaps* contain naphtha or similar grease-dissolving substances. Although such substances improve the action of the soaps in cold or lukewarm water, in hot water they vaporize too rapidly to be very effective.

Soap powders are usually mixtures of soap and washing soda. They may contain other substances, such as borax, trisodium phosphate, or scouring materials. They are made by mixing molten soap with the added ingredients in powerful beaters. The mixture is

made into grains by forcing it through screens of the appropriate size. *Floating soaps* are made by beating air into the soap during its manufacture.

The "soapless soaps" or synthetic detergents. Detergents are cleansing agents and include water, ordinary soaps, and the so-called synthetic detergents. Some detergents are made by the reaction between a fatty alcohol such as lauryl alcohol and sulfuric acid. This produces an acid ester which is then neutralized with sodium hydroxide. The products are water and sodium lauryl sulfate sold under the trade name of *Dreft*. *Drene* is another detergent of this type.

$$1)\quad \underset{\text{lauryl alcohol}}{C_{12}H_{25}OH} + H_2SO_4 \rightarrow C_{12}H_{25}SO_4H + H_2O$$

$$2)\quad C_{12}H_{25}SO_4H + NaOH \rightarrow \underset{\text{sodium lauryl sulfate}}{C_{12}H_{25}SO_4Na} + H_2O$$

The long-chain alcohols used are made from such oils as palm and coconut oils. Another group of detergents are alkylaryl sodium sulfonates made from petroleum hydrocarbons.

These detergents have several advantages over ordinary soaps. They are just as effective in hard water as in soft water. They do not precipitate calcium or magnesium ions and hence do not leave any ring or curd. They do not hydrolyze to produce hydroxyl ions and hence do not attack even the most delicate fabrics. The use of these compounds has been phenomenal. In the five years ending in 1953, the use of ordinary soap products dropped 50 percent while the use of synthetic detergents jumped from less than half a billion pounds to more than two billion pounds (more than ordinary soaps).

How detergents clean. Synthetic detergents belong to the *surfactants* or surface-acting agents all of which reduce surface tension. They clean by making water wetter, that is, they penetrate faster and more completely, thus loosening dirt more quickly by *reducing the surface tension of the water*. The arrangement of the detergent molecule is an important fact. A detergent is composed of two parts or ions. When it dissolves in water the molecules at the surface have their water-attracting heads pointed into the water. This leaves the oil-attraction part pointed away from the water where it is in an excellent position to attach itself to oily or greasy dirt particles (see Fig. 112). The oily film surrounding the dirt is broken up and the dirt is washed away by water. The soap molecule is essentially like that of the detergent. The dirt particles may also be adsorbed by the colloidal soap films, and then carried away by the water.

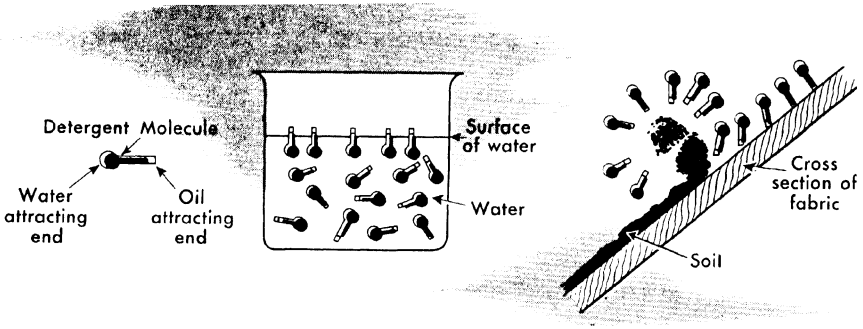
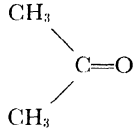


Fig. 112. (left) The detergent molecule. (center) How detergent molecules arrange themselves in water. (right) How the detergent molecules remove and isolate soil particles.

Acetone, ether, and formaldehyde. Acetone, CH_3COCH_3, is a colorless, fragrant, flammable liquid which dissolves acetylene, oils, resins, explosives, and other organic compounds. It is also used to make the methacrylate plastics. It is obtained during the destructive distillation of wood. However, about 80 percent of the acetone now produced is made synthetically from petroleum products, and about 20 percent by the fermentation of corn in the presence of a certain bacterium.

Structural formula of acetone.

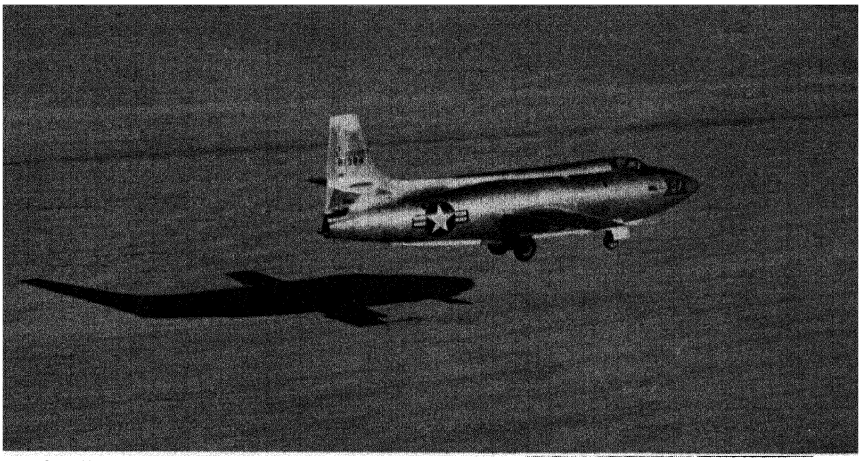


It belongs to the group of compounds called *ketones* which contain the $\diagdown C{=}O \diagup$ group.

Ethyl ether is a low-boiling, flammable, colorless liquid commonly known as *ether*, an anesthetic. It boils at 35°C., is only somewhat soluble in water but is completely soluble in alcohol. It is prepared commercially by the action of sulfuric acid on ethyl alcohol.

$$2C_2H_5OH \rightarrow H_2O + (C_2H_5)_2O \text{ (ether)}$$

Formaldehyde is a colorless gas with a pungent odor. It is used as a disinfectant, in making embalming fluid, and as a preservative of anatomical specimens; but its chief use is in the manufacture of "Bakelite." Formaldehyde $\begin{matrix} H \\ | \\ H-C{=}O \end{matrix}$, is prepared by oxidizing methyl



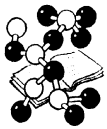
Bell Aircraft Corporation

Liquid oxygen and ethyl alcohol fuel this experimental rocket airplane.

alcohol in the presence of a catalyst such as vanadium pentoxide. It belongs to a group of compounds called *aldehydes.*

$$2CH_3OH + O_2 \rightarrow 2H_2O + 2HCHO \text{ (formaldehyde)}$$

A 40 percent solution of formaldehyde in water is sold under the name of *formalin. Paraform*, a white crystalline solid, is polymerized formaldehyde. On heating, paraform liberates formaldehyde.

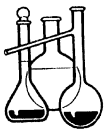


YOU WILL ENJOY READING

Borth, Christy. *Modern Chemists and Their Work.* The New Home Library, New York, 1943. A newspaperman tells the dramatic story of chemurgy and its future possibilities.

de Kruif, Paul. *Microbe Hunters,* pp. 145–184. Harcourt, Brace & Co., New York, 1926. Discusses Pasteur's researches and his explanation of alcoholic fermentation. Written in a breezy style; simple to understand.

Kushner, L. M. and Hoffman, J. I. "Synthetic Detergents." *Scientific American,* Oct. 1951, pp. 26–30. An account of the advantages of detergents over ordinary soaps.



USEFUL IDEAS DEVELOPED

1. An alcohol is an organic compound containing a hydroxyl group.

2. Fermentation is any chemical action brought about by the catalytic action of complex organic compounds called enzymes that are produced by bacteria, yeasts, or molds.

3. Organic acids contain the carboxyl (COOH) group. Because they dissociate only slightly, they are relatively weak acids.

4. An ester is the product formed by the elimination of water from an acid and a hydroxyl compound or alcohol. The process of ester formation is called *esterification.*

5. Animal and vegetable fats and oils are mixtures of esters, chief among which is glyceryl stearate, an ester formed by the union of glycerin and stearic acid.

6. Waxes are the fatty acid esters of some of the higher alcohols.

7. A soap is the metallic salt of a fatty acid. Animal and vegetable fats and oils react with bases, forming soaps and glycerin. This process of soap formation is called *saponification.*

8. Synthetic detergents such as "Dreft" are made by the action of a fatty alcohol and sulfuric acid producing an acid ester which is then neutralized with NaOH.



USING WHAT YOU HAVE LEARNED

Group A

1. (a) What is an alcohol? (b) To what class of inorganic compounds are alcohols analogous?

2. What are the structural formulas of methyl and ethyl alcohols?

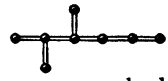
3. Copy and complete the following statements. Do not write in this book. CH_3OH is formed by replacing one of the hydrogen atoms of ... by an OH group. C_2H_5OH, known also as ..., is formed by replacing one of the ... atoms of ... by an OH group. Another alcohol used commonly is .... CH_3OH is obtained by the fractional distillation of ... obtained from wood. C_2H_5OH is prepared by the ... of glucose. Both CH_3OH and C_2H_5OH are used as ....

4. (a) Compare the properties of CH_3OH and C_2H_5OH. (b) Include the principal effect of each on the human body.

5. Name five products of the destructive distillation of wood.

6. (a) How is methyl alcohol synthesized? (b) Write the equation showing the reaction involved.

7. (a) What is fermentation? (b) What is the name and source of the powerful enzyme that brings about this process in the manufacture of alcoholic beverages? (c) Write the equation for the reaction that occurs.



8. (a) By what process are alcoholic liquors changed to almost pure alcohol? (b) What are five important uses of C_2H_5OH?

9. What is power alcohol?

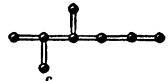
10. Why has the term *John Barleycorn* been used popularly to mean C_2H_5OH?

11. What properties should a denaturant possess to be ideal for preventing the use of C_2H_5OH as a beverage?

12. Why and how is C_2H_5OH denatured?

13. (a) What is C_4H_9OH? (b) How is it made? (c) For what is it used? (d) What other important organic solvent is produced at the same time?

14. (a) Glycerin is a byproduct of what important process? (b) Write the equation for its formation.



15. (a) To what class of compounds does $C_3H_5(OH)_3$ belong? (b) On what hydrocarbon is its molecular structure based? (c) What is a humectant?

16. (a) What is an organic acid? (b) Which organic acid is the most widely used? (c) How is this acid prepared industrially?

17. (a) Why does sweet cider turn *hard?* (b) Why does wine sour? (c) What is the nature of the chemical reaction that takes place? (d) What organic catalyst is necessary to the process? (e) Write the equations.

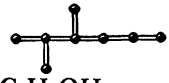
18. What is the structural formula of acetic acid?

19. Only one hydrogen atom of CH_3COOH may be replaced by a metal. Explain.

20. What is glacial acetic acid?

21. (a) Name three organic acids that are crystalline. (b) State their sources.

22. Determine the percentage composition of $H_2C_4H_4O_6$.



23. What weight of C_2H_5OH on oxidation yields 73.2 g. of acetic acid?

24. What volume of CO_2 is formed by the complete combustion of 288 g. of CH_3OH?

25. (a) What is esterification? (b) Write the equation showing the reaction by which the ester, methyl acetate, $CH_3C_2H_3O_2$, could be formed.

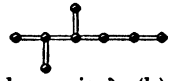
26. (a) What are the usual properties of esters? (b) Give examples.

27. (a) Name a very powerful explosive that is classed as an ester. (b) Why does it come under this classification?

28. (a) What are essential oils? (b) For what are they used?

29. What is the function of H_2SO_4 in the preparation of $C_3H_5(NO_3)_3$?

30. (a) In what respect is esterification similar to neutralization? (b) In what respect is it different?



31. (a) What is dynamite? (b) To what peaceful projects is it essential?

32. What is the composition of an animal or vegetable fat or oil?

33. What is the major difference between mineral oils and esters?

34. Classify the following as hydrocarbons, esters, mixtures of esters, alcohols, or organic acids: (a) castor oil, (b) glycerol, (c) gasoline, (d) oil of wintergreen, (e) butter, (f) "Crisco," (g) carbolic acid, C_6H_5OH.

35. Write the word-equation for the preparation of glyceryl stearate.

36. (a) What are the two principal substances used in making soap? (b) What other product is formed during the process? (c) To what class of chemical compounds does soap belong?

37. Write word-equations for the preparation of (a) hard soap, (b) soft soap, and (c) an insoluble soap.

38. Using an equation, explain what happens when a soluble soap is added to hard water containing $MgSO_4$.

39. (a) What are detergents? (b) How is "Dreft" made? (c) State two advantages of a so-called "soapless soap" over ordinary soap.

Group B

40. (a) How do detergents clean? Explain fully. (b) How do ordinary soaps clean?

41. Why is C_2H_5OH not generally used as the fuel for internal-combustion engines?

42. Is there any connection between "salting out" in soap-making and the common-ion effect? Explain.

43. CH_3COOH has been prepared synthetically by the following system of reactions:

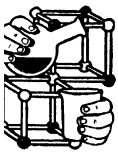
$$1) \quad CaO + 3C \rightarrow CaC_2 + CO$$
$$2) \quad CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$
$$3) \quad C_2H_2 + H_2O \rightarrow CH_3CHO$$
$$4) \quad 2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

What weight of lime would have to be used in preparing 150 tons of glacial acetic acid, assuming a yield of 50 percent?

44. (a) In what respects do soaps differ? (b) How should a soap for a particular purpose be selected?

45. How has the introduction of synthetic detergents affected the soap industry? Cite some statistics.

46. Explain what is meant by *malting.*



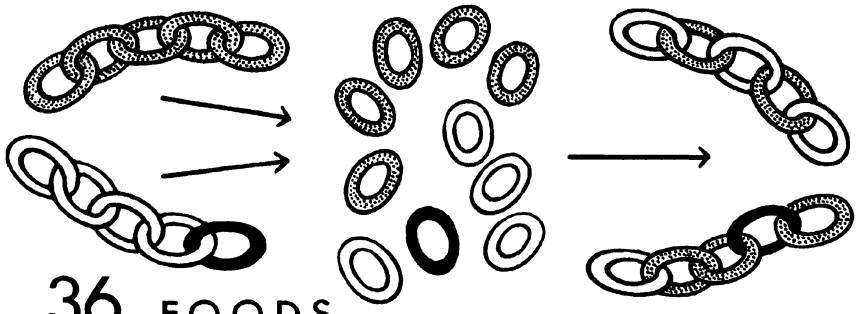
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. In line with an effort to find a new market for farm products in industry, the seventy-fifth Congress in 1938 made provisions for four Regional Research Laboratories "to conduct researches into and to develop new scientific, chemical and technical uses and new and extended markets and outlets for farm commodities and products and byproducts thereof." An annual appropriation of one million dollars was made for each laboratory. Write a two- or three-page report on the results of this effort to help the farmer.

2. Make a display of synthetic chemicals which have either completely or partially displaced natural products. An example of such a synthetic compound would be synthetic methanol, which is displacing wood alcohol. What does such a display seem to indicate?

3. Advertisers sometimes claim that high-priced soaps do not irritate the skin. Some soaps are even said to contain "skin food." Said the trade magazine *Soap,* "If any soap is soothing to any kind of skin, we will eat a bar of it while doing handsprings up Fifth Avenue." One consumer magazine tells its readers that "Soap at $1 a cake cannot be more valuable nor do more than any high-quality soap at 5¢." What are your own reactions to these statements on the basis of what you have learned about the composition of soap?

4. With the aid of either litmus or hydrion paper, test as many soaps and detergents as you can obtain and report your findings to your class.



36 FOODS AND CHEMOTHERAPY

. . . Man, the incurable parasite, lives literally upon the vegetable and animal world: leaf, stem and root. He consumes all plants that have any food value and with the remainder he attempts to make medicines to cure his bodily ills. The dependency of man on the vegetable world has made of him an agriculturist. . . . Secondarily it has made of him a domesticator of food animals. W. D. Richardson, 1927

Why do we have to eat and what should we eat? Our bodies are very complex organisms. We can maintain ourselves and perform our normal functions only within a limited temperature range. The normal temperature of an adult human being, 98.6°F., must be maintained by the body in spite of external temperature changes. To do this, the body must generate heat and also produce enough free energy to enable it to perform such important processes as muscular motion, digestion, breathing, circulation of blood, and so forth. To obtain this free energy, everyone eats, or takes in, food.

Lavoisier first explained accurately how body temperature is maintained by the oxidation of food. Hundreds of other complex chemical processes are necessary to convert the food we eat into the substances necessary for the normal functioning of the human body. Foods are required also to build new tissue and to repair broken down or worn out cells, for the piecemeal exchange of every part of the body goes on at a continuous rushing pace. A man's brain or heart today contains few parts that it did last year. Life is more like a whirlpool than a machine whose parts are replaced from time to time.

In a sense, man is a parasite. We do not synthesize foods in our bodies, but rather we reconstruct them from the various organic and

inorganic materials which we consume. Digestion actually consists of making insoluble food materials into substances that are soluble in water, and of making complex foods into simpler food materials. Digestion is largely a series of chemical processes.

Since most of us know too little about the foods best for us to eat, advice crowds in upon us from all sides. We are deluged with announcements of health-giving foods and diets by faddists. We receive them also from scientists who have made scientific studies of foods. We must learn which teachings should be accepted and which rejected.

In your lifetime probably you will consume some 50 tons of food. This is the estimated average normal food consumption of a human being. The chief nutrients found in these 50 tons of food are *carbohydrates, fats* and *oils, proteins,* and *minerals.* Other substances called *vitamins* are necessary also. Water, even though it does not produce energy, since it is already completely oxidized, is absolutely essential for the proper working of your body. A lack of the minimum amount of water will upset the proper concentrations of the various fluids in your body and will cause many organs to fail to function normally.

Carbohydrates make up part of our diet. A carbohydrate is an organic compound composed of carbon, hydrogen, and oxygen. In a carbohydrate, hydrogen and oxygen are present in the same ratio as in water, that is, two atoms of hydrogen to one of oxygen. The most common carbohydrates are the sugars and the starches.

Carbohydrates are our chief sources of energy. However, we cannot use them as starches. For the human body to use them, they must be changed to sugars, especially glucose, that can be oxidized in body tissues, releasing energy. When, for example, our muscles contract, work is done. This contraction of our muscles is accompanied by the formation of lactic acid, an isomer of the lactic acid found in milk. This acid, which is an oxidation product of carbohydrates, is known as the acid of fatigue since it is believed to be formed during exercise. *Glycogen,* or *animal starch,* is built up from glucose in relatively large amounts in the liver and stored in the liver and muscle tissues. As we need glucose, some of this reserve glycogen is broken down into glucose. *Cellulose* is another carbohydrate, although it differs from sugars and starches.

Starch, the carbohydrate manufactured by photosynthesis. Starch, which is the polymer $(C_6H_{10}O_5)_x$, is one of the most widely distributed substances in the plant world. It is manufactured in green plants by *photosynthesis.*

Starch is composed of microscopic granules whose shape, size, and appearance differ in different plants. Starch is tasteless, odorless, and does not deteriorate in air. Most starches are almost completely insoluble in cold water, but in boiling water the starch granule ruptures and the starch becomes somewhat soluble. Cooking, because it helps make starches available for hydrolysis in digestion, makes starchy foods more digestible. Wheat contains 55 percent by weight, corn about 65 percent, rice about 75 percent of this carbohydrate.

Iodine turns a starch solution a bluish-black color, and this reaction is used as a *test for starch.* In the United States, starch is made from corn almost exclusively. Much starch is used industrially in preparing glucose. When heated to about 180° C., starch changes to another polymer called *dextrin,* a slightly sweet, pale yellow compound which gives toast and zwiebach their sweetish taste. Dextrin is soluble in water and is used as an adhesive on postage stamps, envelopes, and paper boxes.

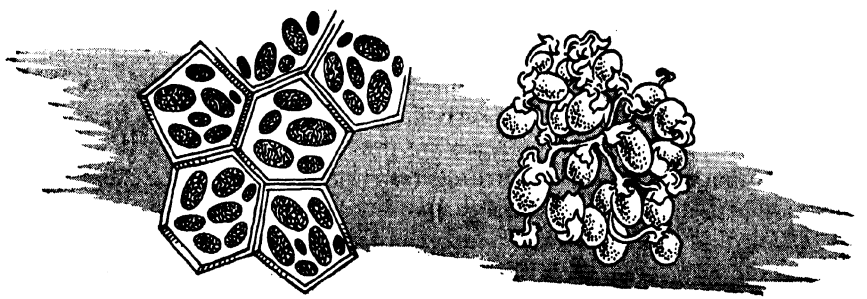


Fig. 113. Starch granules before (left) and after boiling.

Starch in the laundry. Starch is used in the laundry in an effort to replace the original finish of fabrics, most of which is normally removed in washing. In addition, starching helps keep fabrics clean by holding down the small surface fibers that catch dust and dirt.

In this country, cornstarch is the most widely used laundry starch, although wheat, rice, potato, and other starches or combinations of starches are used also.

Soluble or partially soluble laundry starches are made by treating starch with acids or alkalies. Such starches are not likely to rub off during ironing and result in a less "starchy" appearing finish.

Sugars: glucose from starch. The name *sugar* refers to a number of compounds, the most common of which are *glucose, levulose,*

maltose, and *sucrose.* Pure glucose, $C_6H_{12}O_6$, or *dextrose,* is a white crystalline substance, prepared commercially by the *hydrolysis of starch.* The starch is heated in water containing a small amount of hydrochloric acid, which acts as a catalyst only. The reaction is:

$$\underset{\text{starch}}{C_6H_{10}O_5} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6}$$

A similar change takes place in the hydrolysis of starch in the presence of certain enzymes. In digestion, the hydrolysis of starch takes place in the presence of the enzyme *ptyalin,* which is in saliva.

Commercial glucose, an intermediate product in the manufacture of pure glucose, is obtained chiefly from corn. It is a colorless or yellowish, concentrated syrup which contains other compounds, including maltose and dextrin. It is used as a sweetening agent in making candy, jams, ice cream, carbonated beverages, and table syrups. Glucose, also called *corn sugar,* or *grape sugar,* is just as wholesome but not as sweet as cane or beet sugar. Impure glucose has been made from wood chips or cellulose by boiling them under pressure with steam and sulfuric acid. This wood sugar has been used as cattle food and as a source of ethyl alcohol.

When glucose is heated with Fehling's solution, the glucose reduces the latter, forming cuprous oxide, a brick-red precipitate. This reaction is a test for the presence of glucose.

Glucose, the most important food within the body. To furnish every cell with a steady supply of glucose a delicate mechanism maintains a glucose concentration in the blood of about two milligrams per ten milliliters under normal conditions.

Glucose is oxidized in the body to CO_2 and H_2O through a series of catalytic reactions, and the energy formed is chemically trapped rather than liberated as heat. Later this stored energy is utilized to do work as for example in the contraction of muscles. One of the most important intermediate compounds formed is ATP (adenosine triphosphate). Glucose solutions are used in intravenous injections.

Sucrose is obtained from sugarcane or sugar beets. Sucrose, $C_{12}H_{22}O_{11}$, is the white, crystalline solid familiar to us as granulated sugar. It is obtained chiefly from the juice of sugarcane or sugar beets, although about two percent sucrose is found in the sap of the sugar maple tree. This sap is boiled to make maple syrup.

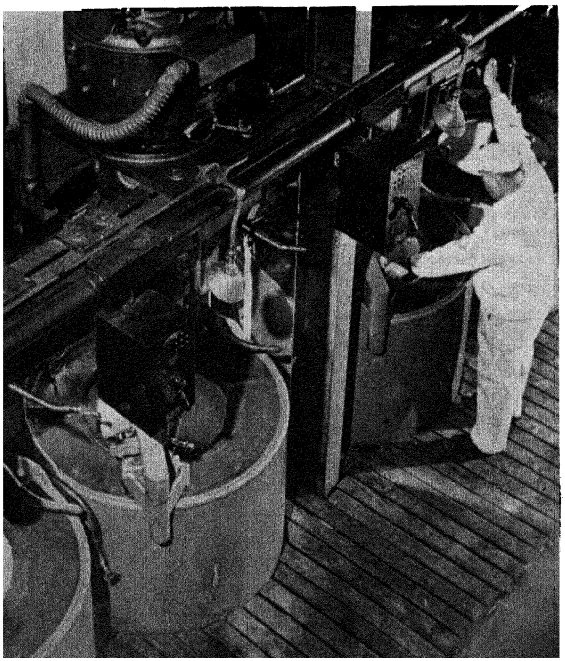
Sugarcane is a species of grass which grows to an average height of about 12 feet. It is a perennial and is grown chiefly in Cuba, which normally produces one-half of the world's supply, Java, the Hawaiian Islands, and the Philippines. In the United States, Florida,

Louisiana, Mississippi, and parts of Texas also grow sugarcane. In a recent year, the United States produced about one-sixteenth but consumed about one-fifth of the world's sugar.

The cane is crushed between rollers, and the juice obtained contains about 15 percent sucrose by weight. The first step in obtaining sugar from this dark, opaque juice is to add calcium hydroxide, which neutralizes the acids present and also precipitates some of the impurities as insoluble calcium compounds. The solution is then passed through boneblack, and diatomaceous earth filters, which remove the coloring matter. The resulting solution is then concentrated by evaporating most of its water content in vacuum pans by *reduced pressure distillation.* The reduced pressure makes it possible to boil off the water in the solution at a temperature below that at which the sugar solution would burn. Evaporation is continued until only a mixture of sugar crystals and molasses remains. This mixture is placed in centrifugal machines, or *centrifuges,* and whirled at high speed. The molasses is thrown off, leaving most of the sugar behind.

Table *molasses,* as you know, is used as a food. It contains about 60 percent sugars and is a rich source of iron. It contains no rejuvenating properties as claimed by some food-faddists. *Black strap molasses* is the raw material from which much of our ethyl alcohol is made. The fiber of the crushed cane, called *bagasse,* is used as a fuel, plastics filler, and in the manufacture of wallboard.

Sugar Research Foundation, Inc.



The centrifuging operation in refining sugar. The molasses is thrown off through the rapidly whirling wire mesh baskets, leaving the white sugar crystals behind.

In the United States we produce about four times as much beet sugar as cane sugar. Sucrose from sugar beets grown in Colorado, Michigan, Utah, and California is becoming a real rival of cane sugar from Cuba. From a forage crop containing less than five percent sucrose, the sugar beet has been so improved by scientific methods that it contains about 20 percent sucrose. It accounts for about one-third of the world's sugar consumption. Other domestic sources of sucrose are the *sorghum plant* grown in Alabama, the *Jerusalem artichoke* grown in Pennsylvania, and *maple syrup* chiefly from Vermont, Ohio, and New York.

Sucrose does not respond to the Fehling test, for it is not a reducing agent, as is glucose. When sucrose is heated to about 210°C., it changes to *caramel,* a yellowish substance used in confectionery. Sucrose is used as a food and in preserving fruits and curing meats.

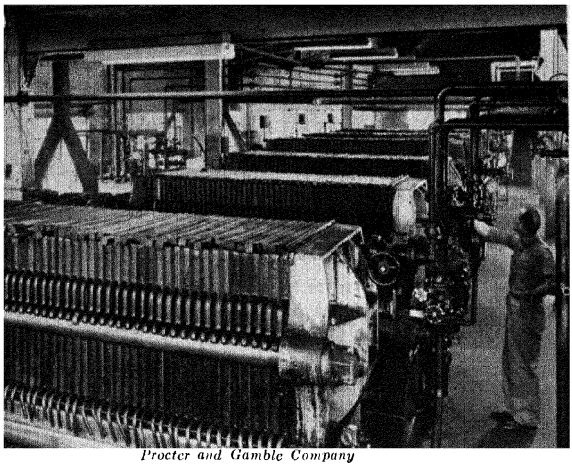
Saccharin is not a sugar. *Saccharin* is a complex organic compound first obtained by Fahlberg and Remsen in 1879 at Johns Hopkins University, as an accidental product of pure research. It is more than 500 times sweeter than sucrose and is used as a substitute sweetening agent (on the advice of a physician) by diabetic patients and others who must cut down their carbohydrate intake in order to help maintain health. Saccharin has no food value. *Sucaryl* is another such organic compound.

The inversion of cane sugar. When sucrose is heated with a small amount of acid, it splits up into a mixture of glucose and levulose, both of which have the same chemical composition but differ somewhat in properties. They are isomers. Glucose is often called *dextrose,* and levulose is called *fructose.*

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 \text{ (dextrose)} + C_6H_{12}O_6 \text{ (levulose)}$$

This process is called *inversion,* and the sugar formed is called *invert* sugar. During digestion also sucrose is broken down into glucose and levulose. Levulose is the sweetest of the sugars. It is found in fruits and in honey.

Fats and oils also constitute part of our diet. These nutrients contain carbon, hydrogen, and oxygen in varying proportions. They are the chief energy reserves in the body, and also function as insulation for various body tissues. Fats are split by water (hydrolyzed) to form fatty acids and glycerine. *Steapsin,* a lipase enzyme, and the bile acids are the two most important agents in the digestion and absorption of fats. "Fat burns in the flame of carbohydrates" because it cannot be used unless much carbohydrate is burned at the same time. One gram of fat produces nine calories, more than twice as



Procter and Gamble Company

After oils have been hydrogenated, they are passed through filter presses such as these to remove the catalyst.

much as an equal weight of either a protein or a carbohydrate. Fats and oils require a longer time for digestion than is required to digest carbohydrates and, hence, delay the sensations of hunger.

The common fats and oils are esters of glycerin and certain acids, virtually all of which are formed from straight-chain hydrocarbons. These acids are known as *fatty acids* and the most common of them contain either 15 or 17 carbon atoms plus a carboxyl group. The glycerin esters of these acids are known as *tripalmitin, tristearin, triolein,* and *trilinolein.* The first two are formed from saturated acids, while the last two are formed from unsaturated acids. As the degree of unsaturation increases, the melting point of the fat or oil decreases. Tripalmitin and tristearin are the chief components of the fats, while triolein and trilinolein are major components of many common oils, including olive oil, cottonseed oil, and soybean oil.

"Mazola," a widely used cooking and salad oil, consists of oil pressed from the germ of the corn kernel, while "Wesson Oil" consists of cottonseed oil.

Hydrogenation of oils produces fats. When unsaturated glycerin esters of fatty acids are heated in the presence of nickel or palladium catalysts and pure hydrogen is admitted to the reaction chamber, hydrogen unites with the unsaturated oil, producing a saturated oil, or fat. Thus, for example, triolein, the chief liquid component of many oils, reacts with hydrogen, forming tristearin, a solid fat. In hydrogenating such oils, the common practice is to stop the process before the hydrogenation is complete, that is, before all molecules of the oil have reacted with hydrogen. This results in a partially hydrogenated product that is much less hard than beef tallow, of which tristearin is a major component.

Many of the common fats used in cooking and baking are hydrogenated oils. Margarine, or oleomargarine, is a widely-used fat. It

may contain hydrogenated soybean, coconut, cottonseed, or peanut oil. Margarine is given a butter flavor by churning it in skim milk, and a butter color by the addition of a harmless yellow coloring matter. In certain cases, beef or lard oil, called *oleo,* may be added. Vitamin concentrates usually are added to vegetable margarines but cannot be added to margarines of animal origin, because of Federal regulations. Most margarines now contain added vitamins A and D, which are normally present in butter but not in the original margarine, plus a small amount of sodium benzoate as preservative.

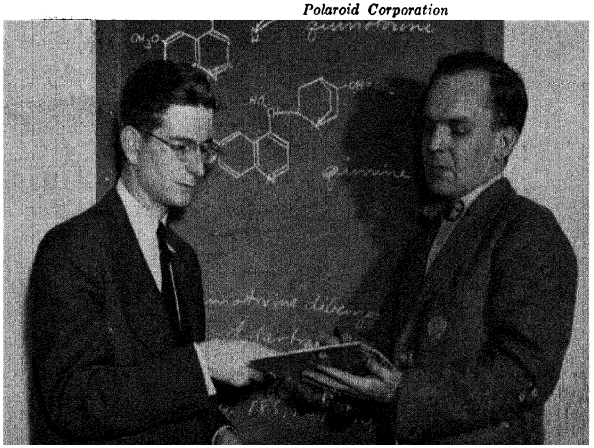
Margarine is an inexpensive and wholesome table and cooking fat. Although many Americans seem to prefer butter, it is nevertheless true that margarine is equally digestible and, as far as food value is concerned, if fortified with vitamin A, is the equal of butter.

Proteins are very complex nitrogen compounds. Carbohydrates and fats are the chief sources of energy used in the activities of the body, but they are not the chief substances of which active body tissues are composed. Muscle tissue, for example, contains but little carbohydrate and often very little fat.

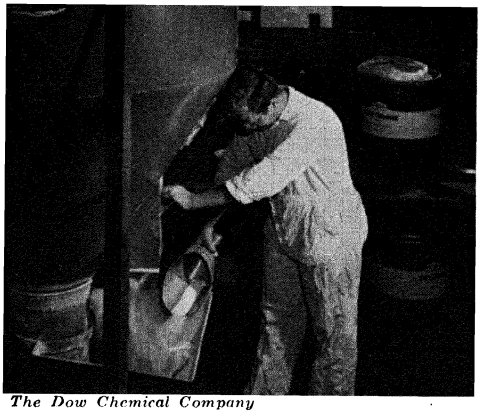
The chief constituents of the muscles and of plant and animal cells generally are compounds called *proteins.* Proteins are distinguished from carbohydrates and fats by the presence of nitrogen, for proteins contain about 16 percent nitrogen. In addition, these complex compounds contain oxygen, carbon, hydrogen, and sometimes small amounts of sulfur and phosphorus. They are very sensitive to heat, acids, and drying which make them insoluble. Raw egg, for example, is soluble in water, but when heated it undergoes *denaturation* and becomes insoluble.

In building the proteins of the human body, animal and vegetable proteins are broken down by digestion into simpler units called *amino acids.* From these amino acids, of which about 25 have been isolated, the much more complex animal and vegetable proteins are

Polaroid Corporation



Robert B. Woodward (left) and William E. Doering who together developed a process for synthesizing quinine. Woodward is also well known for his work with amino acids.



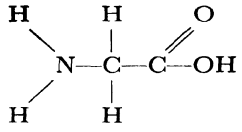
The Dow Chemical Company

Synthetic methionine, one of the essential amino acids being added to broiler feed. Methionine enables broilers to grow more meat per pound of feed.

built up. Proteins can be changed into amino acids by hydrolysis accomplished by boiling several hours with acids. However, in digestion, the process is carried on much more rapidly by means of enzymes.

While amino acids are said to be the simpler units from which proteins are built, they are by no means simple compounds. The simplest is *glycine* (amino acetic acid). Some amino acids have been synthesized.

Structural formula of glycine.



An idea of the complexity of the proteins may be gained from the fact that more than 1000 atoms may be present in one molecule of a typical protein. Molecular weights of typical proteins vary from about 17,500 for *lactalbumin* to about 6,700,000 for *hemocyanin*.

Animals cannot synthesize proteins. There is no known life without proteins, for they are essential components of *protoplasm*, the colorless, jelly-like substance that makes up all living cells. Plants are able to build their own relatively simple proteins from inorganic materials, such as sodium nitrate, carbon dioxide, and other substances obtained from the soil and air. However, animals cannot build up the proteins they need from simple inorganic substances. They must depend upon plant or animal foods to supply them with the simple protein materials.

In digestion, the enzymes *pepsin*, in the stomach, and *trypsin*, in pancreatic juice, break down complex proteins into amino acids. These amino acids can pass through the walls of the intestines into the blood stream. Thus the amino acids originally from plant proteins

are carried by the blood to the cells where they are built up into more complex proteins characteristic of animal tissues. *Keratin* is one of these proteins. It is the horny material of which hair, nails, horns, and hoofs are composed. Skin and muscle tissues are composed chiefly of proteins. Even silk is composed of a complex protein related to keratin and called *fibroin.*

Some pure proteins are *egg albumen, serum albumin* in blood, *casein* and *lactalbumin* in milk, *gliadin* and *glutenin* in wheat, *myosin* in meat, *gelatin* in bones, *zein* in corn, *insulin* in the pancreas, and *hemoglobin* in blood. Certain proteins are of greater value in nutrition than others. *Lysine* and eight other amino acids are essential because the body cannot supply them. The others can be synthesized in the body. Meat, cheese, and eggs contain more of the essential proteins. Gelatin is an incomplete protein of low nutritive value.

Amino acids are important nutrients in another way. In addition to its synthesis from glucose, glycogen is produced in the liver from amino acids not needed by the body. The nitrogen-containing part of the amino acid molecules is split off by certain liver cells and converted into urea, which is excreted. The carbon-containing part of the amino acid molecules is converted into glycogen.

Scientists have not yet been able to determine exactly the chemical structure of natural proteins that have been isolated. However, it has been shown that the typical proteins are essentially anhydrides of amino acids. The protein molecule is a threadlike structure of several hundred amino acids linked to one another. Long chains of amino acids were synthesized in 1947 by Charles H. Schramm and Robert B. Woodward. These chains, containing 10,000 units, somewhat resemble the fibrous proteins.

When concentrated nitric acid reacts with a protein, a yellow compound, *xanthoproteic* (zan'thō-pro-tē'ēk) *acid,* is formed. This yellow coloration is a test for a protein. Since the skin contains proteins, nitric acid leaves a yellow stain on the skin.

Essential minerals in foods. Minerals constitute more than four percent of the weight of the body. Animal tissues contain compounds of calcium, magnesium, sodium, iron, potassium, sulfur, phosphorus, chlorine, iodine, cobalt, and traces of copper, manganese, zinc, aluminum, silicon, fluorine, and other elements. These elements, obtained from foods, become part of different body tissues.

The chief elements which may be lacking in food, thus preventing normal physical and mental development, are calcium, iron, phosphorus, and iodine. Calcium and phosphorus compounds are necessary for building bone and teeth, since the chief constituent of these

structures is calcium phosphate, $Ca_3(PO_4)_2$. *Rickets,* one of the most devastating diseases of children, is caused by the inability of some children to use calcium and phosphorus, with the result that their bones become soft. A diet rich in these minerals and adequate exposure to sunshine will prevent and even cure this disease. Phosphorus also is present in nerve and muscle tissue.

Iron is an important element of hemoglobin, the pigment of the red corpuscles of the blood, which carry oxygen to all parts of the body. Persons whose supply of iron in the blood is insufficient are said to be *anemic,* and should be given foods rich in iron, such as meats, especially liver and kidney, and molasses. Iron salts also help in the clotting of blood, thereby preventing excessive bleeding.

Copper seems to stimulate blood regeneration in cases of nutritional anemia. Cobalt is also tied up with hemoglobin formation. The importance of iodine in the diet has already been discussed (see page 147).

Frequently, these essential mineral salts occur in what many unfortunately consider the waste parts of foods, such as the peelings of tubers and fruits, the coarser, leafy parts of vegetables, and the outer layers of grains. These "wastes," which contain rich mineral content, too often are thrown away. Some of these minerals are often allowed to go down the drain pipe when the liquids in which food is cooked are discarded. These liquids should be incorporated in the meal in one form or another because of the minerals and vitamins they contain.

The public demand for some overrefined foods such as *white* wheat, *choice* starch, and *polished* rice also robs many people of essential minerals. More than 95 percent of the flour milled in this country is changed to white because buyers prefer its taste and texture to whole wheat. On the other hand, whole wheat products are not superior nutritionally to enriched flour to which have been added thiamine, riboflavin, niacin, and iron salts which were removed by the bleaching.

How the heat value (number of calories) of a food is determined. The energy value of a food is generally measured in terms of the heat that it will provide. The unit of heat is the calory. It is, as you know, the amount of heat necessary to raise one gram of water one degree centigrade. Because the gram calory (written with a small *c*) is too small a unit to be conveniently used, the large Calory (written with a capital *C*), equal to 1000 calories, is the unit of heat generally used to measure the fuel values of foods. The heat value of a food is the number of Calories produced during its oxidation.

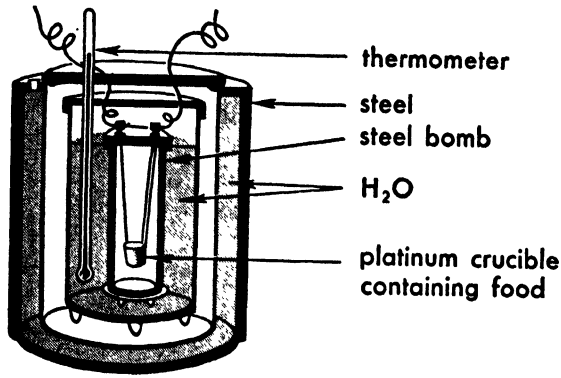


Fig. 114. Cross section of a bomb calorimeter.

One method of determining the calorific value of food is by burning it in a *bomb calorimeter* (kăl-ō-rĭm'ē-tĕr). This is a metal container in which a weighed portion of food can be burned in such a way that the quantity of heat liberated can be accurately measured.

Twelve hours after consuming a meal, an adult lying down at complete bodily rest gives off about one Calory per minute. One Calory per minute is the *basal metabolism* (see page 34) or the heat output of a normal person resting in bed before breakfast. This heat output is equivalent to the heat given off per minute by an average-sized paraffin candle while burning.

What is a balanced diet? An active adolescent boy or girl ordinarily needs a greater number of Calories than the average adult. An average growing boy requires about 3000 Calories daily; an average growing girl requires about 2800. An average adult office worker requires about 2000 if a woman and 2400 if a man. Hard physical work means that a greater number of Calories is needed. A laborer sawing wood needs, for example, as many as 5600 Calories. Lavoisier, in the eighteenth century, deplored the fact that people who have to work hard need more food than those who do not, but generally have less money to buy it than people who do not work so hard.

The energy needed by the body should come from a diet consisting of all the essential nutrients in their proper proportions. Such a diet is called a *balanced diet*. The so-called protective foods are milk, eggs, green leafy vegetables, and fruit. Average milk contains 87 percent water, four percent butterfat, 3.3 percent protein (casein), five percent carbohydrates (milk sugar), 0.7 percent mineral matter, as well as most of the vitamins (see below). With the exception of iron,

which must be supplied by other foods, milk contains all food elements and is, therefore, an ideal food especially for infants and growing children. Cheese is made from the curd which contains the nonsoluble milk solids. Whey is the watery byproduct of cheese and casein manufacture. Skim milk is fresh milk from which all butterfat has been removed and hence has no vitamin A. A table of some common foods showing their approximate compositions and calorific values is given on page 649.

A balanced diet consists of proteins, minerals, vitamins, carbohydrates, and fats in such quantities as may be necessary to meet the needs of the body. At different times during life, and under varying conditions, different amounts of the various nutrients may be required; that is, the balance shifts. For example, the calorific intake of an adult should come from 12 percent proteins, 28 percent fats, and 60 percent carbohydrates and should contain one gram calcium and 12 grams iron. The problem of a balanced diet is complex, but for the promotion of good health must be considered carefully. Excellent free or inexpensive publications on diet may be obtained

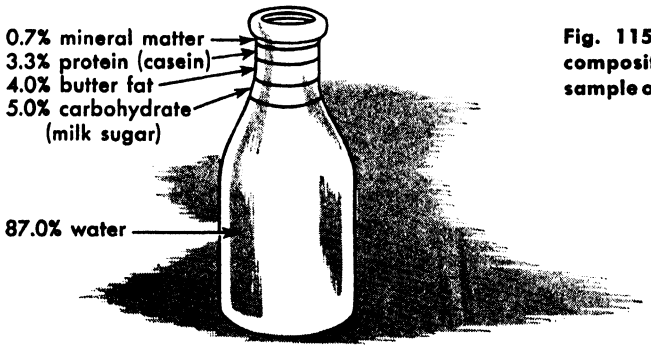


Fig. 115. The percentage composition of an average sample of whole cow's milk.

from the United States Department of Agriculture, the United States Public Health Service, and other government agencies.

What about vitamins? In 1897 Eijkman (īk'man), of Holland, working in Batavia in the Dutch East Indies, discovered that hens fed on *polished* rice exclusively developed a disease causing extreme weakness and creeping paralysis which ended in death. Hens fed on rice from which the outer shell had not been removed did not develop this disease, called *polyneuritis* in animals and *beriberi* in man.

When Eijkman fed his polyneuritic hens with the polishings of the rice, they recovered in a few days. Evidently there was something in the outer portion of the rice grain that was necessary for normal

health. Eijkman had experimentally produced the first case of a food deficiency disease and had cured it. Thirty-two years later he received the Nobel prize in medicine for this discovery.

In the years that followed, scientists found that rats, guinea pigs, and other animals fed with highly refined and *purified* carbohydrates, fats, proteins, and minerals did not thrive, even though they were getting sufficient quantities of these nutrients. However, upon the addition of even minute amounts of milk, fruit juice, or vegetables to their diets they developed normally.

In 1912 Dr. Casimir Funk gave the name *vitamine* (the final *e* was later dropped) to these unknown essentials in foods. The following year Elmer V. McCollum, at the University of Wisconsin, after many years of research, discovered in butterfat the "unidentified dietary factor, fat-soluble vitamin A," the absence of which is responsible for *night-blindness,* a reduced ability to see in dim light, and retardation of growth. Then followed the discovery of vitamins B_1, B_2, C, D, E, K, and several others closely associated with vitamin B_2, such as *niacin, pantothenic acid, inositol, para-amino benzoic acid, choline, pyridoxine* (vitamin B_6), *biotin* (vitamin H), *folic acid,* and B_{12}. The last named, an anti-pernicious anemia vitamin, is a ruby-red crystal vitamin containing one atom of cobalt. It seems probable that other vitamins exist and are yet to be discovered. Substances similar to vitamins are known to stimulate growth in plants; they are called *auxins.*

Vitamins are seldom manufactured in the human body. The absence of vitamins from our diet produces certain vitamin-deficiency diseases or "conditions." For example, the absence of vitamin B_1 results in certain kinds of neuritis and beriberi. Absence of B_2 (riboflavin) brings on skin lesions around the mouth and nostrils, and the absence of niacin (nicotinic acid) produces pellagra. Absence of vitamin C results in scurvy. Absence of vitamin D produces rickets. Absence of vitamin E results in sterility (in rats and probably in human beings). Absence of vitamin K causes blood to fail to coagulate properly and results in excessive bleeding. Vitamins A, D, E, and K are soluble in fats; vitamins B_1, B_2, and C are soluble in water.

The isolation and synthesis of the vitamins. For 20 years vitamins were substances of unknown chemical composition. Vitamin preparations were available, but they were impure products. Then late in 1931, Professor Windaus (vĭn'dous), Nobel prize winner in chemistry, announced the isolation of pure crystalline vitamin D. Its formula was found to be $C_{27}H_{41}OH$. This discovery fulfilled a confident expectation of scientists. Though its final achievement was the work

of Windaus and his assistants, years of experimentation by others led to this epochal event.

A substance similar to vitamin D is obtained by *irradiating,* or exposing to ultraviolet rays, a complex organic compound called *ergosterol.* Steenbock, of the University of Wisconsin, showed the relation between vitamin D and ergosterol subjected to ultraviolet light. Steenbock turned over the profits from his discovery to a foundation which used some of the money to help finance scientific research. Vitamin D is called the *sunshine vitamin* because it is formed in the human body when *dehydrocholesterol,* which is present in the cells of the skin, is exposed to sunshine or other sources of ultraviolet light.

All the vitamins have been obtained in pure crystalline form and all (except D) have been completely synthesized by chemists in the laboratory. American scientists have taken a leading part in vitamin research. (The food table on page 649 indicates various foods rich and deficient in the various vitamins.)

Science protects consumers. There has been a great deal of loose talk and ballyhoo about vitamins. The average adult gets enough vitamins if his diet is well balanced. Vitamin concentrates are needed only by babies, young children, expectant and nursing mothers, persons recuperating from illness, and those following the directions of a competent physician. In general, consumers should be wary of advertisements whose claims are beyond what careful scientists have been able to discover.

The Food, Drug, and Cosmetic Act passed in 1938 deals with cosmetics and healing devices as well as foods and drugs. It gives the Federal Security Agency, through the Food and Drug Administration, power to set compulsory standards, not only of identity, but also of minimum quality for foods sold in interstate commerce. Penalties are listed for misbranding and adulterating food products. The label must bear the names of all the ingredients, net weight, net contents, presence of artificial flavorings, artificial colorings, and chemical preservatives. The success of this law depends to a considerable degree upon the cooperation, alertness, and interest of all consumers.

Hormones and chemical control of body processes. Chemistry and medicine, by joining hands in the study of vitamins, won a great victory over premature death. Together these sciences have not feared to enter upon investigations of other products of the living human body. Among these products are the substances manufactured by the *glands of internal secretion,* or *endocrine glands.* These

glands, also called *ductless glands,* produce complex chemical substances that are emptied directly into the blood stream rather than through ducts into a specific region of the body. Such substances are called *hormones,* from the Greek meaning *I excite,* and enter into the chemical control of various body processes.

Hormones are complex organic compounds which, though present often in extremely minute amounts, act as powerful catalysts and profoundly influence health, growth, mental capacity, and our whole personality. The effects of hormones bear a striking resemblance to the effects of vitamins, and in some cases the action of vitamins and hormones in the human body is interlocked.

The late John J. Abel, of Johns Hopkins University, was the first to isolate a hormone in pure crystalline form. He obtained the hormone *epinephrin,* or *adrenalin* as it is more commonly called, from the suprarenal capsules (glands) located on top of the kidneys. Adrenalin has proved of inestimable value to physicians. As a stimulant and as an astringent it is used both in treating heart ailments and in stopping the bleeding of wounds.

In the human body, adrenalin is necessary whenever unusual physical exertion seems likely. For example, in fright or anger adrenalin in very minute quantities is secreted into the blood stream. As a result, the liver is stimulated to activity, and increased amounts of sugar are poured into the blood. Adrenalin also causes the walls of the arteries leading to the large muscles to relax, thus enabling this larger than normal amount of energy-producing sugar to reach the points at which it is needed. Adrenalin also causes the heart to beat faster and harder and, in apparent anticipation of injury, increases the clotting ability of blood. Adrenalin has been prepared synthetically.

Thyroxin, the hormone secreted by the thyroid gland, which lies like a saddle over the larynx, is a most important hormone. In children, secretion of less than normal amounts of thyroxin results in a marked lack of mental, physical, and sexual development. Such a condition is called *cretinism.* Cretins can be successfully treated by giving them *thyroid extracts* which contain thyroxin.

In adults, secretion of less than normal amounts of thyroxin results in marked reduction in physical and mental vigor, loss of hair, and puffy thickening of the skin. In most cases of too little thyroxin, successful treatment by the use of thyroid extracts is possible. Thyroxin has been prepared synthetically.

One kind of goiter is the result of too little thyroxin, while another type of goiter may be the result of too much. In adults, the secretion

of too much thyroxin results in nervousness, high basal metabolism, and a generally "high-strung" disposition.

Parathormone, the hormone secreted by the parathyroid glands, controls the amount of calcium excreted by the body, maintains a balance between the calcium in the blood and the calcium in the bones, and is very important in muscular control. *Pituitrin,* one of the hormones secreted by the pituitary gland, seems to control the size to which a person grows. In addition, it appears to be related to sexual development and mental ability.

Insulin, discovered in 1922 by Banting and Macleod, is the hormone secreted by certain cells in the pancreas. Its production from the pancreas of animals has saved thousands of diabetic patients from early death. Diabetes (dī-*ă*-bē'tēz) is caused by the partial or complete failure of the body to digest carbohydrates. Insulin, composed almost entirely of nine amino acids, aids in the normal decomposition of carbohydrates. If the body cannot supply its own insulin, the diabetic can get this essential hormone by means of injections.

Estrogen, a hormone of the female sex gland, and *testosterone,* a male hormone, appear to be responsible, among other things, for the development of sex characteristics and certain changes in the reproductive cycle. *Cortin,* a hormone secreted by the outer layer of the adrenal glands, appears to control the sodium, potassium, and chloride content of the blood. Another hormone produced by the same gland is *cortisone,* which is used against rheumatoid arthritis. The pituitary gland manufactures ACTH (*a*dreno-*c*ortico-*t*ropic *h*ormone), used in the battle against both rheumatoid arthritis and rheumatic fever.

While most of the hormones have been prepared in either pure or nearly pure form, usually from the glands of sheep and cattle, not all of them have been prepared synthetically.

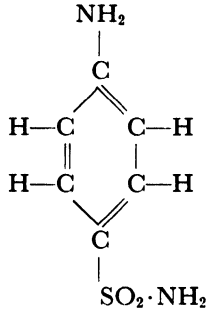
Another group of substances called *chalones* appear to check various kinds of body activity. As yet, chalones are not clearly understood. *Plant hormones* have been used to increase the root growth of seedlings, to retard the sprouting of potatoes, and to reduce the preharvest dropping of apples and pears.

Chemistry in the service of health. Chemistry has given to mankind priceless information concerning foods, vitamins, and hormones, which, if used intelligently by everyone, would no doubt add materially to our health and happiness. In addition, chemistry aids medicine in another important way — in the field of *chemotherapy.*

Chemotherapy is the attack on disease by means of certain chemical compounds known as *specifics.* When Paul Ehrlich (ār'līk), after

trying 605 different arsenic compounds, finally prepared *606,* or "Salvarsan," he gave mankind a magic bullet which could destroy the agent that causes that scourge of mankind, the disease *syphilis.*

The sulfa drugs. Other contributions to medicine are the *sulfonamides,* a group of related compounds known also as the *sulfa drugs.* The first used of these is the now well-known *sulfanilamide.* This group of compounds also includes the very effective *sulfadiazine, sulfapyridine,* and *sulfathiazole.*



Structural formula of sulfanilamide.

Sulfanilamide is the active component of a red dye known as *prontosil,* which was first used in the treatment of bacterial infections of human beings by Gerhard Domagk, a German scientist, and reported in 1935. As a result of his work, Domagk was named to receive the Nobel prize in medicine for 1939, but declined to accept it until 1947 because of the Nazi ban on all Nobel awards.

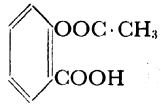
In general, the sulfonamides do not kill bacteria, but make possible their destruction by the body's normal defense mechanisms. In accomplishing this end, the sulfonamides prevent bacteria from multiplying. Robbed of their ability to multiply, the disease-producing bacteria fall easy prey to the white blood cells, called *phagocytes,* and are soon engulfed and destroyed. Unfortunately, not all bacteria are susceptible to the action of the sulfonamides. The many conditions in which the sulfonamides are used include wounds and burns; pneumonia and meningitis; streptococcus sore throat and tonsillitis; ear and mastoid infections; bacillary dysentery; venereal diseases of several kinds; boils and carbuncles; septicemia, or blood poisoning; and trachoma, scarlet fever, impetigo, and peritonitis.

Synthetic quinine and malaria. *Malaria,* one of the most dreadful scourges of mankind, is caused by a peculiarly resistant parasite that is introduced into the blood stream by a certain kind of mosquito. For many years, *quinine,* a drug obtained from the bark of the cinchona tree, was the only specific available to fight the disease. Since

most of the world's natural quinine production was concentrated in Indonesia, which, as World War II quickly proved, is an especially vulnerable territory, substitutes for quinine have long been sought. "Atebrin" and "Plasmochin," products of the synthetic chemists, were finally produced and widely used. In 1944 two 27-year-old American chemists, Robert B. Woodward and William Doering, finally synthesized the drug quinine for the first time. Morphine and caffeine have also been synthesized.

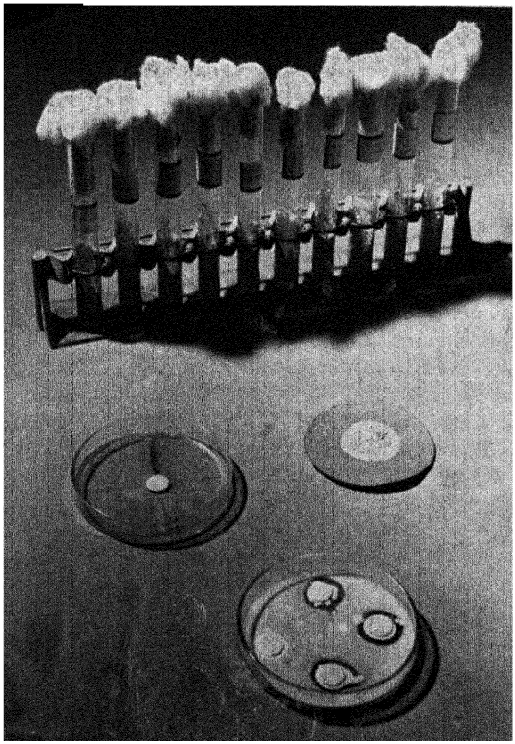
Aspirin, the analgesic or pain reliever, is acetylsalicylic acid with acetic anhydride. Americans consume about five million pounds of it each year.

Structural formula of aspirin.

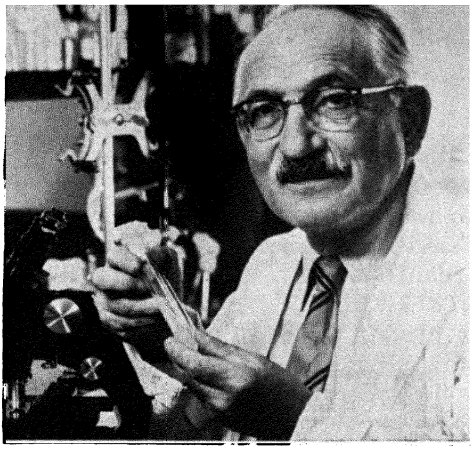


Penicillin from a mold. In 1929, Dr. Alexander Fleming, a Scot, accidentally observed that the growth of certain bacterial cultures that had been contaminated by a mold was slowed down very remarkably. When isolated, this mold was shown to be *Penicillium*

Medical and Pharmaceutical Information Bureau, Inc.



Molds grown in the test tubes are being tested against disease-causing germs in the Petri dishes. Each white disc is a cluster of an experimental mold. A clear area around the discs indicates that germs are being killed by an antibiotic substance produced by the mold.



Dr. Selman A. Waksman, winner of the Nobel prize for his discovery of streptomycin.

By Philippe Halsman, from "My Life with the Microbes," published by Simon and Schuster.

notatum. Fleming gave the name *penicillin* to the antibacterial substance produced by the mold. He found that in the laboratory test tube penicillin is active against the common disease-producing bacteria called *staphylococci, streptococci*, and *pneumococci*.

Because penicillin is unstable and was difficult to obtain except in extremely small quantities, little additional research on its effects or production was carried on until World War II. In 1941, a group of British scientists discovered that penicillin is active against certain kinds of disease-producing organisms in the living body as well as in a test tube. Faced with the enormous demands of the war, additional research was rapidly begun. Production of penicillin in large quantities by fermentation was a triumph of the creative genius of the American chemical and pharmaceutical industries. The pure sodium salt of penicillin was first obtained in 1943. Fleming was knighted in 1944 and in the following year shared the Nobel award in medicine with his collaborators, Florey and Chain, at Oxford.

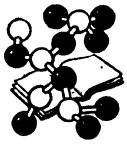
Solutions of penicillin are administered intramuscularly, intravenously, or by mouth in the treatment of septic wounds, blood poisoning, pneumonia, meningitis, venereal diseases, and other infections. The action of penicillin on bacteria is somewhat similar to that of the sulfonamides. Other newcomers among *antibiotics* (substances produced by living organisms which are effective against microorganisms) are also obtained from molds. Among them are *aureomycin, terramycin, chloromycetin,* and *streptomycin* discovered in 1944 in soil by Selman Waksman who also received the Nobel prize. The antibiotics have saved millions of lives and cut down the recovery time of many more millions.

Unravelling the mysteries of virus and enzyme. Many diseases, such as influenza, virus pneumonia, polio, mumps, and measles, are caused by *viruses,* disease-producing agents that are neither bacteria

nor protozoa and are so small that they are not visible under the highest-power optical microscopes. In 1935 the first virus to be obtained in pure crystalline form was isolated by W. M. Stanley, an American scientist. Under the electron microscope this virus, which produces a disease of tobacco plants called *tobacco mosaic disease,* turned out to have a strange, rodlike form. Later investigations indicate that this virus may be a protein molecule with a molecular weight of about 40,000,000. Many other viruses have been identified and isolated. Viruses seem to lie between the worlds of the living and the dead. Outside a living cell of a tobacco plant, the virus of tobacco mosaic disease acts like any other complex molecule. It cannot be grown on synthetic media. However, inside a living cell, it is capable of reproducing itself — a characteristic of living things.

Enzymes, which are complex organic compounds that act as catalysts in amazingly small amounts in many body processes of both plants and animals, are also proteins. In 1926, J. B. Sumner isolated the first enzyme, *urease,* in pure crystalline form. Pepsin, ptyalin, lipase, trypsin, and other enzymes have since been obtained in pure form. In the human body enzymes are especially important in the digestion of foods. Enzymes are used industrially in the manufacture, for example, of beer, cheese, acetone, and acetic acid.

As this brief review indicates, medical scientists and chemists are working together in the study of the chemical processes carried on within and by living cells. This area, *biochemistry,* and chemotherapy promise glorious achievements. Some day the scientists in these fields may give us synthetic antibodies to fight germs and viruses.



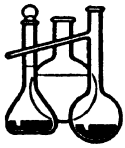
YOU WILL ENJOY READING

Calder, Ritchie. *Profile of Science.* The Macmillan Co., New York, 1951. Part 3, pp. 189–248, contains a very readable account of penicillin and other modern drugs.

Jaffe, Bernard. *Outposts of Science.* Simon & Schuster, New York, 1935. Chapter V contains a popular account of man's efforts to understand the chemistry of the ductless glands. Chapter VII deals with the discovery of the vitamins with particular reference to the work of E. V. McCollum.

Radcliff, J. D. *Yellow Magic.* Random House, New York, 1945. Here is the full story of the discovery, manufacture, and life-saving uses of penicillin.

Rose, Mary S. *Feeding the Family.* The Macmillan Co., New York, 1940. A valuable standard work by one of the world's most competent nutritionists.



USEFUL IDEAS DEVELOPED

1. Among the minerals necessary for normal growth and development are calcium, iron, phosphorus, and iodine. Calcium and phosphorus are needed for building bones and teeth; phosphorus is used in nerve and muscle cells; iron is necessary for the hemoglobin in the blood; iodine is necessary for normal development.

2. The chief nutrients found in food are carbohydrates, fats and oils, proteins, and minerals. Other substances called *vitamins* are necessary also.

3. A carbohydrate is a compound containing carbon, hydrogen, and oxygen. In a carbohydrate, hydrogen and oxygen are present in the same proportion as in water; that is, two atoms of hydrogen for each atom of oxygen.

4. Proteins are complex compounds containing carbon, oxygen, hydrogen, nitrogen, and sometimes sulfur and phosphorus. Protein is used in building muscle and other active body tissues.

5. The fuel value of food is measured in Calories. A Calory is equal to 1000 calories.

6. Basal metabolism is the amount of heat liberated per minute by a person lying down 12 hours after eating. Normally it is equal to about one Calory per minute.

7. Vitamins are complex organic compounds whose absence from the diet causes various deficiency diseases. Scientists now distinguish at least 14 different vitamins, including vitamins A, B_1, B_2, B_6, B_{12}, C, D, E, H, and K.

8. Hormones are chemical secretions from certain glands; they profoundly influence health, growth, and personality. Normally, they are present in the blood in extremely small amounts. Hormones act as catalysts.

9. The Food, Drug, and Cosmetic Act of 1938 protects consumers against false claims, adulterations, and dangerous ingredients. The consumer must, however, be alert.

10. A virus is a disease-producing substance that is so small as to be invisible under the highest power optical instrument. It is neither a bacterium nor a protozoan.



USING WHAT YOU HAVE LEARNED

Group A

1. By what chemical process does the body maintain its temperature?

2. What is digestion?

3. Discuss the dependence of animals upon plants for food.

4. What are the chief nutrients found in food?

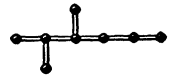
5. What was Lavoisier's contribution to the science of nutrition?

6. In what sense may H_2O be considered a food?

7. Why must starch be changed to sugar in the body before it is used?

8. (a) What is a carbohydrate? (b) Name the most common carbohydrates.

9. (a) In what ways do carbohydrates differ from hydrocarbons? (b) Give two examples of each.



10. What is the appearance of $(C_6H_{10}O_5)_x$ under a microscope?

11. (a) What are the properties of $(C_6H_{10}O_5)_x$? (b) Why is it more digestible when cooked?

12. What is the test for $(C_6H_{10}O_5)_x$?

13. What are the principal uses of $(C_6H_{10}O_5)_x$?

14. State the source, appearance, and chief use of dextrin.

15. Why is glucose so very important?

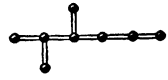
16. (a) Write the equation for the preparation of pure glucose. (b) How is commercial glucose manufactured?

17. Describe a chemical test for the presence of $C_6H_{12}O_6$.

18. (a) What is the chemical relationship between glucose and fructose? (b) What is glycogen?

19. (a) State the three sources of $C_{12}H_{22}O_{11}$ in the order of their importance. (b) What is saccharin?

20. Describe briefly four steps in the preparation of granulated sugar.



21. (a) How is caramel prepared? (b) How is sugar obtained from wood?

22. Using an equation, show the inversion of $C_{12}H_{22}O_{11}$.

23. (a) What foods are almost pure glucose? (b) Where is fructose found?

24. Determine the percentage composition of $C_{12}H_{22}O_{11}$.

25. A growing plant manufactured 12 g. of $(C_6H_{10}O_5)_x$. What volume of O_2 was liberated by the plant during this chemical process?

26. (a) How could you distinguish a protein from either a carbohydrate or an oil? (b) What is the principal difference

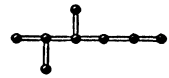
between butter and margarine? (c) May this difference affect health?

27. Name three pure proteins, and state the source of each.

28. How do plants differ from animals in the way in which they obtain proteins for building tissue and for food?

29. Woodward and Schramm are closely connected with the study of proteins. Explain.

30. Some HNO_3 is accidentally spilled on your finger. Explain the chemical action that takes place.



31. What four elements are most commonly deficient in man's diet?

32. How can the elements mentioned in exercise 31 be supplied?

33. What functions do the elements mentioned in exercise 31 play in the life of an individual?

34. What is meant by the *calorific value* of a food?

35. What is considered the normal basal metabolism of an adult?

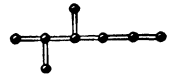
36. Describe one method of determining the calorific value of a food.

37. Why is the calorific value of a diet an unsafe guide to follow?

38. (a) Why is milk often spoken of as an ideal food? (b) In what necessary element is milk deficient?

39. (a) How and by whom was the first vitamin-deficiency disease produced experimentally? (b) Give an account of the experiment.

40. (a) Make a list of four vitamin-deficiency diseases. (b) Opposite each write the name of the vitamin that will prevent it and (c) mention at least one food that contains this vitamin.



41. (a) What are the "protective foods"? (b) Name four foods especially rich in vitamins.

42. (a) Have any vitamins been obtained in pure form? (b) What danger might accompany the taking of pure vitamins without the advice of a competent physician?

43. (a) What are hormones? (b) How do they function?

44. (a) Name one hormone that has been synthesized, and (b) another that is used in the treatment of diabetes.

45. (a) What is chemotherapy? (b) Name three recent discoveries in this field.

Group B

46. (a) Why is the formula of starch written $(C_6H_{10}O_5)_x$? (b) What is an "essential" amino acid?

47. Make a list of at least five principles suggested in this chapter to use in selecting your diet.

48. What is the most inexpensive way to get all the vitamins you need?

49. A manufacturer advertises a cosmetic cream as a skin food and rejuvenator. (a) What do you think of these claims? (b) Explain.

50. (a) What is a specific? (b) Discuss the history and uses of one specific.

51. How do (a) the sulfonamides and (b) penicillin act as antibacterial agents? Explain fully.



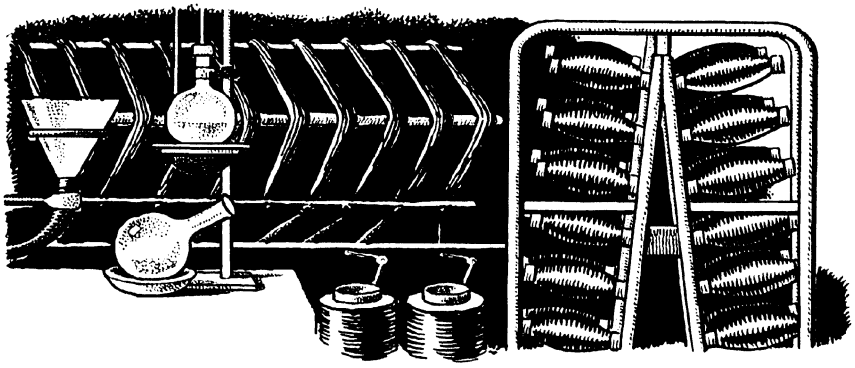
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. Make an accurate list of all the foods you have eaten during one full day. Make an analysis of your food consumption on the basis of what you have learned regarding a balanced diet.

2. Obtain some Benedict's solution from your chemistry or biology teacher and test several sweetening agents found at home for the presence of glucose. Report your results to the class.

3. *Consumers' Guide* says skim milk has everything in it except butterfat. Would it be safe to use skim milk and some animal fat which has been substituted for the butterfat as a substitute for whole milk?

4. Several thousand cases of pellagra are reported each year in spite of the fact that we know the cause and how to prevent this disease. Is this situation the result of ignorance or poverty or both? Explain your answer fully.



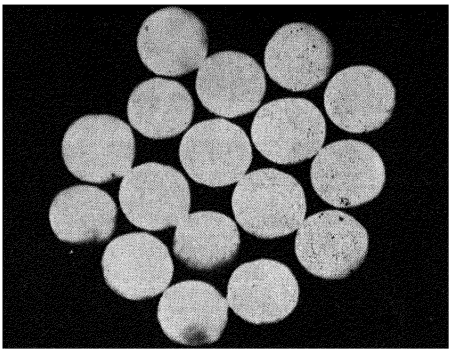
37 FIBERS AND PLASTICS: TEXTILES, PAPER, AND DYEING

There might be a way found out, to make an artificial glutinous composition, much resembling if not fully as good, nay better, than that Excrement, or whatever other substance it be made of which, the Silkworm wiredraws his clew. Robert Hooke, 1664

The long, slow road from skins to nylon and "Orlon." It is a far cry from the raw skins and furs that covered ancient man to the richly colored fabrics, both natural and synthetic, with which we clothe ourselves today. This tremendous change represents in part the difference between the ancients' utter ignorance of chemistry and the know-how of modern chemists.

Our many fibers — animal, vegetable, mineral, and man-made. The word *textile* refers to all products of the loom. Natural fibers are those parts of animal and vegetable tissues used chiefly in textiles. The most commonly used fibers of vegetable origin are *cotton* and *flax,* from which linen is made. Other vegetable fibers are *jute* used in making burlap sacking, *hemp* and *sisal* for ropes, and *ramie* for fire hoses and for clothing in China, India, and the Philippines. The most important animal fibers are *wool* and *silk.*

Rayon, really rayons, for there are several kinds, was at one time incorrectly called *artificial silk.* It is only one of the many synthetic fibers employed today. Glass and, to a lesser extent, the mineral *asbestos* have been spun and woven into waterproof and fireproof fabrics (see page 513). *Fiberflax* is a very thin fiber, cotton-like in appearance and very resilient. It is made by air-blasting a molten



Cross section of nylon thread magnified about 660 times. Each filament is smooth and almost perfectly round. Thread of this type is used for sheer stockings.

E. I. du Pont de Nemours and Company

stream of Al_2O_3 and SiO_2. Even some metals, including gold, silver, aluminum, and certain alloys, are drawn into fine threads which are spun and woven into textiles.

The characteristics of a good fiber. Molecules linked together to form a long chain-like polymer structure give us a fibril — building block of a fiber. All natural fibers except silk come in short lengths, a few inches long. Man-made fibers are continuous filaments. In general, a *good* fiber consists of very long, straight, parallel, and moderately rigid and interconnected molecules. The *good* of anything should be measured in terms of the use to which it is to be put. For example, glass or asbestos fabrics make excellent curtains and draperies for use where fireproof characteristics are desirable. Cotton, silk, or rayon fabrics would be *no good* in these situations because they burn easily.

For all-purpose usage, however, a textile fiber should be: (1) *tough* (stands up under hard use); (2) *strong* (not easily broken by moderate longitudinal stretching); (3) *elastic* (returns to original size and shape after slight stretching); (4) *heat resistant* (not damaged by moderate heat such as that used in ironing); (5) *water and cleaning liquid resistant* (not damaged by water or ordinary cleaning fluids, retains strength when wet); (6) *light resistant* (not damaged by much ultraviolet light from sunlight and other sources). Few fibers possess all these characteristics, but the most commonly used fibers possess most or all of them in varying degrees.

King cotton. Of all plant fibers, cotton is the one most widely used in the manufacture of textiles. Because cotton requires a long growing season, it can be raised only in rather warm climates. In the United States, the southern states and California and Arizona raise much cotton. India, China, Russia, Egypt, and Brazil are other principal raisers of cotton. In a recent year, the world output of cotton was 30 million bales, of which the United States produced approximately one-third.

A cotton fiber consists of only one cell, varying in length from $\frac{3}{8}$ inch to $2\frac{1}{2}$ inches, attached to the seed of the cotton plant. Under

a microscope, a cotton fiber appears as a flat and twisted thread resembling an empty, twisted fire hose.

Cotton fiber is almost pure cellulose, a carbohydrate whose formula is $(C_6H_{10}O_5)_y$. Cellulose molecules are very long chains of glucose molecules so bound by oxygen atoms as to be relatively straight. This compound like other plant fibers resists alkalies, but is attacked by strong acids. When cotton fibers are immersed under tension in a cold, concentrated solution of sodium hydroxide, they become smoother and stronger, and take on a silky luster. Cotton treated in this manner is called *mercerized cotton,* after the inventor of the process, John Mercer, an English chemist.

Wool, the most widely used animal fiber. Animal fibers are usually spoken of as *hair,* with the exception of that of sheep, which is called *wool. Camel's hair,* the *mohair* of the angora goat, the *alpaca* of the llama, and *felt* made from rabbit hair are used in making cloth; but wool is by far the most widely used animal fiber. The world produced about three billion pounds of wool in a recent year, of which about 15 percent was produced in the United States.

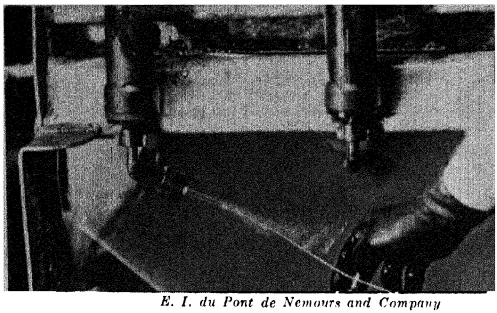
After sheep are sheared, the wool is sorted, scoured, and treated with carbon tetrachloride, CCl_4, to remove the *suint,* or wool grease, which, as you remember, is a source of potassium salts and of lanolin oil. The wool is then combed, forming continuous lengths, drawn, and twisted, by spinning, into yarns.

Under the microscope, wool fibers appear circular and serrated, or notched like a saw. The fiber generally coils up like a spring and can therefore be easily stretched. Wool fiber is composed of protein material, which accounts for the burnt feathers or ammonia smell when wool is burned. Unlike cotton, wool and other animal fibers are soluble in alkalies. They should not be washed with strong soap in hot water. Wool is not easily attacked by acids, except nitric acid, which turns it yellow. Why?

Wool textiles are much warmer than cotton, because the mesh between the fibers is filled with air, which conducts heat poorly. A wool-cotton mixture can be identified by boiling it in a five percent potassium hydroxide solution. The wool dissolves; the cotton does not.

Silk, marvellous product of a worm. *Sericulture,* the raising of silkworms, originated in China more than 40 centuries ago. In spite of the care with which its secrets were guarded, sericulture spread to Japan and later to France and Italy.

Silk fiber is made by the caterpillar of an ashy-white moth about half an inch long, which feeds on the leaves of the mulberry tree.



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Birth of a textile fiber. A viscose rayon filament coming from the spinneret into an acid precipitating bath.

From its spinning glands, the caterpillar squeezes out a viscous liquid which solidifies in the form of a cylindrical thread. With this thread, the silkworm spins a cocoon in which it is soon enclosed and thus protected. Before the moth is ready to emerge, the thread is reeled from the cocoon, and several such threads are brought together and twisted.

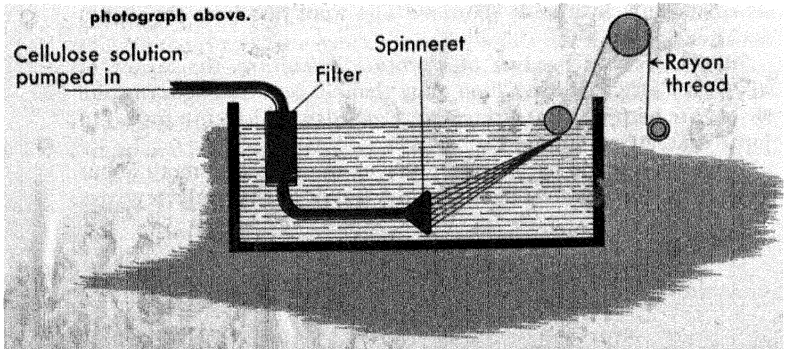
Silk, like wool, is composed of protein material. Its structure is like wool. Therefore it reacts chemically very much like wool, except that wool resists the action of sulfuric acid somewhat better than silk does.

Rayon, first rival of natural silk. In 1884, Chardonnet (shär-dô-nā′), a Frenchman, who was a student of Pasteur while the latter was investigating the silkworm disease, took out the first patent for the manufacture of "artificial silk." His process consisted of forcing a solution of *nitrocellulose* through fine openings into a chemical solution. Three years later at the Paris Exposition the first gown made from "artificial silk" was displayed. This event marked the birth of the great man-made fiber industry of today.

The rayon industry grew so phenomenally that by 1950 almost 100 times as much rayon cloth was manufactured as natural, or worm, silk cloth. In a recent year, world production amounted to more than 3.5 billion pounds of rayon yarn as compared with about three billion pounds of wool and 12 billion pounds of cotton.

Viscose rayon. Various methods are now used for the manufacture of this man-made fiber. There are several kinds of rayon, depending

Fig. 116. Simplified apparatus for manufacturing rayon thread. Compare with the photograph above.



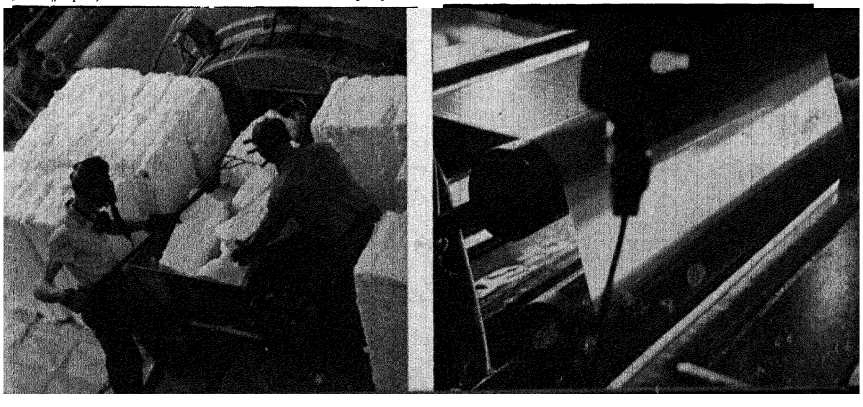
upon the chemical process used. Each kind has its own individual characteristics. Today more rayon is produced by the *viscose process* than by any other process. This is perhaps because of both the low cost of the raw material and the dyeing quality of the product.

Cellulose is obtained from spruce, pine, or other wood pulp, or from cotton *linters*. Linters are short cotton fibers left on the seed after separation from the plant. The bleached cellulose in the form of sheets is first steeped in a 17 percent sodium hydroxide solution, torn into shreds, and then dried and treated with carbon disulfide — 100 parts cellulose to 60 parts CS_2. After further treatment, the cellulose dissolves and the resulting orange-colored cellulose-carbon disulfide solution, called *cellulose zanthate,* becomes an amber-colored gelatinous syrup called *viscose*. This viscose syrup is then forced through a number of very tiny holes in a small metal cup (about the size of a dime) called a *spinneret*. From the spinneret, named after the organ through which the silkworm ejects its filament of silk, it enters a *setting bath,* which is a solution of sulfuric acid and sodium sulfate. Here the viscose hardens into filaments. The viscose forced through each hole in a spinneret forms a filament, and these many filaments are twisted into a thread by a revolving spindle. The threads are then treated to remove any excess chemicals, dried, and wound on spools or into skeins. This viscose rayon fiber, like natural cotton fiber, is almost pure cellulose, but under a microscope it appears a solid round filament rather than a flat thread. Its chemical action with acids and alkalies resembles that of cotton. Rayon made by the viscose process is really a regenerated cellulose, man-made rather than synthetic.

Cellophane is made by the same process. However, the viscose is forced through a narrow slit instead of through a spinneret. The acid into which it is forced solidifies the viscose into a soft and pliable sheet. It may be less than 0.001 inch in thickness.

(left) Cotton linters are placed in an acetator to be reduced to a liquid. (right) A sheet of Cellophane leaves the coagulating bath in which it was formed.

Photographs, E. I. du Pont de Nemours and Company



Acetate. *Acetate,* an ester of cellulose, is a kind of rayon made by the next most widely used process of rayon manufacture. Cellulose acetate dissolved in acetone is the liquid that is forced through the spinneret in making acetate. A current of warm air evaporates the acetone leaving a solid filament. Today about ten percent of the world's rayon production is made by the acetate process, while the remainder, except for a negligible amount, is made by the viscose process. *Celcos* is a combination fiber of viscose and acetate.

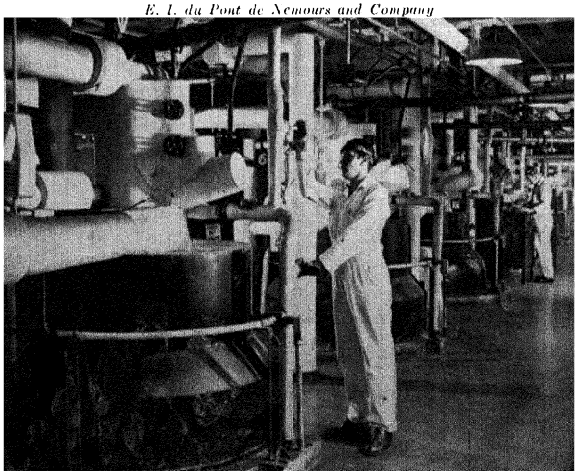
Nylon yarn, a wholly synthetic fiber. Both rayons and acetate are made from very complex organic compounds. None of these compounds has been synthesized by chemists. In 1939 du Pont began the manufacture, on a commercial scale, of an entirely new synthetic fiber that can be made from chemicals derived from coal, natural gas, petroleum, water, and air. This fiber is called *nylon.*

The chemical character of nylon is such that many different nylons of different long-chain structures are possible. One common member of the nylon family is made by polymerization from hexamethylene diamine and adipic acid obtained from petroleum, natural gas, or coke ovens.

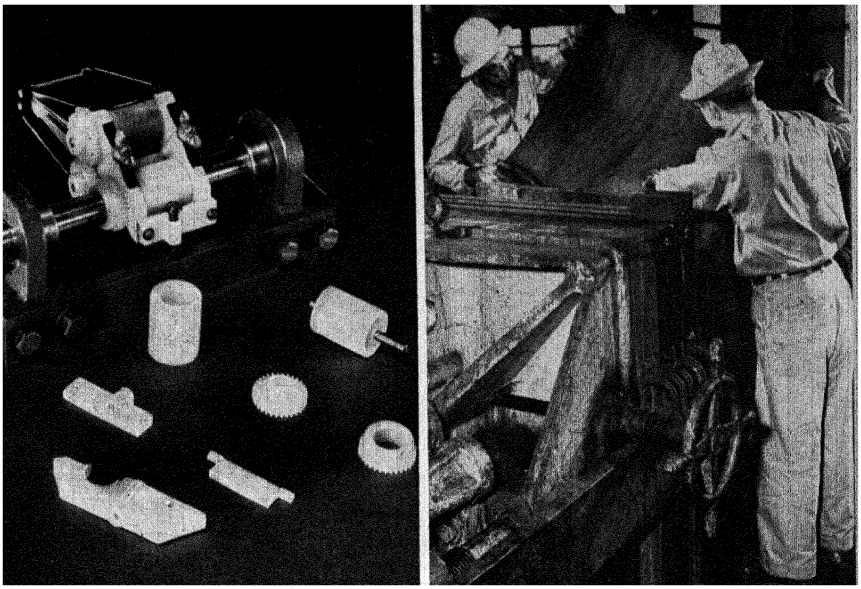
Nylon yarn is used wherever fibers possessing its characteristics are required — in women's stockings, curtains, dress fabrics, shirts, fishing lines, and as nylon cords in tires. Nylon's chief advantages over natural silk are that it is somewhat tougher, stronger, more elastic, more water resistant (less water absorptive), and is not attacked by moths or by mildew. It may be stored in darkness without deterioration.

When nylon is forced through relatively large holes, coarse filaments of nylon are formed. This form of nylon is being used for bristles for brushes of various types. Nylon is also used for coating fabrics and for rods, tubing, and window screens.

E. I. du Pont de Nemours and Company



Autoclaves in a nylon plant. In these receptacles, small molecules join to form the nylon polymer.

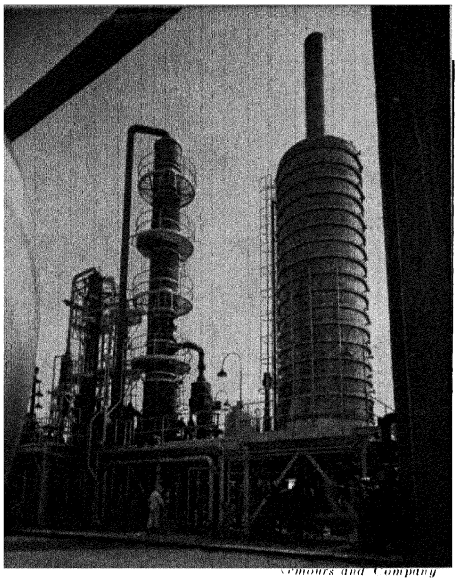


Photographs, E. I. du Pont de Nemours and Compa

The new synthetics are adaptable to many uses. (left) Nylon elements of a spinning unit. (right) An "Orlon" filter for a large filter press.

"Orlon," "Dacron," and other synthetic, wool-like fibers. Several other synthetic fibers soon came out of the chemist's test tubes. Among them were *"Orlon"* (acrylic fiber), *"Dacron"* (Terylene), *dynel* (*"Vinyon N"*), *lanital, "Vicara,"* and *saran*. They are all long-chain polymers. *"Orlon"* and *dynel* are made from acronitrile, a volatile, water-like liquid obtained from petroleum. *"Dacron"* is a polyester fiber which retains its high resilience even when wet, resists wrinkling, and dries easily. It is mildew and moth resistant. *Dynel* is sensitive to heat and dries quickly. *Saran* is a vinylidine chloride-vinyl chloride copolymer made from natural gas and petroleum. It is highly resistant to light, heat, and chemical agents and absorbs little moisture. It is used primarily for awnings, upholstery, curtains, screens, and the like.

The first of the protein fibers to be introduced was *lanital*. It was made in Italy from the casein of milk. Casein is similar in chemical composition to wool. *"Vicara"* is the trade name of an American fiber of the lanital type. It is made from zein extracted from the corn kernel. *Ardel* is made from the peanut. Combinations and blends of synthetic and natural fibers are used in making various types of cloth. For example, men's suits are made from a mixture of "Dacron" and wool, and tropical suits from "Orlon," viscose, and acetate rayons. Blankets, rugs, and carpets are woven from rayon and natural



Courtesy du Pont de Nemours and Company

Units of the first full-scale plant in the world for manufacturing "Orlon" acrylic fiber. These units recover essential materials for re-use in the process.

wool. Special dyes and techniques are constantly being developed for processing these new synthetic fibers.

Economic effects of artificial fibers. In 1940, 85 million pounds of raw silk were produced by the world largely in Japan and China. By 1952 silk imports by the United States had dropped to five percent of this figure. Nylon had almost completely supplanted silk in hosiery manufacture and in the making of fabrics for many purposes. The silk shortage of World War II proved conclusively that synthetic fabrics could take the place of silk. However, it is likely that in spite of plentiful rayon, nylon, and other artificial fibers, silk will continue to be used to some extent. With the evergrowing uses of other man-made fibers will come far-reaching effects on the agricultural patterns of the great centers of production of silk, wool, and cotton. This will take some time, for the present production of all synthetic fibers (not including the rayons) constitutes only five percent of the world's wool production.

Paper, another cellulose product. Practically all of the paper manufactured in this country is made from cellulose obtained from wood. Rice hulls, jute, straw, linen and cotton rags, or esparto grass are also used. The art of making paper was invented about 150 A.D. by Tsai-Lun in China. He made the first true paper from macerated vegetable fiber on flat, porous molds.

The modern method of making paper consists of first making *wood pulp. Mechanical,* or *groundwood, pulp* is made by pressing short logs peeled clean of their bark against a rotating stone or steel

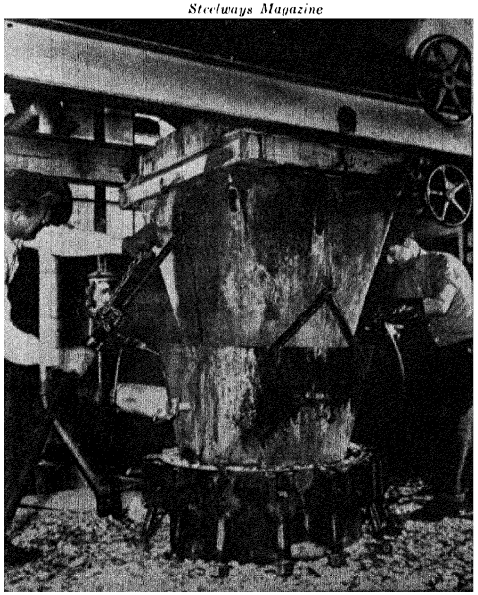
pulping wheel in the same manner as grinding an ax against an old-fashioned grindstone. Water cools the pulping wheel and washes the wood pulp formed into a pit below the wheel. Such pulp is made chiefly in the forest lands of Canada and Scandinavia near the raw material.

The fiber mass in mechanical pulp contains most of the components of the wood from which it was made, including lignin and cellulose. Short-lived paper products are made from mechanical pulp. Mixed with about 15 percent of sulfite pulp, mechanical pulp is made into newsprint and wallpaper. The presence of some lignin in newsprint accounts for the fact that it becomes yellow very quickly.

Chemical wood pulp is made by treating wood chips with various chemicals to rid them of the noncellulose portion, chiefly the resinous, glue-like substance lignin which binds the cellulose fibers. This comprises about 25 percent of the weight of the wood and is today the most abundant unexplored organic byproduct in the world. Different treatments are used with different kinds of woods. Chief among these are the *sulfite process, soda process,* and *sulfate process.*

In the *sulfite* process, chips of spruce, fir, hemlock, or pine are *digested,* or heated, in a liquor of calcium bisulfite, $Ca(HSO_3)_2$, held in solution by an excess of SO_2. The lignin is dissolved out of wood, leaving almost pure cellulose fibers. These are washed with sodium carbonate solution and then bleached with chlorine or bleaching powder. When poplar or cottonwood is used, the *soda* process is employed. Sodium hydroxide instead of calcium bisulfite is used in digesting the wood chips.

Steelways Magazine



Through this unit, wood chips are fed into a "digester," three stories high. In the digester, the chips are steam-cooked with caustic soda. This process frees the chips of wood gums and resins, and reduces them to a pulp.

After the pulp has been thoroughly beaten, a thin, even layer of wet pulp containing about 99 percent of water is placed on an endless wire screen of very fine mesh. Most of the water present in the pulp passes through the screen. A *sizing material,* such as *rosin* (a gum from pines), and fillers, such as barium sulfate, chalk, or clay, are added (to prevent ink from running), and finally the paper is *glazed* by passing it between heated rollers. The whole process is continuous.

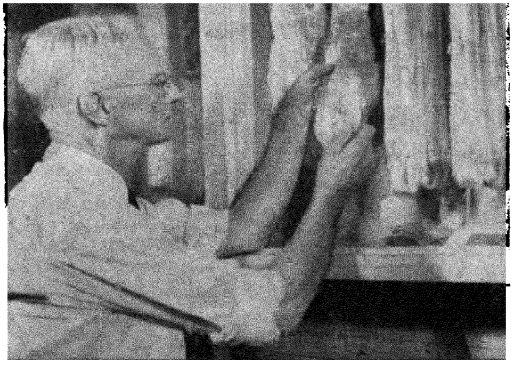
Filter, cigarette, and bank-note papers are made from cotton or linen rags. Filter paper is almost pure cellulose. Coarse papers and insulating boards are made from cornstalks and straw. Writing and printing papers are made from a mixture of wood pulp and esparto grass. This grass, which grows in southern Spain and northern Africa, attains a height of four feet. Its leaves contain more than 50 percent cellulose fiber. A tough, semi-transparent *parchment* paper is obtained by treating paper with dilute sulfuric acid.

Paper is now being used at a staggering rate. In this country alone almost one-half million tons of wood pulp are used each week in the manufacture of paper and paperboard. To save our forests, to cut down our tremendous imports of wood pulp, and to help the South economically, successful attempts have been made to obtain wood pulp from several species of pine (such as loblolly or slash pine) which grow in the South. Southern slash pine matures in about 20 years compared with 70 years for northern spruce. Why?

A great expansion has taken place in the South in the manufacture of wood pulp from slash pine. Because of the resinous nature of this wood, a third process, the *sulfate* process, is used. Sodium sulfide is one of the chemicals employed. Kraft paper for wrapping and grocery bags is made by this method.

Nitrocellulose and some amazing products made from it. When cellulose is treated with nitric acid, in the presence of sulfuric acid, which acts as a dehydrating agent, it is changed into a mixture of cellulose nitrates called *nitrocellulose.* If the product is highly nitrated, it is used as smokeless powder, or *guncotton;* if it is mixed

FPG



Dr. Charles H. Herty (1867–1938), of Georgia, inspecting skeins of rayon made from southern pine. Dr. Herty developed a process for making newsprint paper from these trees.

with nitroglycerin, it is used as *blasting gelatin*. Nitrocellulose that is less highly nitrated is known as *pyroxylin*. This is the basis of the pyroxylin finish, which has revolutionized automobile painting by cutting down the drying time from several days to just a few hours.

Pyroxylin finishes, of which "Duco" nitrocellulose lacquer is an example, are made by dissolving nitrocellulose mixed with varnish gums in a suitable solvent, such as amyl acetate or ethyl lactate. After the solvent has evaporated, a transparent, durable, flexible film is left. Pyroxylin is used also to coat or impregnate many fabrics used in bindings for books, upholstery, traveling bags, and brief cases.

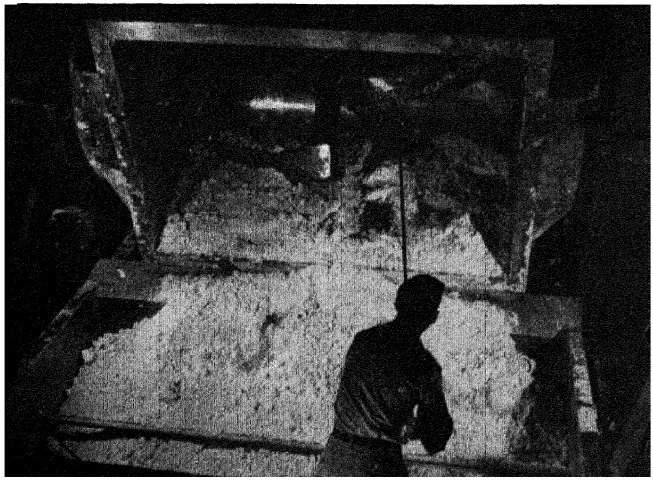
Collodion is a solution of nitrocellulose in a mixture of alcohol and ether. It is an ingredient of fingernail lacquers and of certain liquid substances used to treat corns.

Plastics, another giant that grew almost overnight. In 1868 John Hyatt, an Albany printer and son of a village blacksmith, set out to make a substitute for the ivory billiard ball. After a long series of unsuccessful trials, he blended camphor and cellulose nitrate, producing "Celluloid," which, next to cellulose nitrate which had been produced in England thirteen years earlier, was the world's first synthetic plastic.

The white "Celluloid" collar of the gay nineties and the "Bakelite" panel of the early radio cabinets are both examples of *plastics*, a fairly new class of substances that are now very widely used and extremely important in our daily lives. In 1953 nearly three billion pounds of plastics were manufactured — more than any single nonferrous metal.

A plastic is an organic substance, generally synthetic, that can be given a more or less permanent shape by the use of heat, pressure, or both. There are two groups of plastics and they have somewhat different physical properties. The first group consists of substances that

American Cyanamid Company



A step in the manufacture of melamine, a plastic used for dinnerware and sink and table tops. Here, the cellulose filler, impregnated with liquid resin, is scraped from an open mixer. It will be screened and oven-dried before it is molded.

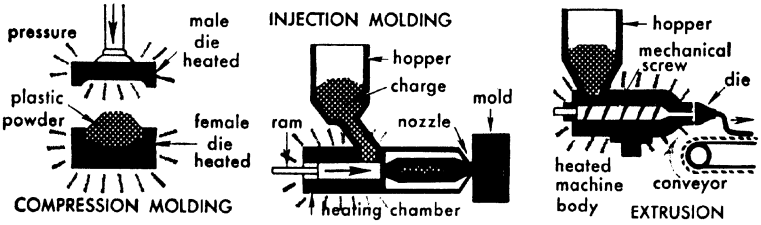


Fig. 117. Simplified cross sections of the apparatus used in molding plastics.

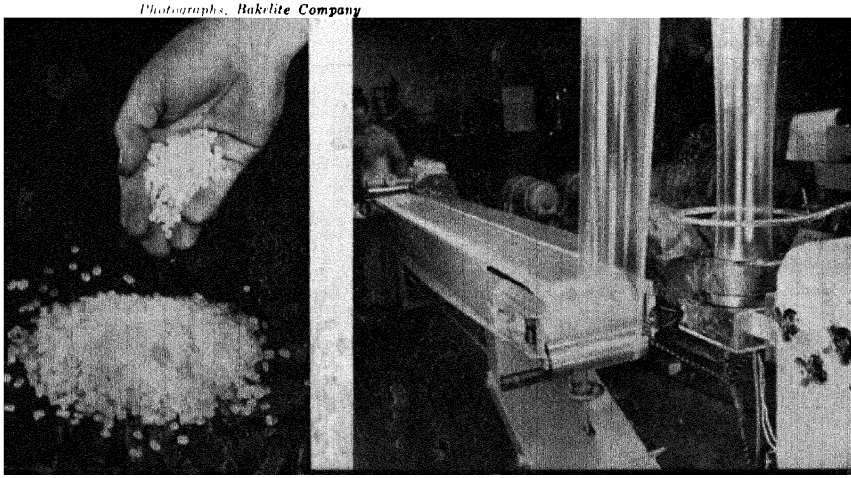
are softened by heat, may be molded by means of heat and pressure, and become soft as often as sufficient heat is applied. Such plastics may be melted as often as desired and are called *thermoplastics*. The second group consists of substances that are softened by heat during the making of a plastic article, but, after cooling, they cannot be melted again. Such plastics are called *thermosetting plastics*.

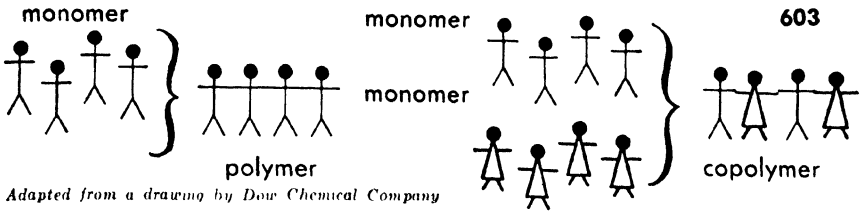
The molding of plastics. In general, thermosetting plastics are molded into shape by placing sufficient *molding powder* in a steel die of the desired shape, raising the temperature, and applying pressure until the plastic powder melts and assumes the contours desired. This process is known as *compression molding*.

The method generally used in molding thermoplastic materials is to force molten plastic under pressure into a mold, where it is cooled and hardened. This process is called *injection molding*, from the fact that the molten plastic is forced, or injected, into the mold. *Extrusion molding* consists of forcing molten thermoplastics through dies of the desired shape, after which the plastic cools and hardens. Color which is added to plastics is more than skin deep. It goes all the way through.

(left) Polyethylene resins used to make packaging and insulating materials. (right) Extrusion of polyethylene film tubing through a circular die.

Photographs, Bakelite Company





Adapted from a drawing by Dow Chemical Company

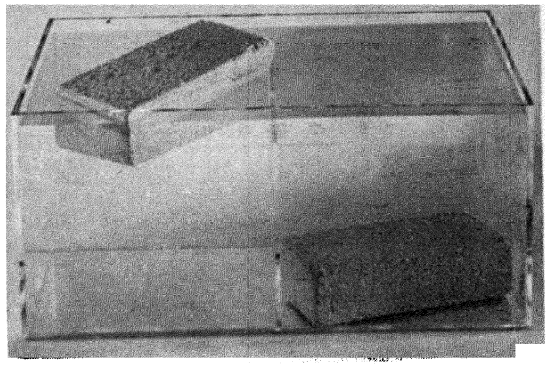
Fig. 118. A representation of the manner in which molecules join to form long "chain" polymers and copolymers.

A few important "tailor-made" plastics. Some of the most widely used plastics and the trademarks under which they appear may be chemically grouped into (1) the thermoplastic cellulose derivatives, including nitrocellulose ("Celluloid," "Pyralin"), cellulose acetate ("Plastacele," "Tenite"), and ethyl cellulose ("Ethocel"); (2) the synthetic resins, including the thermosetting phenol-formaldehyde resins ("Bakelite," "Redmanol," "Durite"), the urea-formaldehyde resins ("Plaskon"), the methacrylate resins ("Plexiglass," "Lucite"), the tetrafluorethylene resins ("Teflon"), the vinyl resins ("Vinylite," "Koroseal"), and the polystyrene thermoplastics ("Styron"); and (3) the protein resins made by treating certain proteins with formaldehyde. For example, milk casein is powdered, mixed with water, and shaped. On being placed in a solution of formaldehyde, the casein sets or hardens. Plastics have even been made from fibrinogen, a protein in blood. Many synthetic fibers such as nylon and saran are plastics.

Plastics are usually polymers; that is, their molecules consist of chains of chemical units sometimes numbering as many as 1000. Polyethylene, for example, is a thermoplastic made by polymerizing ethylene, C_2H_4, under pressure. Each molecule of polyethylene contains about 1000 CH_2 units. These chain molecules help to explain the elastic properties of plastics. Polyethylene bottles are flexible and are used as containers for deodorants, hand lotions, and the like.

Many plastics are oil-soluble and are used in paints, lacquers, and other finishes. Some are lighter than aluminum; others are tough enough to stop a bullet; many are resistant to chemicals, are electric insulators, and can be machined on a lathe, sawed and drilled with woodworking tools, milled, and ground. Their properties and uses are almost limitless. They have replaced nonferrous metals, wood, and natural fibers for many uses. The manufacturing chemist today can produce a plastic of almost any reasonable specifications.

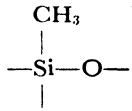
Silicones, a new family of plastics. When the carbon of certain organic compounds is replaced by the element silicon, polymerized compounds called *silicones* are formed. They are very inactive, do



The firebrick on the left has been coated with a silicone which makes it watertight. The brick floats because of the air trapped within it. The untreated brick soaks up water and sinks.

not corrode metals, and can stand extremely high and low temperatures. Their resistance to heat is so much greater than that of the carbon-based plastics that silicones have found use in making gaskets for use at extremely high temperatures. Some silicones can be vulcanized in very much the same manner as rubber. Silicones have been used also in greases, lubricants, paints, varnishes, as water repellents, and as pan glaze to keep bread from sticking to pans in bread factories.

The general formula of silicones. They are long-chain polymers.



The new fluorocarbons. This is a group of chemicals which resists acids, bases, and other chemicals, and which may in the future be used in the manufacture of paints, plastics, rubber, fibers, and solvents. They also do not burn and do not decay. *They contain carbon and fluorine only,* and may some day become a branch of chemistry even larger than the hydrocarbons. C_5H_{12} (pentane) and C_5F_{12} (pentforane) are both clear liquids which boil at about room temperature, are nonelectrolytes, and are insoluble in water.

How dyes are classified. The textile industry is intimately bound up with the use and, hence, the manufacture of dyes. Although the investment in dye factories represents only a small fraction of the wealth invested in textiles, the dye industry is a key industry.

Dyes may be broadly divided on the basis of origin into four groups: (1) mineral, (2) vegetable, (3) animal, and (4) coal-tar. A typical mineral dye is *iron buff.* For many years natural *indigo* was the most important and widely used of the vegetable colors. It has been replaced almost entirely by *synthetic indigo.* A representative animal dye is *Tyrian purple,* extracted from a species of mollusk found in the Mediterranean. It was used by wealthy Romans who, "born to the purple," could afford to pay fabulous prices for fabrics dyed with this rich coloring material.

The triumph of coal-tar, or aniline, synthetic dyes. Until only about a century ago the world had to depend upon natural dyes, and the variety of such coloring matters was limited both in range of color and in other important properties. When, in 1856, 17-year-old William Perkin accidentally discovered a method of preparing *mauve,* a purple dye not found in nature, from the distillate of coal tar, a new era in dye-making began.

Within the next 50 years, hundreds of new dyes were synthesized from aniline, one of the products of the destructive distillation of coal. Not only has the chemist prepared new dyes, but he has actually duplicated nature and made pure and inexpensive synthetic indigo in his test tube.

The rise of synthetic indigo was accompanied by the death of the natural indigo industry, which, 50 years ago, employed thousands of men who cared for hundreds of thousands of acres of indigo plants. Of course, the synthetic dye industry, either directly or indirectly, created thousands of new jobs. This is but another of the social and economic changes brought about by the advance of chemistry.

In the development of synthetic dyes, a new industry sprang up almost overnight. Since synthetic dyes are definite chemical compounds, they are more uniform in composition than natural dyes and, hence, more dependable. In general, synthetic dyes are more colorful, more lasting, cheaper, and more varied than dyes made from natural products. The research chemist can point with pardonable pride to this new branch of creative chemistry.

Some dyeing processes. The ability to dye a certain fiber with a particular color depends upon the chemical, as well as the physical, properties of both the fiber and the dye. In general, wool is the most easily dyed fiber. Next comes silk, and then cotton and the rayons. Nylon is somewhat similar to animal fibers in dyeing characteristics. The other man-made fibers require special dyeing assistants.

We may group dyes according to dyeing processes in the following manner: (1) *Direct dyes* such as *Congo Red* are mainly used on cotton and viscose rayon, and do not run when washed. *Orange II* when applied to wool boiled with dilute acetic acid is another such dye. (2) *Mordant dyes* will not remain fixed, unless the fiber is steeped in a *mordant,* such as aluminum hydroxide, forming an insoluble compound, or *lake,* within the fiber. *Alizarin* (ă-lĭ′zə-rĭn), a vegetable dye, which is now prepared synthetically, produces Turkey red when aluminum hydroxide is used as the mordant. (3) *Vat,* or *reduction, dyes* are very fast dyes and are used in dyeing shirts and other cotton, linen, and rayon goods that must be fast to perspiration,

light, washing and chlorine treatment. Indigo is such a dye. *Indigo white* is placed in a vat with the substance to be dyed. The oxygen of the air gradually oxidizes this soluble substance into insoluble indigo blue in the fibers.

If a fabric is composed of wool and acetate, one dye can be selected to color only the wool and another dye to color only the acetate. Interesting color combinations can thus be obtained. Synthetic fibers may be colored by the addition of desired coloring agents to the fiber-forming liquid before placing the fiber in the setting bath.



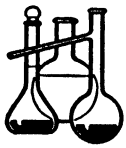
YOU WILL ENJOY READING

Robinson, C. N. *Meet the Plastics.* The Macmillan Co., New York, 1949. This small book deals with the history of plastics, opportunities in this field, and consumer education in plastics.

Haynes, Williams. *Cellulose: the Chemical That Grows.* Doubleday and Company, New York, 1953. Deals with rayon, paper, lacquer, film, cellophane, plastics, and natural and synthetic fibers. A popular treatment.

Williams, Simon. "Synthetic Fibers." *Scientific American,* July, 1951, pp. 37–45. An excellent article on the history, production, and properties of fibers. Very clear photographs.

Webb, Hanor A. "Dyes and Dyeing." *Journal of Chemical Education,* Oct., 1942, pp. 460–470.



USEFUL IDEAS DEVELOPED

1. *Textile* is the name applied to all products of the loom. Natural fibers are those parts of animal or vegetable tissues used in making textiles.

2. The most widely used vegetable fibers are cotton and linen. Wool and silk are the most widely used animal fibers. Rayon and nylon are the chief synthetic fibers used today. Other synthetic fibers are "Orlon," "Dacron," dynel, and "Vicara."

3. The cotton fiber is almost pure cellulose $(C_6H_{10}O_5)_y$. It resists alkalies, but is attacked by strong acids. Fibers are made of molecules linked together to make a long chain-like polymer.

4. Animal fibers are usually spoken of as *hairs,* with the exception of those of sheep, which are called *wool.* Wool is composed of protein material; it is soluble in alkalies, but is not readily attacked by acids.

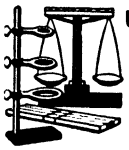
5. Silk fiber is made by the caterpillar of the silk moth, which feeds on mulberry leaves. Silk is squeezed out as a viscous liquid and solidifies as a cylindrical thread. Like wool, silk is a protein.

6. Today, most rayon is made by the viscose process from cellulose obtained from either wood pulp or cotton linters.

7. The viscose rayon fiber, like the cotton fiber, is almost pure cellulose. Therefore, it behaves chemically like cotton.

8. Nylon's chief advantages over silk are that it is somewhat tougher, more elastic, more water resistant (less water absorptive), is not attacked by moths, and may be stored indefinitely in darkness without deterioration.

9. A plastic is an organic substance, generally synthetic, that can be given a more or less permanent shape by the use of heat, pressure, or both. Plastics are either thermoplastic or thermosetting.



USING WHAT YOU HAVE LEARNED

Group A

1. What are the chief classes of fibers in use today?

2. Name the most commonly used fiber of each class.

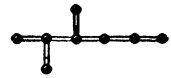
3. Is an asbestos curtain a textile? Explain your answer.

4. (a) What are the characteristics of a good fiber? (b) What is "fiberflax"?

5. Describe a cotton thread as seen under a microscope.

6. (a) What is the composition of cotton fiber? (b) Tell how it behaves in an acid solution, and in an alkaline solution.

7. (a) What is mercerized cotton? (b) Why is it called *mercerized?*



8. What is the difference between hair and wool?

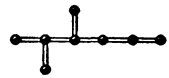
9. Copy and complete the following. Do not write in this book. After sheep are sheared, the wool is immersed in ... to remove the suint, which is a source of ... . Under a microscope, a wool fiber appears circular and .... The fiber's composition is ....

10. How can you determine the percentage of wool in a cotton-wool mixture?

11. Account for the burnt feathers odor when wool is burned.

12. Why is woolen clothing warmer than cotton clothing?

13. Why should Cl_2 not be used in bleaching wool or silk, although it may be used in bleaching cotton and linen?



14. What is the appearance and composition of silk fiber?

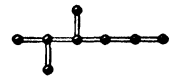
15. When and by whom was the first patent for the manufacture of "artificial silk" obtained?

16. In what ways is the manufacture of rayon from cellulose similar to the making of natural silk by the silk moth?

17. What is viscose?

18. Compare the composition and chemical action of a natural silk fiber and an artificial fiber.

19. (a) What is acetate and how is it made? (b) What is nylon?



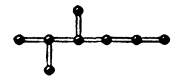
20. (a) Name five other synthetic fibers. (b) Describe several differences between them.

21. Compare cellophane and rayon as to composition and manufacture.

22. (a) What are plastics? (b) Name three plastics.

23. What is lignin?

24. (a) What is a silicone? (b) Name another branch of carbon compounds which may be of tremendous importance in the future.



25. Describe briefly the manufacture of newsprint.

26. What is the purpose of $NaHSO_3$ in paper-making?

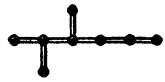
27. (a) Name eight fabrics and papers. (b) From what is each prepared?

28. What volume of CO_2 is formed by the complete combustion of the $(C_6H_{10}O_5)_y$ in 50 lb. of absorbent cotton, 98 percent $(C_6H_{10}O_5)_y$?

29. (a) What is pyroxylin? (b) What is pyroxylin paint?

30. In the burning of a certain weight of pure $(C_6H_{10}O_5)_y$, 250 l. of CO_2 were liberated. What volume of water vapor was formed?

31. Concentrated H_2SO_4 is added to pure $(C_6H_{10}O_5)_y$, and 20 g. of pure C are formed. How much $(C_6H_{10}O_5)_y$ is decomposed?



32. Why is the dye industry called a *key industry*?

33. (a) According to dyeing processes, name the chief classes of dyes. (b) Give an example of each class.

34. Name two natural dyes that have been almost completely replaced by synthetic dyes.

35. Why are certain dyes called *coal-tar*, or *aniline*, dyes?

36. Name four requisites of a good dye.

Group B

37. Describe *vat dyeing*, emphasizing the chemistry of the process.

38. (a) How do we explain the elasticity and other similar properties of such different substances as rubber, fibers, and plastics? (b) Illustrate your answer.

39. What is a mordant? (b) How is it used?

40. How are the textile and high explosive industries linked?

41. What tests are used to identify three different fibers?

42. What is the difference between virgin wool, reprocessed wool, and shoddy?



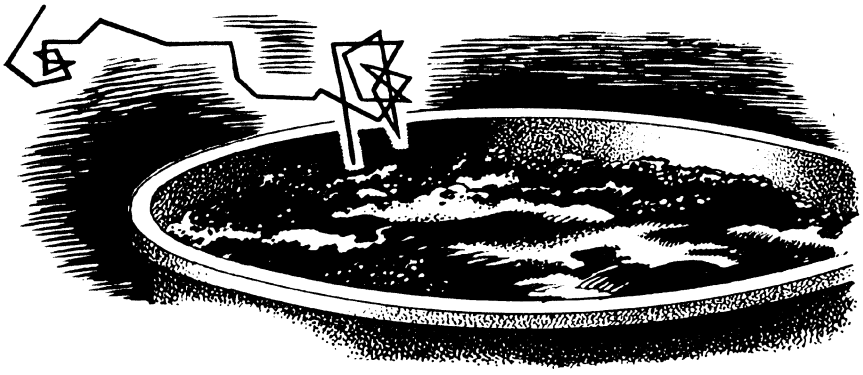
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. What precautions do you, your sister, or your mother take in washing clothing to prevent fading or running? Explain.

2. Make a report on the aniline dye industry, and show how its phenomenal development was the result of heavily subsidized research. In 1914 the United States produced only ten percent of the dye we used. Twenty-five years later we made 96 percent of all the dyes we consumed.

3. Make a collection of swatches of as many different natural and synthetic fibers as you can obtain. Paste them on a chart and label them with such pertinent information as source, composition, special properties, and uses.

4. Prepare a discussion on the mechanical cotton-picker developed by the Rust brothers. How has the success of this new machine affected (a) the chemical industries, and (b) farm workers?



38 COLLOIDS: THE COLLOIDAL STATE OF MATTER

. . . When it is recalled that Nature has selected matter in the colloid state to be the vehicle of life and as the medium in which all life processes take place, the importance and interest of a study and knowledge of the colloidal state become obvious.
Alexander Findlay, 1930

What is a colloid? In 1861, Thomas Graham performed some simple experiments on the passage of certain substances through parchment paper; and, on the basis of the results obtained, he grouped all substances into two classes. Those like sugar and salt, whose solutions passed through the parchment, he called *crystalloids,* and those like albumen and gelatin, which did not pass through the parchment, he called *colloids* from Greek words meaning *gluelike* (Fig. 119). For a long time this was the only generally accepted classification until experiments indicated that crystalloids could be changed to colloids, and vice versa.

Today we do not recognize Graham's hard and fast method of classification but speak about a *colloidal state,* or *colloidal condition,* of matter caused essentially by the size of the particles. The terms *colloid* and *crystalloid,* however, are still used to designate matter having definite and distinct general properties.

Characteristic properties of matter in the colloidal state. Matter in a colloidal state has several distinctive properties. These are:

1) *Brownian movement.* Thirty-four years before Graham coined the word *colloid,* another Scottish scientist, Robert Brown, while examining pollen grains under a microscope, noticed that they made

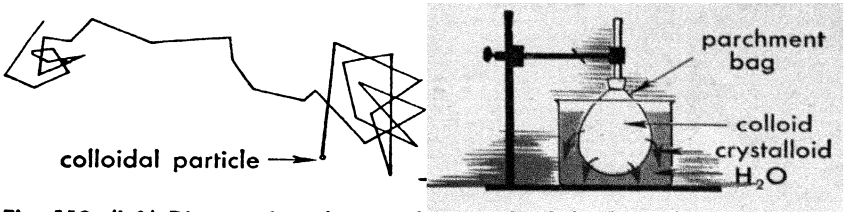


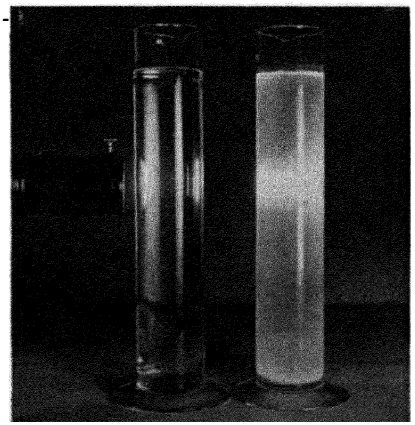
Fig. 119. (left) Diagram based on a photograph of the Brownian movement of a colloidal particle. (right) The principle of dialysis. The colloid will not pass through the parchment bag.

peculiar jiggling movements. Later investigation showed that all particles in the colloidal state exhibit this fascinating Brownian movement. Today we know it is caused by the uneven bombardment of colloidal particles by the moving molecules of the surrounding liquid.

2) *Tyndall effect.* When a beam of light is passed through a true solution, the beam is not visible in the solution. If, however, a beam of light is passed through a colloidal substance, the path of the beam is visible. We could pass a beam of light through a perfectly dust-free room without being able to see the path of the light, yet the path of a beam of sunlight passing through a room containing dust particles can be seen easily. The beam of a searchlight passing through a fog (a colloidal dispersion of water droplets in air) is visible because of the Tyndall effect. This effect, though noticed by Faraday before the term *colloid* was introduced, was named after John Tyndall, an eminent English physicist, who studied it many years later.

3) *Size of colloidal particles.* In 1903, Zsigmondy (shĭg'mŏn-dē) and Siedentopf (sĭ'dĕn-tŏpf) invented the *ultramicroscope.* An intense Tyndall cone of light is projected into the liquid under investigation. The microscope is placed at right angles to the path of the light.

By means of the ultramicroscope, the particles of matter in the colloidal state have been examined and found to range from 0.0001



The Tyndall effect. Note that the beam of light is not visible as it passes through the true solution (left), but its path may be easily detected in the colloidal solution (right).

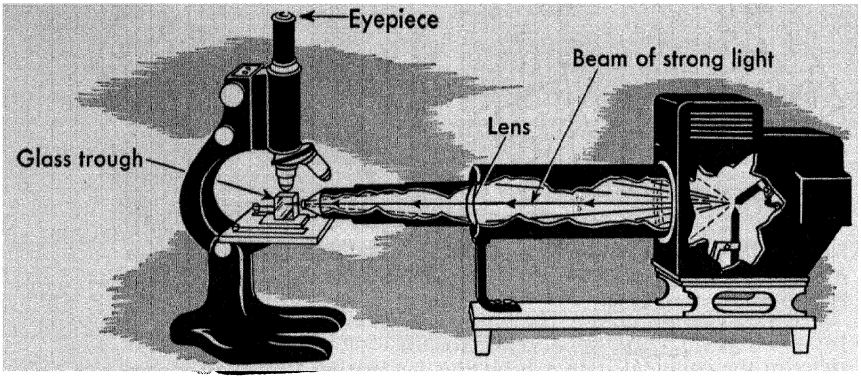


Fig. 120. Simplified drawing of an ultra-microscope. Note how the light from the electric arc is focused on the object under scrutiny.

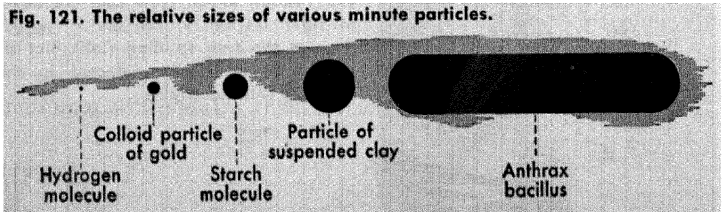
millimeter to 0.000001 millimeter in diameter. The diameter of the colloidal particle, therefore, lies between the diameter of a particle of a suspended material and the size of a molecule of a true solution. The diameter of the smallest known colloidal particle is still 100 times as great as the diameter of the hydrogen atom. Any substance, then, that can be divided into particles small enough to fall within this range will show the characteristics of a colloid.

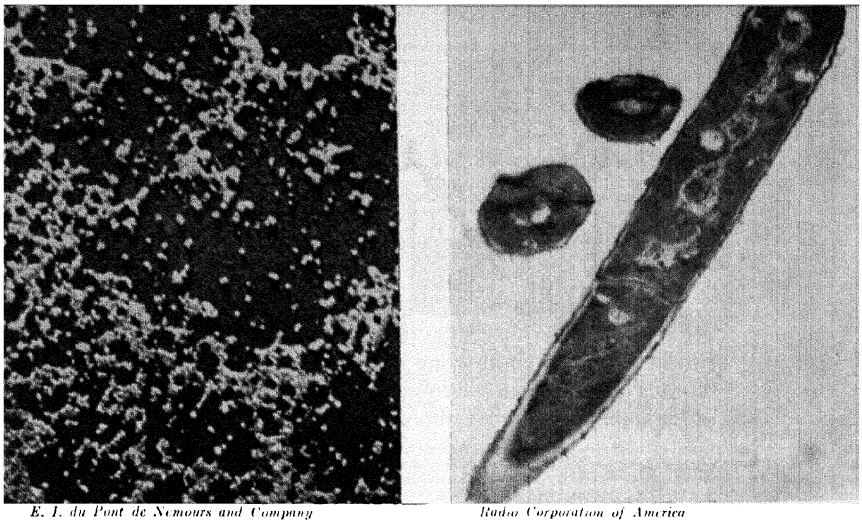
The more recently developed *electron microscope* has also been of great help in the study of colloidal particles, viruses, and protein molecules. The electron microscope can magnify up to 500,000 times as compared with the 2000 power of the best optical microscope.

Although colloids cannot be filtered by ordinary filters, they may be separated by an *ultrafilter*. This consists of a layer of some *gel* (see page 614) on porous porcelain. Colloids may also be separated from crystalloids by *dialysis* (dī-ăl'ĭ-sĭs). If a mixture of a colloid and a crystalloid is placed in a parchment bag in water, the crystalloid passes through the parchment, but the colloid remains behind (see page 611).

4) *Electric charge of colloidal particles.* A particle in the colloidal state is a group of molecules that is electrically charged as a whole, that is, as a group of molecules. All particles of certain colloids are charged positively, while all particles of other colloids are charged negatively. Thus, all particles of colloidal copper, ferric hydroxide, albumen, and hemoglobin are positively charged; and all colloidal particles of clay, silver chloride, starch, and oil emulsions possess a

Fig. 121. The relative sizes of various minute particles.





E. I. du Pont de Nemours and Company *Radio Corporation of America*

Photomicrographs taken by the electron microscope. On the left are particles of colloidal silica, magnified 25,000 times; on the right, longitudinal and transverse cross sections of a bacillus, magnified 59,500 times.

negative charge. The electric charge on a *suspensoid* (see page 614), such as colloid gold, may be 50 times the electric charge carried by a univalent ion.

Scientists believe that the electric charge on a colloidal particle is caused by positive or negative ions which it adsorbs on its surface. These ions are mainly the H^+ and OH^- present in water. This electric charge on colloidal particles can be readily shown by *electrophoresis* (ė-lĕk'trō-fō-rē'sis), the movement of colloidal particles under the influence of an electric current. This movement is sometimes used in the separation of colloidal materials from water.

How colloidal dispersions are prepared. A colloidal dispersion of a substance may be prepared by bringing about a very fine division of the particles of that substance. This may be accomplished by either of two methods: (1) *peptization*, that is, breaking down coarser particles into a finer state of subdivision, and (2) *condensation* or *coagulation*, that is, building up colloidal particles from single molecules.

The most common methods of peptization are: (a) grinding the material in special mills called *colloid mills*, (b) shaking drops of material with an emulsifying agent (see page 615) until they are broken down to proper size, and (c) passing an electric arc between two metal electrodes under water.

Colloidal fuels, which flow like water, and colloidal paint pigments are prepared commercially by grinding the materials in colloid mills. Mayonnaise, a typical colloid, is made by beating some oil such as

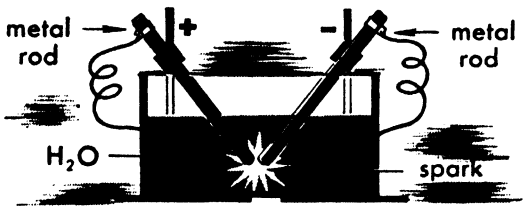


Fig. 122. Producing a colloidal dispersion by passing an electric arc between two metal rods under water.

olive oil in vinegar or lemon juice with egg white or white and yolk which act as the emulsifying agents. Whipped cream is a colloid. Shaving cream is an oil-in-water emulsion and cold cream is a water-in-oil emulsion. Colloidal gold is prepared by passing an electric spark between two gold electrodes under water. "Argyrol," and "neo-silvol," used as antiseptics, contain colloidal silver and a protective colloid.

One example of the preparation of a colloid by coagulation is the preparation of colloidal ferric hydroxide by adding ferric chloride to warm water. The equation is:

$$FeCl_3 + 3H_2O \rightarrow 3HCl + Fe(OH)_3 \text{ (colloidal)}$$

What are sols (suspensoids) and gels (emulsoids)? Although the terminology of colloid chemistry is not yet entirely standardized, we can group all colloidal matter broadly into two classes: (1) *sols,* and (2) *gels.* An egg is a *sol* before, and a *gel* after heating.

The sols (also called *lyophobes,* that is, haters of solution, and *suspensoids*) are not viscous, and are easily precipitated out by electrolytes. Most of them are made artificially and exhibit electrophoresis. They include the colloidal metals, sulfides, and hydroxides.

The gels (also called *lyophiles,* that is, lovers of solution, and *emulsoids*) are viscous, set to a jelly on cooling, and are not much affected by the presence of electrolytes. Gelatin, which is obtained from skins, bones, and the intestines of animals, belongs to this group. As little as five percent of this solid will mix with water and form a thick jelly. Even one percent of *agar-agar* in 99 percent water will form a thick jelly. So-called "canned heat" is a mixture of 85 percent alcohol and 15 percent saturated solution of calcium acetate.

Fruit jellies are made with the aid of *pectin,* present in many fruit juices. Certain kinds of fruits contain little or no pectin and, unless pectin is added, the fruit will not jell (gel).

How colloids may be kept from precipitating. A present classification of colloids is based on stability. *Intrinsic* colloids are stable and include mainly polymers such as rubber, protein, and cellulose. *Extrinsic* colloids are unstable, are usually inorganic dispersions or ordinary insoluble material obtained by subdivision.

Many colloidal particles have a tendency to precipitate gradually. The addition of a small quantity of another substance, called a *protective colloid,* prevents this. For example, Faraday was the first to notice that a sol could be made more stable by the addition of a minute amount of gelatin. The gels act as protective colloids. Thus, in the preparation of mayonnaise, egg albumen (a gel) keeps the oil from coming out of the colloidal state. Mayonnaise should be kept at a temperature between 50°F. and 70°F. Below 50°F. it may freeze and the emulsion will break. The role of the protective colloid is extremely important. Certain body fluids contain proteins which act as protective colloids.

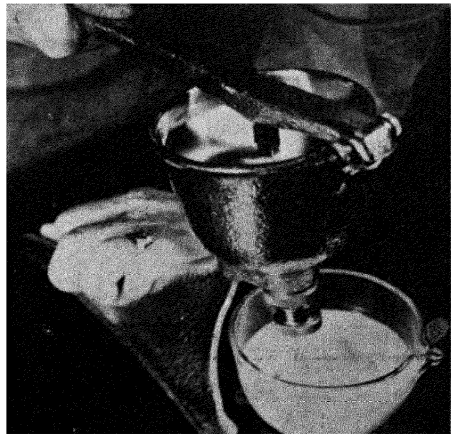
These protective agents are called *emulsifying,* or *peptizing, agents* also. They seem to collect on the surface between the oil and water of emulsions and prevent the oil droplets from running together, or *coalescing,* which would produce precipitation.

Tannic acid, found in straw, tea, and nutgalls, acts as a protective colloid, and its presence explains the colloidal condition of clay particles used in brick-making and other ceramic processes. Acheson used tannic acid to keep graphite in colloidal suspension in water, thus giving us *aquadag,* which is used as a lubricant. *Tar oil* is used to keep coal suspended in petroleum. *Gum arabic* acts as the protective colloid in India ink. *Gelatin* in ice cream prevents the precipitation of the sugar.

How colloids are precipitated. Since a substance in the colloidal state owes its properties to some extent to the fact that it is electrically charged, if these charges are neutralized, the colloid ought to precipitate. This is actually the case. Two oppositely charged colloids, such as ferric hydroxide, $Fe(OH)_3$, and arsenious sulfide, As_2S_3, when brought together, precipitate out of the colloidal state.

It has been found also that the presence of electrolytes (that is, ions) destroys the colloidal condition. This is especially true in the

International Emulsifiers, Inc.



A hand homogenizer for producing emulsions. Pumping the piston forces liquid at a pressure of 600 pounds per square inch through the dispersing nozzle.

case of sols. Thus, the addition of a small amount of salt solution will precipitate a *gold sol*. The great delta of the Mississippi River was formed by the precipitation of colloidal clay by sodium ions from the salt water of the Gulf of Mexico. It is also true that the higher the valence of the ion added, the greater is its power to precipitate colloids. Thus a cupric salt has greater power to destroy a colloid than has a sodium salt.

The precipitation of colloids by neutralizing the electric charge of colloidal particles has been used industrially. The smoke nuisance has been abated, and valuable products which formerly escaped in smoke have been saved by a method of electric precipitation developed by F. G. Cottrell, an American chemist. This method consists of passing the gases, smokes, and vapors from the flues of factories up a strongly electrified metal pipe or stack, which acts as an electrode. Within this pipe a fine wire is suspended. This wire is connected to one side of a source of high-voltage current and the pipe to the other. The gases, smoke, and mist, passing through the pipe, become ionized, and the suspended particles are precipitated upon the smooth interior of the pipe as soon as they lose their charge.

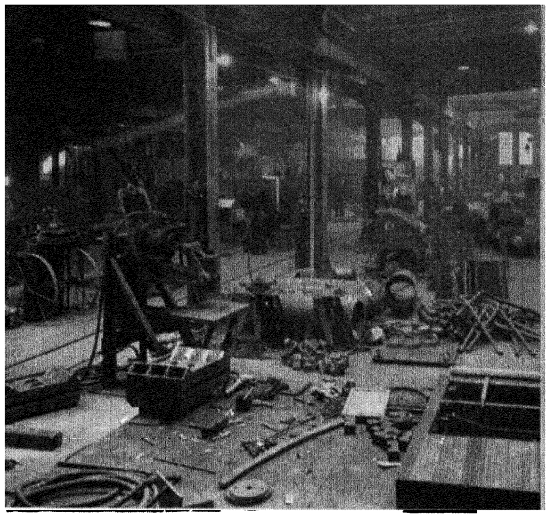
The "Precipitron," a machine that removes dust, pollen, and other particles from air, is used in air conditioning. The "Precipitron" operates on the same principle as the *Cottrell precipitator*.

Acids and alkalies also precipitate colloids. Milk is an emulsion of butterfat in a water solution of milk sugar and certain salts, with casein acting as the protective colloid, or *emulsifier*. In the souring of milk or cream, the milk sugar, under the influence of certain bacteria, changes to lactic acid. This acid precipitates the casein which

Westinghouse Electric Corporation



A view in a metalworking plant showing a heavy concentration of smoke particles.



Westinghouse Electric Corporation

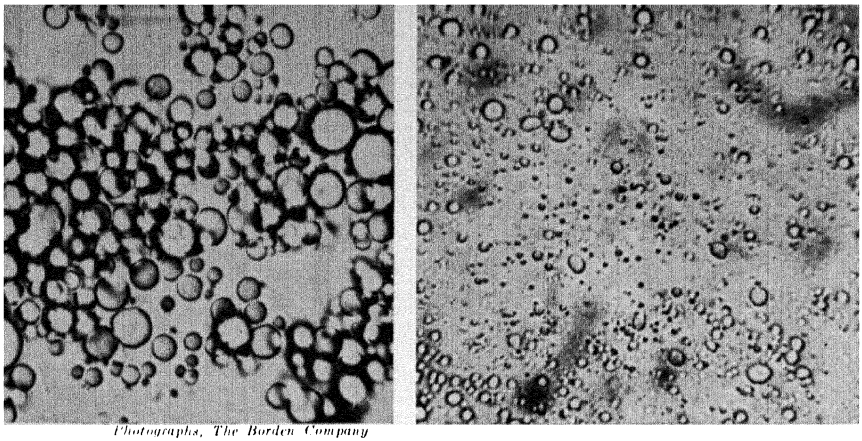
The same plant shown in the photograph on page 616. A "Precipitron" unit has been in operation for 30 minutes.

coagulates into a curd. The emulsion is thus broken, and it is easier to separate the curd containing the butterfat from the whey. We may thus see why it is easier to churn butter (an emulsion of butterfat in water) from sour cream than from sweet cream.

In general, negative suspensions such as clay, As_2O_3, and oil emulsions are precipitated by acids. Rubber is separated from the colloidal rubber *latex* by the addition of acetic acid. It may also be precipitated in an electrolytic cell on an anode mold. Rubber gloves are made this way. Positive suspensions such as albumen, hemoglobin, and $Fe(OH)_3$ are precipitated by alkalies.

Adsorption and the colloidal state. Essentially, the colloidal state is caused by the extreme smallness of the particles. The small size of the particles results in an extremely large total surface area. For example, it has been calculated that a cube only one centimeter on each side would, if ground into a powder of colloidal dimensions, expose a surface equal to 15 acres.

It has been found that the molecules on a surface have a tendency to hold on to molecules of other substances in contact with them. The surface of a solid fairly bristles with energy. Fine particles tend to coat their surfaces with layers of the substances to which they are exposed. This surface phenomenon is a physical property and probably explains adsorption. Irving Langmuir, who has carried on very important research work in this field, believes that the adsorbed substance is only one molecule thick on the adsorbing surface. The ability of animal charcoal to adsorb coloring matter and the ability of activated carbon to adsorb gases are well known. Gasoline is recovered from natural gas in this way.



Photographs, The Borden Company

Photomicrographs of non-homogenized milk (left) and homogenized milk (right). By homogenization, fat globules are reduced in size and spread evenly throughout the milk.

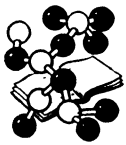
Fuller's earth, which contains about 60 percent silicon dioxide, is used to adsorb impurities in the manufacture of white Vaseline and colorless cottonseed oil. Clay adsorbs many colors. In ore flotation, mentioned in Chapter 28, water is adsorbed by the gangue, and the valuable ore is adsorbed by the oil. Adsorption, fortunately, is a *selective process;* that is, only certain substances will be adsorbed.

Catalysis and the poisoning of catalytic agents are often adsorption phenomena. In industrial processes, the adsorbed substances may be removed by heat and washing, thus permitting the adsorbents to be used almost indefinitely.

The colloidal state is vital. *Colloid chemistry* has been defined as the study of drops, filaments, bubbles, grains, and films. Nature and the arts are filled with examples of colloidal phenomena. The baking of bread, the dyeing of fibers, tanning (the conversion of natural skins into leather), the manufacture of rubber articles and rayon, fertilizing of soil, brewing, ore flotation, the action of detergents, and the purification of water by coagulation, and cooking are only a few of such phenomena. The surfaces of the fine clay particles in the soil are as important to the soil's fertility as the humus. These fine particles concentrate the minerals and other plant nutrients by attracting their ions when water is present. Soluble salts are thus prevented from being washed away. More important than these examples are many of the vital processes of life which depend upon selective adsorption in the body. For example, toxins in the body are adsorbed and made harmless by antitoxins produced in the body.

Protoplasm itself, the physical and chemical basis of life, is colloidal. Theodor Svedberg, Swedish Nobel prize winner in chemistry

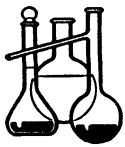
in 1926, said, "The central point in colloids is the particle — like the molecule in chemistry and the cell in biology. The colloid particle possesses the properties of the molecule, and has the complicated properties of the cell. We know that the main part of all living things is built up of colloids." The colloidal nature of living material makes possible the localization of chemical reactions within the body. Without colloids, a hopeless chaos of chemical reactions would result.



YOU WILL ENJOY READING

Weiser, H. B. *Colloid Chemistry* (2nd edition). John Wiley & Sons, Inc., New York, 1949. This is an execellent textbook for college students.

Mills, John. *Electronics: Today and Tomorrow,* pp. 126–139. D. Van Nostrand Co., New York, 1944. The electron microscope and its application to colloids.



USEFUL IDEAS DEVELOPED

1. The colloidal state of matter is caused essentially by matter in a state of subdivision, ranging between the size of molecules (true solution) and size capable of being seen under a microscope (suspension).

2. Some typical properties of matter in the colloidal state are (a) Brownian movement, (b) Tyndall effect, (c) smallness of particle, (d) electric charge.

3. Brownian movement is a peculiar jiggling motion caused by the uneven bombardment of colloidal particles by molecules of the surrounding liquid.

4. The Tyndall effect is the appearance of a cone of light in a colloid when a beam of light is sent through it.

5. Colloids can be separated from crystalloids by ultrafilters and by dialysis. In dialysis the mixture is placed in a parchment bag immersed in water. The crystalloid passes through the parchment and the colloid remains.

6. Colloidal dispersions may be prepared by (1) peptization, and (2) coagulation.

7. Peptization is the breaking down of coarser particles into a finer state of subdivision by grinding, shaking, or passing an electric spark between two pieces of metal under water. Grinding is done in a colloid mill.

8. Coagulation is used in preparing colloidal dispersions by hydrolysis.

9. All colloidal matter may be divided broadly into sols (lyophobes, or suspensoids) and gels (lyophiles, or emulsoids).

10. Colloids may be precipitated by (1) adding a colloid of opposite charge, (2) adding an electrolyte (ions of high valence have greater power than those of low valence), or (3) neutralizing the charge of the colloid by an electric current (Cottrell's process). Acids and alkalies precipitate colloids.

11. Adsorption is a surface phenomenon. The molecules on the surface of a colloidal particle hold on to molecules of foreign material passing over the surface.



USING WHAT YOU HAVE LEARNED

Group A

1. Who is usually considered the father of colloid chemistry?

2. How does the original definition of a colloid differ from that accepted today?

3. How would you separate sugar from a colloidal dispersion of gelatin?

4. What are four characteristics of substances in the colloidal condition?

5. How is Brownian movement explained?

6. There is a difference in the effect produced when a beam of light is passed through a solution of copper sulfate and through a gold sol. Explain.

7. Copy and complete the following statements. Do not write in this book. Colloidal particles can be carefully studied by means of an instrument called the ... invented by ... and ... in ... (date). Colloidal particles are smaller than ... but larger than .... Colloidal particles are larger than ... mm., but smaller than ... mm.

8. How would you show that colloidal particles of $Fe(OH)_3$ are electrically charged?

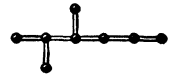
9. Name three negatively and three positively charged colloids.

10. What is electrophoresis?

11. Explain briefly the two methods generally used for preparing colloidal dispersions.

12. How would you prepare a silver sol? Explain.

13. Describe an experiment for preparing a colloid by coagulation.



14. In what two ways do sols differ from gels with respect to their sensitivity to electrolytes?

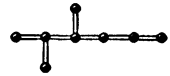
15. Illustrate the difference in viscosity of a sol and a gel.

16. What is an emulsion?

17. (a) What is a protective colloid? (b) Give an example.

18. Why is gum arabic added in the making of ink?

19. Explain the addition of egg albumen in the preparation of mayonnaise. State your answer in terms of a surface phenomenon.



20. Explain how Acheson produced colloidal graphite.

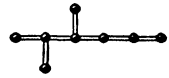
21. What are three methods of precipitating colloids?

22. (a) Which will have greater precipitating effect on a colloid, a solution of KCl or a solution of $CuSO_4$? (b) Explain.

23. What is the principle of Cottrell's process of electric precipitation?

24. What are two important benefits that come from the use of the electric precipitation of smoke, mists, and dusts?

25. Explain why finely divided C will decolorize a sugar solution, but a solid mass of coal will not.



26. (a) Is adsorption a physical or chemical process or both? (b) Explain.

27. Why do we say that adsorption is a *selective* process?

28. What are three industrial uses of adsorption?

29. (a) Is there a difference between adsorption and absorption? (b) Explain.

30. Rivers carrying colloidal particles form deltas when their mouths are in the sea. Deltas are not formed when their mouths are in fresh water. Explain.

31. Clouds have been caused to condense and form rain by sprinkling finely divided silver iodide crystals over them. Explain.

Group B

32. Soap cleanses partly by adsorption. Explain.

33. Is there any relationship between adsorption as a phenomenon of large surface areas and the increase in the speed

of chemical reactions when finely powdered materials are used? Explain.

34. As little as one percent of agar-agar in 99 percent of water will form a jelly. Explain this phenomenon.

35. How do colloidal particles (a) resemble ions and (b) differ from ions?

36. Explain why colloidal particles do not settle by gravitation.

37. Explain why soluble fertilizers thrown upon certain soils are not easily washed away by rains.

38. Suspensions do not exhibit the Brownian movement. Why?

39. Why are eggshells sometimes put in the coffee pot while coffee is being prepared?



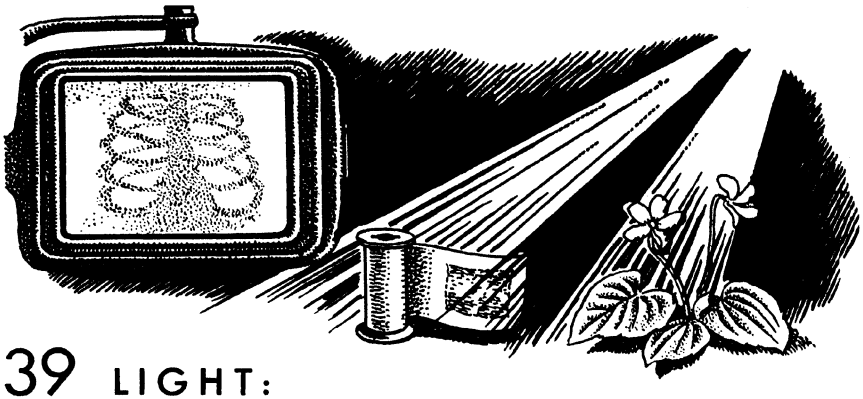
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. For a long time the nomenclature of colloid chemistry was very unstandardized, and a great deal of confusion resulted from reading the literature dealing with colloid researches. Can you give examples in social and economic fields of confusion resulting from the use of vague terms or labels?

2. Report on how you, your sister, or your mother makes jams or jellies. Explain the chemistry of the methods described.

3. Describe how your mother makes whipped cream. Why does not this colloid break down immediately? What is the latest method of making whipped cream? Does the chemistry of this method differ from the chemistry of the method used by your mother?

4. Construct a model of a Cottrell precipitator and describe it to your class.



39 LIGHT: ITS CHEMICAL EFFECTS

The engineer still finds Newton's laws useful though they are inapplicable within the atom or bodies millions of times more massive than the sun or stretches of space that are measured in light-years. . . . A theory does not have to be true, but it must work. And the old theories still work within limits. Waldemar Kaempffert, *The New York Times Book Review,* June 20, 1954

The nature of light. The radiations that we call *heat* and *light* are thought to be wave motion in the ether. The eye is able to interpret as light only those ether waves whose wave lengths are between 0.00004 centimeter and 0.00007 centimeter. The shortest ether waves known are the *cosmic rays;* the longest known ether waves are the *Hertzian,* or *radio, waves.* All ether waves are electromagnetic in character. Table 17 shows the electromagnetic spectrum.

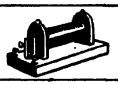
This *wave theory of light* has not been accepted by all scientists. Newton, himself, in 1675 thought light to be made up of minute particles, or *corpuscles,* of matter (*corpuscular theory*). Lately, the corpuscular theory has again received very serious attention.

Max Planck, who postulated that all radiation, like matter, is atomic in structure, called a unit of radiation the *quantum.* In the field of light, the quantum is also called the *photon,* or unit of light. Its mass is believed to be only about 1/200,000 of an electron. It has been estimated that the sun is losing mass as radiated energy at the rate of four million tons a second!

Light produces chemical changes. The chemical manufacture of starch from carbon dioxide and water plants (photosynthesis) has

TABLE 17. ELECTROMAGNETIC SPECTRUM

By studying this chart, you can gain a clear picture of the electromagnetic spectrum. The wavelength, frequency, and source of each type of ray are given

Wavelength in cm. and frequency in cycles	KIND OF RADIATION	HOW OR WHERE EMITTED	
500,000,000 cm.			
60,000 cm. (600 meters) 1,500,000 cycles 20,000 cm. (200 meters) 500,000 cycles	Radio broadcasting range		Radio tube
0.02 cm. 1,500,000,000,000 cycles	Short-wave radio waves		Induction coil
0.000,08 cm. 375,000,000,000,000 cycles	Infrared rays		Heated flatiron
0.000,04 cm. 750,000,000,000,000 cycles	Visible-light rays		Electric lamp
0.000,001 cm. 30,000,000,000,000,000 cycles	Ultraviolet rays		Ultraviolet lamp
0.000,000,01 cm. (1Å) 3,000,000,000,000,000,000 cycles	X-rays		Coolidge X-ray tube
0.000,000,000,75 cm. 40,000,000,000,000,000,000 cycles	Gamma rays		Radium dial
0.000,000,000,000,1 cm. 300,000,000,000,000,000,000,000 cycles	Cosmic rays		Cyclotron

already been discussed, as has the decomposition of hydrogen peroxide into water and oxygen in the presence of light. A mixture of hydrogen and chlorine, when exposed to light, changes with explosive violence to hydrogen chloride. The chemical effect of light on ferric ammonium citrate, which is changed to a ferrous compound, was discussed in Chapter 32. For centuries cotton and linen fabrics have been bleached, that is, chemically changed, by the action of sunlight (grass-bleaching). Photography based upon the effect of light upon certain silver salts has been practiced for over a century. These, and many more illustrations which could be cited, demonstrate light is an important factor in certain chemical changes.

How light produces chemical changes. *Photoelectric effect.* In 1888 Hertz found that light falling on a metal causes the metal to become positively charged. This charge was later shown to be caused by the emission of electrons from the metal. The *photoelectric cell* that is used in television and in countless industrial processes acts as it does because the rays of light strike a coating of potassium, cesium, or rubidium inside the glass bulb, and the emission of electrons from the potassium, cesium, or rubidium sets up a flow of electrons, or an electric current. Light, therefore, ionizes certain elements.

Photochemical effect. The ionization of certain elements and compounds by light explains how light produces chemical changes, since most chemical changes are reactions between ions. Light has the power both to excite molecules and to decompose them. This power of light causes the chemical change in certain compounds. The amount of change is proportional to the product of the intensity of light and the duration of illumination. According to Einstein, each molecule absorbs one quantum of energy in a chemical change caused by light.

Since the real nature of light is still in doubt, the photoelectric effect and the photochemical effect have not yet been fully explained. Nevertheless, both effects are widely utilized in industry.

The chemistry of silver photography. Familiar to most of us is the chemical change produced by light in the coating of photographic film.

As we have said, silver chloride is sensitive to the action of light. In fact, all the silver halides — silver chloride, silver bromide, and silver iodide — undergo a change in chemical composition and color when exposed to light. On this sensitivity of the silver halides to light, photography is based. The five steps in the process of silver photography are:

1) *Preparing the sensitive film.* Silver bromide, AgBr, and a small amount of silver iodide, AgI, are precipitated in gelatin as tiny crystals. This emulsion is spread as a very thin layer on a plate of glass, a sheet of paper, or a transparent film made of cellulose acetate. The gelatin acts as a protective colloid and prevents the silver salt crystals from separating out of the emulsion. The silver bromide and silver iodide are light-sensitive chemicals, and a trace of impurity in the gelatin acts as a catalyst. Most camera films are covered completely with black paper to shut out light, thus making them suitable for daylight loading.

2) *Exposing the film.* The sensitized film is placed in the back of the camera. Light reflected from the object being photographed

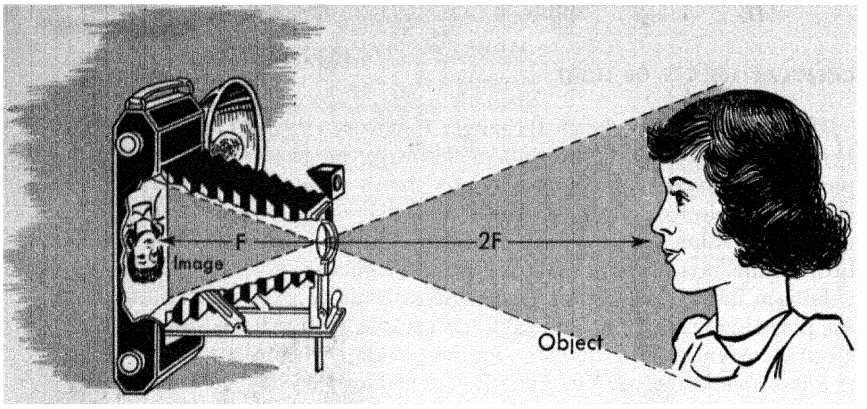


Fig. 123. Principle of the camera. Why is the image upside down?

passes through an opening in the front of the camera and falls upon this film for a short period of time. Since the intensity of light varies according to the lights and shadows on the object, the intensity of the light that strikes the film varies also. Wherever light strikes the emulsion, some chemical change eventually takes place. The greater the intensity of the light, the more marked the change.

The chemical change may be represented simply as follows:

$$AgBr \rightarrow Ag + Br$$

The silver formed is in a finely divided (colloidal) state. Because colloidal silver is black, a black mark is left after development wherever the light has struck the film. The silver bromide that has not been struck by the light remains unchanged. The free bromine formed is probably taken up by the gelatin. Thus an image is formed on the film.

3) *Developing the film.* If the sensitized film is exposed to light too long, all the silver bromide is, upon development, changed to black silver. Such a picture is *overexposed.*

To continue the action of the light and yet prevent overexposing, the film is developed in a darkroom by means of certain chemicals called *developers.* The sodium salts of pyrogallol (*pyro*) and *metol* are selective reducing agents which confine their action solely to the silver salts that have been exposed (the *latent image*). The unexposed surface of the film remains unaffected. Sodium carbonate is added to pyrogallol, metol, and other substances (1) to produce their sodium salts (developers), and (2) to cause the gelatin to swell and thus permit the developer to reach the silver bromide embedded therein.

Developers continue the decomposition of the silver bromide wherever the light has reached it. Those places reached by strong

light become very black. By examining the film in the developing bath, a photographer can watch the picture appear, and thus know when to remove the film from the developing solution. However, by properly timing the development, most commercial photographers dispense with observing the chemical action.

4) *Fixing the film.* After the film is developed, the image appears as a pattern of deep black, white, and various shades of gray. If the film is exposed to light at this stage, the unattacked silver bromide will darken. To *fix* the film, that is, to make the image permanent so that it will no longer be affected by light, any remaining silver bromide on the film must be removed. This is accomplished by immersing the film in a suitable solvent, usually sodium thiosulfate (hypo) solution. All the remaining silver salts are thus dissolved and later washed away together with the hypo in running water.

5) *Making the print.* The developed film is now called the *negative* because the picture is the reverse of the object photographed with respect to light and dark areas. To reverse this pattern and give a picture that resembles the object photographed, a positive *print* is prepared from the negative by superimposing the negative upon a sensitized film. Light is allowed to strike this negative. The part of the negative that is black does not allow the light to pass through it, and hence the silver salt under it does not undergo decomposition. The areas of light and shade are thus reversed. This print, of course, must also be developed and fixed.

Some other chemical reactions in silver photography. Additional chemical processes have been devised to improve the quality of the finished picture. These include:

1) *Toning.* To improve the color of a print, the colloidal silver may be replaced by silver sulfide, which varies in color from light brown to black. This chemical process is called *toning.* Salts of other metals, such as gold, copper, uranium, and iron, may be used instead of silver sulfide. In the sulfide process, which gives a *sepia,* or brown, finish, sulfur combines with the silver directly, forming silver sulfide.

$$2Ag + S \rightarrow Ag_2S$$

The sulfur is obtained by the reaction of hypo, $Na_2S_2O_3$, and potassium alum, $KAl(SO_4)_2$.

2) *Reduction.* When a negative is too dark, because of *overdeveloping* or *overexposure,* the darkness can be lessened, or reduced, by changing some of the dark insoluble silver on the negative to a soluble silver salt, which can be washed away in water. This can be done by treating the negative with a *reducer,* a solution of potassium

permanganate and sulfuric acid. As a result, the silver is oxidized and silver sulfate is formed.

$$2KMnO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$$
$$2Ag + H_2SO_4 + O \rightarrow Ag_2SO_4 + H_2O$$

In this reaction the valence of silver is changed from zero to plus one. In other words, an electron is removed from the silver. The reaction is therefore really an oxidation. However, it has unfortunately been named a reduction. Why?

3) *Intensification.* Exposure for too short a time, that is, *underexposure,* may produce a negative that is too light. To correct this, it is possible to deposit some other metal on the weak silver deposits. Usually, a chromium or mercury compound is deposited upon the image. The mercury intensifier consists of a solution of mercuric chloride, $HgCl_2$. The following reaction takes place.

$$Ag + HgCl_2 \rightarrow AgCl + HgCl$$

The underexposed intensified negative is then developed.

The story of silver photography. Scheele was among the earliest investigators to notice the effect of light on silver salts. The first permanent paper photograph made with silver chloride was the work of Niepce (nyĕps), a French scientist, in 1822. Seven years later, Daguerre (dà-gâr′), a leading scene painter for the Paris stage, made *daguerreotypes* by exposing silver iodide on a plate to light and then bringing out the image with mercury vapor. Following the lead of Sir John Herschel, he used hypo to fix the image. Niepce and Daguerre formed a partnership.

More than 20 years passed before collodion was introduced as a base on which the sensitive silver salt was deposited for photographic film. Another 20 years went by before the gelatin emulsion plate began to be used. The roll-film was not invented until 1884, and the following year a young bank clerk of Rochester, New York, George Eastman, of "Kodak" fame, patented a machine for continuous coating of rolls of photographic paper.

The earliest films were sensitive only to blue light. Then came the *chrome* films, which are fairly sensitive to all colors except red. These films can be developed in the presence of a red *safelight. Panchromatic* film is sensitive to all colors, including red. Hence it must be handled in total darkness. Sometimes it is necessary to cut out the violet and ultraviolet rays to get a more natural appearing picture. They may be cut out by using a *filter,* a small piece of colored glass (usually pale yellow), over the lens of the camera.

A recent development in rapid, low-cost, *nonsilver photography* makes use of a mixture of *diazo* compounds which are light-sensitive. The image is developed and fixed by passing ammonia gas over the cellophane film containing the sound track. This is done in subdued light, and the ammonia causes the formation of a dye. The result is a positive print.

Infrared photography is used for distant landscapes which are rendered invisible by atmospheric haze. Special infrared-sensitive plates are also affected by the invisible heat rays given off, for example, by a heated electric iron in a dark room.

Color photography. The chemistry of color photography is much more complex than that of black-and-white photography. As you know, there are three *primary colors:* red, blue, and green. By combining these three colors, or by slight modifications of them, it is possible to produce most of the colors to which the eye is sensitive. For example, yellow and blue *light* produce white light. Mixing paints or pigments is altogether different. Yellow and blue *paints* make a green paint.

Since both color prints and color transparencies require three separate colors, the films on which they are made must contain three very thin separate emulsions, each sensitive to a particular color, and two very thin filters, instead of a single emulsion, as in black-and-white photography. The lowest emulsion, that is, the emulsion next to the film base, is sensitive mainly to red light. On top of this emulsion is a layer of clear gelatin. Next is an emulsion that is sensitive chiefly to green light. On top of this is a layer of yellow gelatin, which acts as a filter. On top of this yellow gelatin is an emulsion that is sensitive chiefly to blue light. The bottom surface of the film is coated black to prevent reflection of light.

When light from an object being photographed is focused on a film, the blue light is absorbed and recorded in the top emulsion. Because of the yellow filter, no blue light passes on to the middle emulsion; only red light and green light are transmitted. Green light is absorbed and recorded in the middle emulsion and red light in the bottom emulsion. The developed film contains a series of full-color pictures, which, when viewed against light or projected on a screen, blend together, producing different hues of the original scene.

How x-rays may be used in photography. The light that affects our vision is made up of light waves of between 80,000 and 40,000 to the inch. Radiations of even shorter wave length also affect sensitive silver bromide. X-rays, for example, have much shorter wave lengths than visible light. Also, they have great penetrating power.

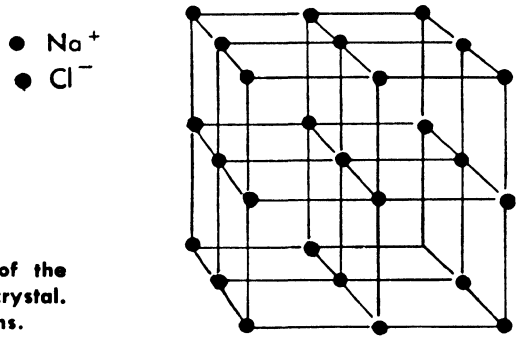


Fig. 124. Modern conception of the structure of the sodium chloride crystal. Note the arrangement of the ions.

X-rays are used in photographing the inside of solid objects. After passing through a solid object, the x-rays strike an ordinary sensitized film and decompose the silver bromide with greater or less intensity, depending upon the amount of the rays that have managed to pass through the solid object in front of the film. The film is then developed and fixed in the same way as an ordinary picture.

X-ray photography is used in detecting the internal structure of steel (see Chapter 27). It is used also in dentistry, medicine, and surgery. For example, when the stomach or intestines are to be examined, the patient takes some barium sulfate, $BaSO_4$, internally. This salt coats the internal organs, and, since barium sulfate is more impervious to x-rays than the stomach or intestines, a fairly clear outline of these organs appears on the photographic plate.

Diseases such as tuberculosis can also be detected by x-ray. *Lipiodol* is a harmless oil containing iodine. A little of it is allowed to trickle into the lung and air cavities, which then show up quite clearly in a radiograph of the chest.

A *fluoroscope* is a device consisting of a screen coated with a chemical such as barium platinocyanide which glows, or fluoresces, when x-rays strike it. When such a device is placed on one side of a patient and an x-ray machine is operating on the other side, the bones are shown on the screen, and the physician can make a preliminary examination of the patient. The x-rays used in photography or in the fluoroscope are obtained generally from a Crookes' (x-ray) tube.

How x-rays may be used in determining crystal structure. X-ray photography has been of great service to the scientist in finding out the structure of crystals. It had long been known that if parallel lines are scratched very close together on a plate of glass, and a beam of light is directed against this grating, the light is broken up and a spectrum is formed, from which the wave length of the light can be

determined. Scientists tried to apply this method to x-rays in order to find the length of the wave, but they found it impossible to draw parallel lines close enough together.

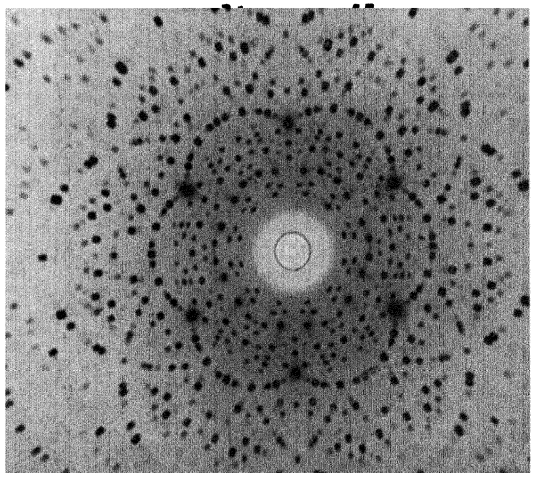
It occurred to Max von Laue (fŏn lou'ĕ), in 1913, that perhaps a crystal, which many people believed was an arrangement of atoms in orderly rows, could be used as a grating. Consequently he directed a narrow beam of x-rays through a crystal of zinc sulfide to a photographic plate of silver bromide, and found that he could get a picture of the beam as a central spot, surrounded by a series of fainter spots distributed in a symmetrical pattern. From this picture he was able to determine the wave length of the x-ray.

This photographic method is known as the *x-ray diffraction method*. X-ray fingerprints of hundreds of compounds have already been made. The method works in two ways. If the structure of the crystal is known, the wave length of the x-ray can be determined. If the wave length of the x-ray is known, the structure of the crystal can be determined. In other words, from the x-ray picture of a crystal, a scientist can determine the position of the ions in the crystal. It has been found that crystals of polar compounds are made up not of groups of molecules, as was supposed, but of ions (or atoms) arranged in a definite pattern. The distance between ions is about one twenty-millionth of an inch.

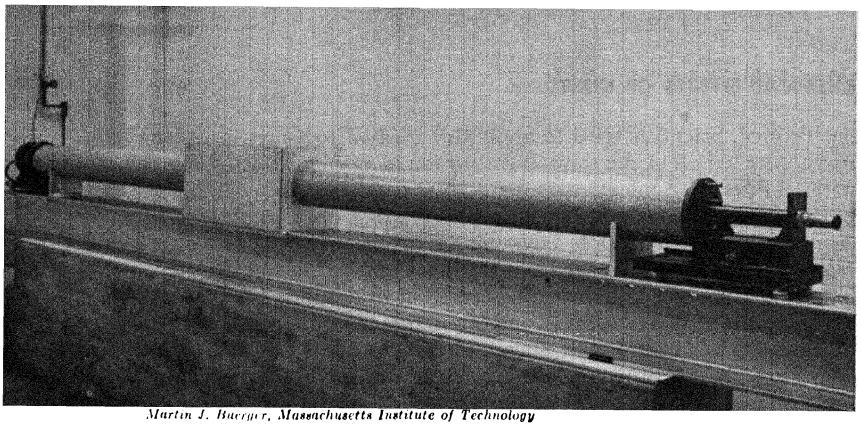
Sir William H. Bragg and his son, working at Leeds, England, did some brilliant pioneer work in this field. They found that the ions in a crystal of table salt are arranged in a definite pattern, as shown in Fig. 124. When this *ion-molecule* of NaCl dissolves in water, its ions separate and dissociation is said to have taken place.

The crystals of nonpolar compounds, on the other hand, show a different structure. Thus ferric oxide and organic substances seem to be made up of electrically neutral molecules and not ions. Hence,

Eastman Kodak Company



The x-ray diffraction pattern of beryllium aluminum silicate. An x-ray diffraction pattern does not look at all like the crystalline structure from which it was produced. It does, however, tell scientists the nature of the crystal.



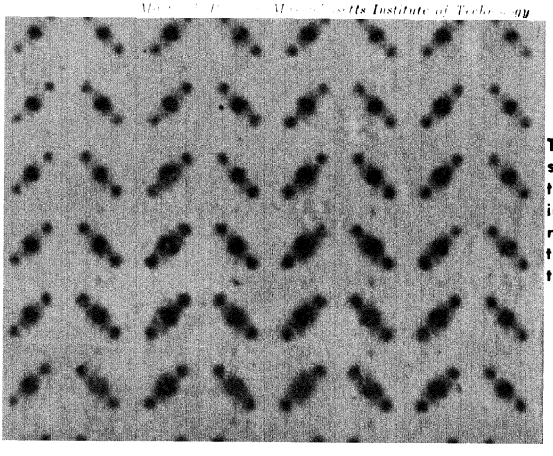
Martin J. Buerger, Massachusetts Institute of Technology

This experimental instrument for studying crystal structure makes use of both x-ray diffraction and magnification by an optical microscope.

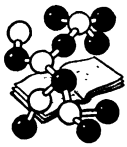
when they go into solution, dissociation does not take place. They are nonelectrolytes. This fits in perfectly with Arrhenius' theory of electrolytic dissociation (see pages 232–233). This important research earned for the Braggs the Nobel prize in physics in 1915.

By developing the Bragg method, scientists of the Kodak Research Laboratories have taken pictures of complex molecules, which look very much like the drawings and models made from theory.

The future of chemistry. Between the fanatical search of the old alchemists for gold and the elixir of life, and the far-reaching effects of the conquest of nuclear energy, as well as the uses of chemical research in modern industry, stretches a vast, fascinating land. The world of chemistry that remains unexplored is even more alluring. The age of nuclear energy is upon us, and to its possibilities and to the dominion of chemistry there is no end. In man's universal use of the rich fruits of scientific discovery lies hope for the happiness of all mankind. Here is a goal worthy of all our efforts!



This photograph, made with the instrument appearing above, shows the actual structure of a crystal of iron pyrites, FeS_2, magnified 2.2 million times. The larger spots are the atoms of iron; the smaller are the atoms of sulfur.



YOU WILL ENJOY READING

Eastman Kodak Co., Rochester, N. Y. *Elementary Photographic Chemistry,* 1951. This book was written in response to the demand for a simple account of photographic chemistry for the practical photographer.

Hawley, Gessner G. *Seeing the Invisible.* Alfred A. Knopf, New York, 1945. This is a beautifully illustrated description of the electron microscope, a valuable tool of research.



USEFUL IDEAS DEVELOPED

1. Light is thought to be a wave motion in the ether, the various colors of light being caused by differences in wavelength.

2. A unit particle of energy is called a *quantum.* The unit of light energy is called a *photon.* The mass of a photon is about 1/200,000 of an electron.

3. Some chemical changes produced by light are: photosynthesis, decomposition of H_2O_2, the union of Cl_2 and H_2, the reduction of ferric ammonium citrate to a ferrous compound, the bleaching of fabrics by the sun, and silver photography.

4. When light falls on a plate coated with potassium, cesium, or rubidium, electrons are emitted. This phenomenon, called the *photoelectric effect,* is used in the photoelectric cell.

5. Light excites molecules and decomposes them. The energy absorbed produces the *photochemical effect.*

6. Radiation which affects our vision is made up of light waves ranging between 80,000 and 40,000 to the inch. X-rays have much shorter wave lengths and greater penetrating power.

7. In x-ray photography, the ordinary sensitized silver bromide film is placed behind the object to be photographed. The film, after exposure, is developed and fixed in the usual way. X-ray photography is used in dentistry, medicine, surgery, metallurgy, and engineering.

8. When x-rays are passed through or reflected from a crystal, the layers of atoms of the crystal act like a grating (fine lines drawn close together) and a spectrum is produced. This x-ray spectrum is photographed, and from this the scientist can determine the distances between the atoms. It has been found that crystals of polar compounds are built up not of molecules but of ions.

9. Crystals of nonpolar compounds seem to be made up of molecules and not ions. Hence they do not dissociate in solution.



USING WHAT YOU HAVE LEARNED

Group A

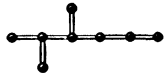
1. In what way does visible light both resemble and differ from x-rays?

2. What are three important chemical changes produced by light?

3. What is the photoelectric effect?

4. What are the five steps in the making of a silver print?

5. Describe the preparation of the sensitive film used in photography.



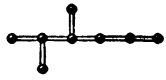
6. Write an equation for the effect of exposing a sensitized film to light.

7. What is the purpose of developing a film?

8. What is a negative?

9. Describe the process of *fixing* in photography.

10. How is the print prepared from the negative?



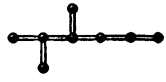
11. What are the advantages and disadvantages of panchromatic film?

12. (a) What is the purpose of *toning*? (b) What is its chemistry?

13. (a) When and (b) by whom was the first permanent paper silver print made?

14. What weight of Ag is needed in preparing a ton of AgBr?

15. Determine the percentage composition of hypo.



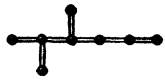
16. How would you treat a film that has been overdeveloped?

17. How could you correct a film that has been underdeveloped?

18. What is the purpose of adding washing soda to the developer?

19. What is the function of gelatin on a sensitized film?

20. How does the sensitized film used in color photography differ from that used in black-and-white silver photography? Explain.



21. What are the chief uses of x-ray photography?

22. (a) How does x-ray photography differ from ordinary silver photography? (b) What is a fluoroscope?

23. Who did the pioneer work in the structure of crystals?

24. (a) What is a grating? (b) How is it made? (c) How is it used? (d) How does a crystal resemble a grating?

25. Is a crystal made up of groups of molecules or groups of ions?

26. Make a diagram of a crystal of NaCl showing the relative position of the ions.

Group B

27. Describe (a) the construction, (b) operation, and (c) a use of a photoelectric cell.

28. How does light produce a chemical change?

29. Why does a photographic "proof" fade?

30. What is the complete electromagnetic spectrum?

31. Describe the x-ray diffraction method of photography.



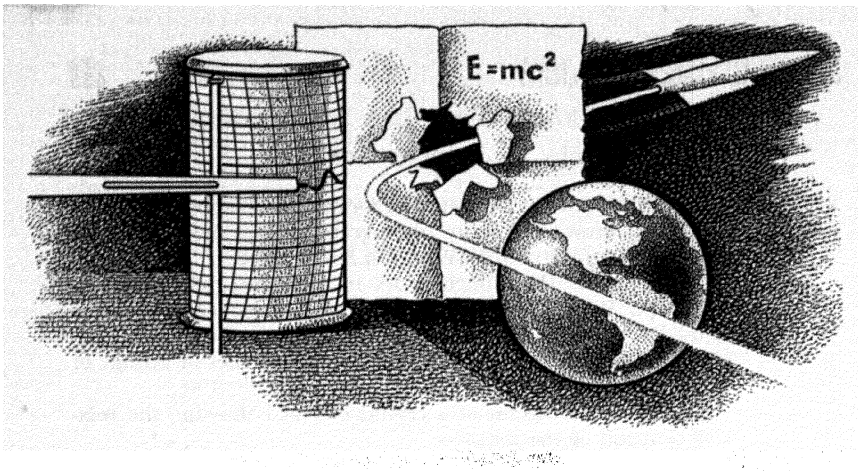
PROJECTS, ACTIVITIES, AND INVESTIGATIONS

1. All industrial applications of the x-ray machine came as the result of scientific research conducted not for any practical objective, but rather as a part of the search for truth. Can you give two similar examples?

2. Write a report on the present paradox of the nature of light, pointing out how light behaves as a wave motion and also as minute particles of matter.

3. Demonstrate in class the various steps in the making of a photographic print. Carry on a verbal description of what you are doing as you carry out the various steps.

4. Visit your dentist or doctor and ask him to let you examine his x-ray equipment. Report to class on what you have learned.



40 MORE CALCULATIONS

. . . Number may be said to rule the whole world of quantity, and the four rules of arithmetic may be regarded as the complete equipment of the mathematician. James Clerk Maxwell, 1831–1879

In addition to the three types of chemical problems discussed in Chapters 9 and 19, there are two other types which deal with the determination of the formula of a compound. In your work in chemistry, you may need to know also how to convert thermometer readings from one scale to another, and how to reduce gas measurements to standard conditions of temperature and pressure. To help you solve problems of these types, a brief discussion of them is included.

TYPES OF PROBLEMS

TYPE FOUR: TO DETERMINE THE SIMPLEST FORMULA OF A COMPOUND FROM ITS PERCENTAGE POSITION

According to the law of definite proportions, elements always combine in the same ratios to form compounds. This knowledge enables us to write the *simplest formula* of a compound when we know the relative amounts, or percentages, of each of its elements. The percentage composition is determined by laboratory analysis of the compound.

EXAMPLE: Find the simplest formula of a compound that contains 63.6 percent nitrogen and 36.4 percent oxygen.

Procedure.

1. Divide the percentage of each element by its atomic weight.

$$\frac{\text{Percentage of N}}{\text{Atomic weight of N}} = \frac{63.6}{14} = 4.54$$

$$\frac{\text{Percentage of O}}{\text{Atomic weight of O}} = \frac{36.4}{16} = 2.28$$

2. Divide the quotients from step (1) by their highest common factor. The highest common factor (H.C.F.) of two or more numbers is the largest number by which each of the numbers is divisible. The quotients from step (1) may not always be *exactly* divisible by the H.C.F., but the answers may be rounded off to the nearest whole number. The H.C.F. of 4.54 and 2.28 is 2.28. Each quotient is therefore divided thus:

$$\text{For nitrogen } \frac{4.54}{2.28} = 1.99, \text{ which is rounded off to } 2$$

$$\text{For oxygen } \frac{2.28}{2.28} = 1$$

3. The numbers obtained in step (2) represent the smallest number of atoms of each element that can be present in one molecule of the compound. Therefore, used as subscripts for the symbols of their respective elements, they give the *simplest formula* of the compound:

$$N_2O$$

Problems of this type can be checked by finding the percentage composition of the formula that is determined. This percentage composition should, of course, agree with the data given in the problem.

PRACTICE WORK ON PROBLEMS OF TYPE 4

1. Calculate the simplest formula of a compound containing 7.7 percent hydrogen and 92.3 percent carbon.

2. An oxide of barium contains 81 percent barium and 19 percent oxygen. What is the formula of this compound?

3. Acetic acid contains 40 percent carbon, 6.67 percent hydrogen, and 53.3 percent oxygen. Find its simplest formula.

4. Analysis of 100 parts of an oxide of manganese shows the presence of 63.2 parts of manganese and 36.8 parts of oxygen. Find its formula.

5. A compound contains one percent hydrogen, 11.98 percent carbon, 47.96 percent oxygen, and 39.06 percent potassium. Find its formula.

6. 70 g. of nitrogen unite completely with hydrogen, forming 85 g. of ammonia. What is the simplest formula of ammonia?

7. 168 lb. of iron were oxidized to 240 lb. of iron oxide. Find the simplest formula of this oxide.

The true formula of a compound. The simplest formula is not necessarily the *true formula,* or *molecular formula,* of a compound; that is, it may not show the actual composition of one molecule of the compound. In many cases, the simplest formula merely shows the ratio of the atoms of the various elements in a compound, not their actual number. Since we cannot tell the actual number of atoms of each element without further information, we write the subscript x after the simplest formula in order to indicate the true formula.

Thus in the example above, the simplest formula, N_2O, tells us that in the compound, the nitrogen atoms outnumber the oxygen atoms two to one. However, this same ratio would exist if the formula were N_4O_2, N_6O_3, or N_8O_4. We cannot tell which of these combinations is the true formula. Therefore, we represent the true formula by $(N_2O)_x$, where the subscript x stands for any number.

In the case of solid compounds, the simplest formula is usually, although not always, the same as the true formula. In general, however, the simplest formula differs from the true formula. Given certain experimental data, the true formula may be determined from the simplest formula.

TYPE 5A: TO FIND THE TRUE FORMULA OF A COMPOUND WHEN ITS VAPOR DENSITY IS KNOWN

The true formula of a gas or a compound which vaporizes without decomposition may be found if both the percentage composition and *vapor density* are known. Like the percentage composition, the vapor density must be determined experimentally by methods such as those described on page 642.

The vapor density (V.D.) of a gas is the ratio of the weight of a certain volume of the gas to an equal volume of hydrogen under standard conditions of temperature and pressure.

Since the weight of one liter of hydrogen is 0.09 gram, the following formula applies:

$$\text{V.D.} = \frac{\text{weight in grams of 1 liter of the gas}}{0.09}$$

It has been determined experimentally that the vapor density of a gas is always equal to half its molecular weight, that is:

$$\text{Molecular weight} = 2\text{V.D.}$$

EXAMPLE: Find the true formula of a compound that contains 63.6 percent nitrogen and 36.4 percent oxygen, and whose vapor density is 21.9.

Procedure.

1. Determine the simplest formula of the compound. In this instance we know it to be:

$$N_2O$$

2. Determine the molecular weight of the simplest formula.

$$\begin{matrix} N_2 & O \\ 2(14) & + 16 = 44 \end{matrix}$$

3. Using the vapor density of the compound, find the *true* molecular weight.

$$\text{mol. wt.} = 2\text{V.D.}$$
$$\text{mol. wt.} = 2(21.9) = 43.8$$

4. Compare the *true* molecular weight and the molecular weight based on the simplest formula, in this instance 44 and 43.8. Since they are approximately the same, we know that the simplest formula, N_2O, is also the true formula. If the true molecular weight had been a multiple of the molecular weight of the simplest formula (that is x times it), we should have multiplied the simplest formula by this number x to get the true formula.

In writing the formula of a compound, group together those elements which form radicals. Thus a compound whose composition shows one atom of K, one atom of N, and three atoms of O is written KNO_3, since NO_3 is a radical.

PRACTICE WORK ON PROBLEMS OF TYPE 5A

1. The vapor density of a compound is 38.8. It contains carbon and hydrogen in the proportions of 92.3 percent and 7.7 percent, respectively. Find the true formula of this compound.

2. A compound contains 27.4 percent carbon and 72.6 percent oxygen. Its vapor density is 21.9. What is its true formula?

3. A compound contains 96.7 percent iodine, 3.05 percent carbon, and 0.25 percent hydrogen. Its vapor density is 197. Find its true formula.

4. A compound is made up of equal weights of sulfur and oxygen. Its vapor density is found to be 31.9. What is its true formula?

5. Carbon, hydrogen, and oxygen unite in the ratio, by weight, of 39.9 percent, 6.7 percent, and 53.4 percent, respectively. The vapor density of the resulting compound is 30.5. Determine its true formula.

6. A compound was vaporized and its vapor density was found to be 76.9. It contained 22.7 percent phosphorus, 10.9 percent oxygen, and 66.4 percent chlorine. Find the true formula of this compound.

TYPE 5B: TO FIND THE TRUE FORMULA OF A COMPOUND WHEN ITS VAPOR DENSITY MUST BE DETERMINED

In solving probems of this type, we first find the simplest formula. Then the vapor density of the gas is determined from data which have been obtained by experiment. Finally, the steps outlined for problems of Type 5A are followed.

EXAMPLE: What is the true formula of a compound that contains 92.3 percent carbon and 7.7 percent hydrogen, if 2.2 g. of its vapor occupy 628 ml. at standard conditions?

Procedure.

1. Find the simplest formula of the compound.

a) Divide the percentage of each element by its atomic weight.

$$\frac{\text{Percentage of carbon}}{\text{Atomic weight of carbon}} = \frac{92.3}{12} = 7.69$$

$$\frac{\text{Percentage of hydrogen}}{\text{Atomic weight of hydrogen}} = \frac{7.7}{1} = 7.7$$

b) The highest common factor by which we may divide each quotient is 7.7. Perform the division.

$$\text{For carbon } \frac{7.69}{7.7} = 1$$

$$\text{For hydrogen } \frac{7.7}{7.7} = 1$$

c) The smallest number of atoms of each element which can be present in a molecule of the compound is in each case one. Therefore, the simplest formula of the compound is:

$$CH$$

2. Determine the molecular weight of the simplest formula.

C H

12 + 1 = 13, the mol. wt. of the simplest formula.

3. We have learned that:

$$\text{V.D.} = \frac{\text{weight in grams of 1 l. of the gas}}{0.09}$$

Using this formula, determine the vapor density of the compound.

a) We are told that 628 ml. weigh 2.2 grams. Therefore 1 liter (1000 ml.) will weigh:

$$\frac{1000}{628} \times 2.2 = 3.5 \text{ g., weight of 1 liter}$$

b) Substitute the weight of one liter of the gas in the vapor density formula:

$$\text{V.D.} = \frac{3.5}{0.09} = 38.9$$

4. Since mol. wt. = 2V.D., the true molecular weight of the compound is 77.8. This true molecular weight is approximately six times as great as 13, the molecular weight based on the simplest formula. Therefore, the true formula is $(CH)_6$ or, more properly, C_6H_6 (benzene).

PRACTICE WORK ON PROBLEMS OF TYPE 5B

1. 500 ml. of SO_2 gas weigh 1.44 g. Find (a) the weight of 1 l., (b) the vapor density, and (c) the molecular weight of this gas.

2. The vapor density of HCl gas is 18.25. (a) What is the weight of 1 l. of this gas? (b) What is its molecular weight?

3. NH_3 has a vapor density of 8.5. (a) Find its molecular weight, and (b) the weight of 500 ml. of this gas.

4. 1 l. of a gas weighed 1.98 g. and contained 27.27 percent carbon and 72.73 percent oxygen. What is the true formula of this compound?

5. A compound contains 94.1 percent sulfur and 5.9 percent hydrogen. 100 ml. of the substance weighs 0.154 g. Determine its true formula.

6. A compound is made up of 25.93 percent nitrogen and 74.07 percent oxygen. 0.097 g. of this gas occupy 20 ml. under standard conditions. What is its true formula?

7. 500 ml. of the vapor of a compound weighed 3.1 g. It contained 22.6 percent phosphorus and 77.4 percent chlorine. Find its true formula.

8. Find the true formula of a compound containing 42 percent chlorine, 1.2 percent hydrogen, and 56.8 percent oxygen. 250 ml. of this vapor weigh 0.94 g.

9. Find the true formula of a gas containing 30.4 percent nitrogen and the rest oxygen. 1 l. of this gas weighs 2.06 g.

How the molecular weight of a compound is determined experimentally. 1) *When the substance may exist as a vapor.* Avogadro's law makes it possible to find the molecular weights of such substances. Using this law, we have learned that the weight of 22.4 liters of any vapor under standard conditions* equals the gram-molecular weight of the compound. Hence, by weighing 22.4 liters, or some convenient fraction of this volume, of vapor, we can determine the molecular weight of the compound. Both the Dumas and the Victor Meyer methods are based on this law.

2) *When the substance cannot be changed to a vapor.* It is apparent that the molecular weight of substances which cannot be changed into gaseous form cannot be determined by the method just explained. However, in our discussion of solutions, we learned that solutes alter the freezing point and boiling point of solvents. The addition of a *definite weight of solute* to a solution raises the boiling point and lowers the freezing point of the solution a definite number of degrees. Thus, the addition of one gram-molecular weight of sugar, 342 grams, raises the boiling point of one liter of water from 100°C. to 100.52°C., and lowers its freezing point from 0°C.

* Standard conditions of temperature and pressure: Temperature = 0°C. Pressure = 760 mm. barometer reading.

to — 1.87°C. From these facts, formulas have been derived which enable us to find the molecular weights of such substances.

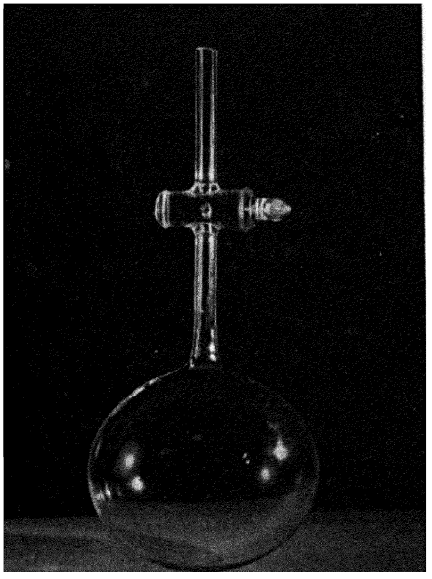
How the atomic weight of an element may be determined experimentally. A) *When the element occurs in gaseous compounds.* This method involves four distinct steps: (1) The molecular weights of a number of gaseous compounds containing an element are determined. (2) By means of chemical analysis, the percentage of this element in each of its gaseous compounds is found. (3) The weight attributable to the element is found by multiplying the percentage of the element by the molecular weight of the compound. (4) The smallest number found is the probable atomic weight. The larger the number of compounds used, the greater is the chance that the smallest number is the correct atomic weight. These four steps are outlined as follows:

Example: Determine the atomic weight of sulfur.

COMPOUNDS	MOL. WT.	PERCENTAGE OF SULFUR	WEIGHT OF SULFUR	H.C.F.	CONCLUSION
Sulfur dioxide	64	50.0	32	32	The atomic weight of sulfur is 32
Sulfur trioxide	80	40.0	32		
Carbon disulfide	76	84.2	64		
Hydrogen sulfide	34	94.1	32		

B) *When the element does not exist in gaseous compounds.* It has been found experimentally that the product of the atomic weight of a solid element and its specific heat is *approximately* 6.4.

Specific heat × atomic weight = 6.4 (approximately)



A Dumas bulb of measured capacity used to weigh a definite volume of a gas.

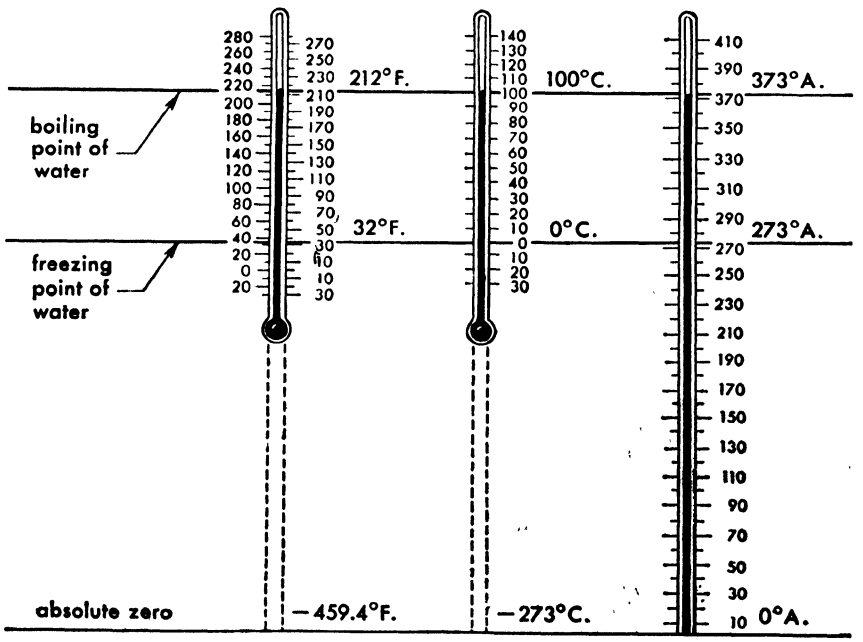
This is known as the *"law" of Dulong and Petit.* As you know, the specific heat of a solid element is the number of calories necessary to raise the temperature of one gram of the substance 1°C.

How thermometer scales are related. You are probably familiar with two kinds of thermometers — those using the centigrade scale and those using the Fahrenheit scale. On the centigrade scale, the zero mark is the point to which the mercury falls when the thermometer is immersed in a mixture of ice and water when the atmospheric pressure is 760 mm. The 100 mark is the point to which the mercury rises when the thermometer is placed in boiling water, or in steam when the atmospheric pressure is 760 mm. On the Fahrenheit scale, the freezing point of water is marked 32° and the boiling point of water is marked 212°.

You have learned that theoretically at −273°C. all motion of particles of matter ceases. This temperature is called *absolute zero.* A thermometer scale based on the centigrade scale but with 0° meaning absolute zero is called the *absolute,* or *Kelvin, scale.* On this scale, the freezing point of water is 273°A.; the boiling point is 373°A.

Careful study of Fig. 125 will help you to understand the relation between Fahrenheit, centigrade, and absolute scales. A centigrade

Fig. 125. The three thermometer scales.



degree is what part of a Fahrenheit degree? A Fahrenheit degree is what part of a centigrade degree?

Converting thermometer readings from one scale to another. 1) To convert centigrade readings to the corresponding Fahrenheit readings, multiply the centigrade reading by 1.8 and add 32.

Example: What is the Fahrenheit reading corresponding to 20°C.?

$$(20 \times 1.8) + 32 = 36 + 32 = 68°\text{F}.$$

2) To convert Fahrenheit readings to the corresponding centigrade readings, subtract 32 degrees from the Fahrenheit reading and divide by 1.8.

Example: What is the centigrade reading corresponding to 100°F.?

$$\frac{(100 - 32)}{1.8} = \frac{68}{1.8} = 37.77°\text{C}.$$

3) To convert centigrade readings to the corresponding absolute scale readings, add 273° to the centigrade readings.

Example: What is the absolute scale reading corresponding to −43°C.?

$$-43° + 273° = 230°\text{A}.$$

4) To convert Fahrenheit readings to absolute scale readings, first convert the Fahrenheit reading to the centigrade reading, and then add 273°.

Example: What is the absolute scale reading corresponding to 68°F.?

$$\frac{(68 - 32)}{1.8} + 273 = 20 + 273 = 293°\text{A}.$$

Changing gas measurements from one set of conditions of temperature and pressure to a different set of conditions. In Chapter 19 you learned two laws concerning the behavior of ideal gases, that is, gases whose molecules are so far apart, they do not attract each other appreciably. These were Boyle's law and Charles' law. These laws may be expressed as equations, in which p_1 represents the *initial pressure*, p_2 the *final pressure*, v_1 the *initial volume*, v_2 the *final volume*, T_1 the *initial absolute temperature*, and T_2 the *final absolute temperature*.

Boyle's Law: $p_1/p_2 = v_2/v_1$ or $p_1v_1 = p_2v_2$
Charles' Law: $v_1/v_2 = T_1/T_2$ or $v_1T_2 = v_2T_1$

By using these equations, gas measurements made under one set of conditions may be changed to fit another set of conditions. Usually, these equations are used in changing gas measurements from existing conditions to standard conditions.

1) *Change in volume caused by change in pressure (Boyle's law).*

Example: A quantity of chlorine gas has a volume of 50 ml. when the barometer reads 740 mm. What is its volume under standard conditions?

The temperature is not mentioned, so we assume that it does not change.

$$p_1v_1 = p_2v_2$$
$$740(50) = 760(x)$$
$$37000 = 760x$$
$$x = 48.7 \text{ ml. of chlorine}$$

2) *Change in volume caused by change in temperature (Charles' law).*

Example: A quantity of carbon dioxide gas measures 450 ml. when the room temperature is 22°C. What is its volume under standard conditions?

The pressure is not mentioned, so we assume that we are working under standard, or 760 mm., pressure.

$$\frac{v_1}{T_1} = \frac{v_2}{T_2}$$
$$\frac{450}{273 + 22} = \frac{x}{273}$$
$$\frac{450}{295} = \frac{x}{273}$$
$$295x = 450(273)$$
$$x = 416.4 \text{ ml. of } CO_2$$

3) *Change in volume caused by change in both temperature and pressure (laws of Boyle and Charles combined).*

Example: At 27°C. and 800 mm. pressure a quantity of nitrogen gas measures 20 ml. What is the volume under standard conditions?

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2}$$
$$\frac{800(20)}{273 + 27} = \frac{760(x)}{273}$$
$$800(20)(273) = 760(300)x$$
$$x = \frac{800(20)(273)}{760(300)}$$
$$x = 19.2 \text{ ml. of nitrogen}$$

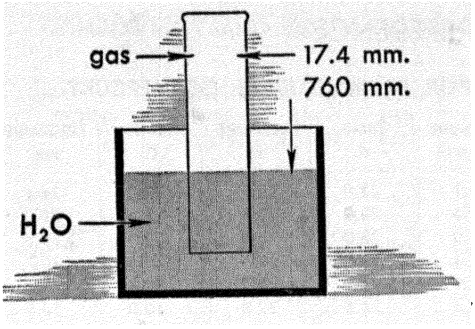


Fig. 126. When a gas is collected over water, its volume must be corrected to compensate for water vapor pressure.

4) *Correction of gas volumes to compensate for water-vapor pressure.*

If we are measuring the volume of a gas collected over water at 20°C. and 760 mm., the gas is saturated with water vapor, which, according to the table of water vapor pressures, exerts its own pressure of 17.4 mm. Since 760 mm. represent the sum of the water pressure and the gas pressure, the pressure of the dry gas is 760 minus 17.4, or 742.6 mm. Similarly, the volume of any gas collected over water must be corrected, using the data given in the table on page 648.

USEFUL MATERIAL FOR REFERENCE

PRESSURE OF WATER VAPOR IN MILLIMETERS OF MERCURY

TEMP. C.	PRESSURE mm.	TEMP. C.	PRESSURE mm.	TEMP. C.	PRESSURE m.	TEMP. C.	PRESSURE mm.
0.0°	4.6	15.5	13.1	22.0	19.7	28.0	28.1
5.0	6.5	16.0	13.5	22.5	20.3	28.5	28.9
10.0	9.2	16.5	14.0	23.0	20.9	29.0	29.8
10.5	9.5	17.0	14.4	23.5	21.5	29.5	30.7
11.0	9.8	17.5	14.9	24.0	22.1	30.0	31.6
11.5	10.1	18.0	15.4	24.5	22.8	40.0	54.9
12.0	10.5	18.5	15.9	25.0	23.5	50.0	92.1
12.5	10.8	19.0	16.4	25.5	24.2	60.0	149.2
13.0	11.2	19.5	16.9	26.0	25.0	70.0	233.8
13.5	11.5	20.0	17.4	26.5	25.7	80.0	355.4
14.0	11.9	20.5	17.9	27.0	26.5	90.0	526.0
14.5	12.3	21.0	18.5	27.5	27.3	100.0	760.0
15.0	12.7	21.5	19.1				

SOLUBILITY OF COMMON COMPOUNDS AT DIFFERENT TEMPERATURES*

COMPOUND	WEIGHT IN GRAMS SOLUBLE IN 100 g. OF H_2O AT		
	0°C.	20°C.	100°C.
$C_{12}H_{22}O_{11}$ (sugar)	179.0	204.0	487.0
$CaCl_2$	59.5	74.5	159.0
$Ca(OH)_2$	0.185	0.165	0.077
$CaSO_4$	0.176	0.203	0.162
$CuSO_4$	14.3	20.7	75.4
KCl	27.6	34.0	56.7
KNO_3	13.3	31.6	246.0
K_2SO_4	7.6	11.3	24.3
NaCl	35.7	36.0	39.8
NH_4Cl	29.4	37.2	77.3
$NaNO_3$	73.0	88.0	180.0

* See page 243 for further information on solubility.

COMPOSITION AND FOOD VALUES OF SOME COMMON FOODS

FOOD	PERCENTAGE WATER	PERCENTAGE PROTEIN	PERCENTAGE FAT	PERCENTAGE ASH (Mineral)	PERCENTAGE CARBOHYDRATES	NUMBER OF CALORIES PER POUND	VITAMINS
Apples	84.1	0.3	0.4	0.29	14.9	290	A, B_1, B_2, C
Asparagus	93.0	2.2	0.2	0.67	3.9	120	A, B_1, B_2
Bacon	29.0	12.2	53.0	4.7	1.4	2410	B_1
Beans, lima	66.5	7.5	0.8	1.71	23.5	595	B, C
Beef, chuck	71.0	19.2	9.0	0.94		720	B_1, B_2
Beets	87.6	1.6	0.1	1.11	9.6	205	A, B_1, B_2, C
Bread, white	35.9	8.5	2.0	1.3	52.3	1185	B_1
Butter	15.5	0.6	81.0	2.5	0.4	3325	A, B, D
Cabbage	92.4	1.4	0.2	0.75	5.3	130	A, B_1, B_2, C
Carrots	88.2	1.2	0.3	1.02	9.3	205	A, B_1, B_2, C
Cheese, Swiss	34.0	28.6	31.3	4.2	1.9	1830	A
Clams	85.8	8.6	1.0	2.6	2.0	235	A, B_2, C
Codfish	82.6	16.5	0.4	1.2		315	B_1, B_2, C
Corn, sweet	73.9	3.7	1.2	0.66	20.5	490	A, B_1, C
Eggs	74.0	12.8	11.5	1.0	0.7	715	A, B_1, B_2, K
Gelatin	13.0	85.6	0.1	1.3		1555	
Lamb	66.3	17.1	14.8	0.9		910	B_1
Liver, beef	69.7	19.7	3.2	1.4	6.0	600	A, B_1, B_2, C, E, K
Macaroni	75.0	3.7	0.4	1.5	19.4	435	
Milk, whole	87.0	3.5	3.9	0.7	4.9	310	A, B_1, B_2, C, D, E
Oatmeal	84.8	2.3	1.2	0.7	11.0	290	B_1
Onions	87.5	1.4	0.2	0.58	10.3	220	B_1, B_2, C
Oranges	87.2	0.9	0.2	0.47	11.2	230	A, B_1, B_2, C
Oysters	80.3	9.8	2.0	2.0	5.9	365	A, E
Peanuts	5.1	27.6	48.5	2.3	16.5	2780	B_1
Peas, green	74.3	6.7	0.4	0.92	17.7	460	A, B_1, B_2, C, E
Potatoes	77.8	2.0	0.1	0.99	19.1	385	A, B_1, B_2, C
Rice, white, boiled	74.4	2.2	0.1	0.1	23.2	465	
Spinach	92.7	2.3	0.3	1.53	3.2	110	A, B_1, B_2, C, K
Squash	90.4	1.2	0.3	0.76	7.3	165	B_1
Strawberries	90.0	0.8	0.6	0.50	8.1	185	A, B_1, B_2, C
Tomatoes	94.1	1.0	0.3	0.57	4.0	105	A, B_1, B_2, C, K
Turnips	90.9	1.1	0.2	0.73	7.1	155	B_1, B_2, C
Veal	71.0	19.7	8.0	1.0		680	B_1, B_2
Whole wheat flour	11.0	13.0	2.0	1.6	72.4	1630	B_1, E

Food composition and vitamin content based on U. S. Department of Agriculture, *Proximate Composition of American Food Materials,* Circular No. 549, and *Vitamin Values of Foods in Terms of Common Measures.*

MELTING POINTS, DENSITIES, AND DISCOVERY DATES OF COMMON ELEMENTS

ELEMENT	MELTING POINT (centigrade)	DENSITY (g./cc.)	WHEN AND BY WHOM DISCOVERED OR ISOLATED
Aluminum	658.7	2.70	1825 Oersted
Antimony	630.0	6.618	Known to Ancients
Arsenic	850.0	5.73	1649 Schroeder
Bismuth	271.0	9.747	Known to Ancients
Boron	2200.0	2.535	1808 Gay-Lussac, Davy
Bromine	−7.3	3.12	1826 Balard
Cadmium	320.9	8.54	1817 Stromeyer
Carbon	3500.0	3.52	Known to Ancients
Chromium	1615.0	6.52	1798 Vauquelin
Cobalt	1480.0	8.71	1735 Brandt
Copper	1083.0	8.30	Known to Ancients
Gold	1063.0	19.3	Known to Ancients
Iodine	113.5	4.940	1812 Courtois
Iridium	2350.0	22.42	1804 Tennant
Iron	1530.0	7.85	Known to Ancients
Lead	327.0	11.342	Known to Ancients
Lithium	186.0	0.534	1817 Arfwedson
Magnesium	651.0	1.741	1808 Davy
Manganese	1230.0	7.42	1774 Gahn
Mercury	−38.87	13.596	Known to Ancients
Molybdenum	2535.0	9.01	1781 Hjelm
Nickel	1452.0	8.60	1754 Cronstadt
Osmium	2700.0	22.5	1804 Tennant
Phosphorus	44.2	1.83	1669 Brand
Platinum	1755.0	21.73	1740 Wood
Potassium	62.3	0.870	1807 Davy
Silicon	1420.0	2.42	1824 Berzelius
Silver	960.8	10.42	Known to Ancients
Sodium	97.5	0.9712	1807 Davy
Sulfur	112.8	2.0	Known to Ancients
Tantalum	2900.0	16.6	1802 Ekeberg
Tin	231.9	7.29	Known to Ancients
Titanium	1795.0	4.5	1795 Klaproth
Uranium	1150.0	18.7	1842 Péligot
Vanadium	1720.0	5.69	1831 Sefstrom
Wolfram	3400.0	18.6	1783 d'Elhuyer brothers
Zinc	419.4	7.04	1746 Marggraf

HEATS OF FORMATION OF COMMON COMPOUNDS

(IN CALORIES)

CaO	131,000	$Hg(ONC)_2$	−64,500
CO	29,000	HNO_3	41,600
CO_2	97,000	H_2S	4,800
C_2H_2	−54,000	KCl	105,000
$C_{12}H_{22}O_{11}$	536,000	$KClO_3$	90,000
CS_2	−19,000	MgO	146,000
FeS	24,000	NH_3	12,000
HgO	21,500	$NaCl$	97,800
HCl	22,000	$NaOH$	103,000
HBr	8,400	NO	−21,600
HF	37,600	P_2O_5	370,000
HI	−6,100	SO_2	69,000
H_2O	68,400	ZnS	46,000

APPROXIMATE ATOMIC WEIGHTS OF COMMON ELEMENTS

ELEMENT	SYMBOL	APPROX. AT. WT.	ELEMENT	SYMBOL	APPROX. AT. WT.
Aluminum	Al	27	Lead	Pb	207
Antimony	Sb	121.8	Lithium	Li	7
Arsenic	As	75	Magnesium	Mg	24.3
Barium	Ba	137.4	Manganese	Mn	55
Bismuth	Bi	209	Mercury	Hg	200.6
Boron	B	11	Nickel	Ni	58.7
Bromine	Br	80	Nitrogen	N	14
Cadmium	Cd	112.4	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Platinum	Pt	195
Chlorine	Cl	35.5	Potassium	K	39
Chromium	Cr	52	Radium	Ra	226
Cobalt	Co	59	Silicon	Si	28
Copper	Cu	63.5	Silver	Ag	108
Fluorine	F	19	Sodium	Na	23
Gold	Au	197	Strontium	Sr	87.6
Hydrogen	H	1	Sulfur	S	32
Iodine	I	127	Tin	Sn	118.7
Iron	Fe	56	Zinc	Zn	65.4

THE METRIC SYSTEM

The *metric system* was devised in France about the time of the French Revolution to bring order to the chaos that then existed with respect to weights and measures. In France alone several hundred different systems of weights and measures were in use in different sections of the country. Very confusing, to say the least.

The metric system, *based throughout on multiples of ten,* is simple to understand and easy to use. Established by law in France in 1793, it has since been adopted as official by many countries. In the United States and Great Britain it is not the official system, but both permit its use. Scientists throughout the world use the metric system. Why?

LENGTH	WEIGHT
1 decimeter (dm.) = 0.1 meter (m.)	1 decigram (dg.) = 0.1 gram (g.)
1 centimeter (cm.) = 0.01 meter (m.)	1 centigram (cg.) = 0.01 gram (g.)
1 millimeter (mm.) = 0.001 meter (m.)	1 milligram (mg.) = 0.001 gram (g.)
1 kilometer (km.) = 1000 meters (m.)	1 kilogram (kg.) = 1000 grams (g.)

UNIT EQUIVALENTS (APPROXIMATE)

1 inch (in.)	=	2.54	centimeters (cm.)
1 square inch (sq. in.)	=	6.45	square centimeters (sq. cm.)
1 square meter (sq. m.)	=	10.76	square feet (sq. ft.)
1 cubic inch (cu. in.)	=	16.4	cubic centimeters (cc.) or milliliters (ml.)
1 cubic foot (cu. ft.)	=	28.3	liters (l.)
1 cubic foot (cu. ft.)	=	7.48	gallons (gal.)
1 liter (l.) (1000 ml.)	=	61	cubic inches (cu. in.)
1 liter (l.)	=	1.06	quarts (qt.)
1 gallon (gal.)	=	231	cubic inches (cu. in.)
1 gallon (gal.)	=	3.79	liters (l.)
1 cubic meter (cu. m.)	=	1.31	cubic yards (cu. yd.)
1 cubic meter (cu. m.)	=	35.32	cubic feet (cu. ft.)
1 ounce (oz.) fluid	=	29.57	milliliters (ml.)
1 ounce (oz.) avoirdupois	=	28.35	grams (g.)
1 ounce (oz.) Troy	=	31.10	grams (g.)
1 gram (g.)	=	15.43	grains
1 kilogram (kg.)	=	2.2	pounds (lb.)
1 ton, 2000 pounds	=	907.2	kilograms (kg.)
1 liter (l.) of water	=	2.2	pounds (lb.)
1 cubic foot (cu. ft.) of water	=	62.4	pounds (lb.)
1 gallon (gal.) of water	=	8.34	pounds (lb.)
1 atmosphere (atm.) pressure	=	1033	grams per square centimeter (g./sq. cm.)

WINNERS OF THE NOBEL PRIZE IN CHEMISTRY

In 1896, Alfred B. Nobel, the Swedish scientist who invented dynamite, died, bequeathing to a special body, to be known as the Nobel Foundation, the sum of nine million dollars. The interest of this sum, in the form of prizes, is awarded annually to persons judged to have contributed most to the benefit of mankind in various fields of endeavor. The value of the Nobel award varies, but the award in each field was about $35,000 in a recent year.

The chemistry awards are made by the Swedish Academy of Science. Thus far ten Americans have won or shared the prize in chemistry. The chemistry awards were not made in 1916, 1917, 1919, 1924, 1933, 1940, 1941, and 1942.

YEAR	WINNER	COUNTRY	CONTRIBUTION
1901	J. H. van't Hoff	Holland	Theory of solutions, molecular structure
1902	Emil Fischer	Germany	Proteins. Chemistry of sugars
1903	Svante Arrhenius	Sweden	Theory of dissociation
1904	William Ramsay	England	Isolation of the rare gases of the air
1905	Adolf von Baeyer	Germany	Synthesis of indigo
1906	Henri Moissan	France	Isolation of fluorine. Electric furnace
1907	Eduard Buchner	Germany	Chemistry of enzymes and fermentation
1908	Ernest Rutherford (born New Zealand)	England	Radioactivity
1909	Wilhelm Ostwald	Germany	Theory of solutions, fixation of nitrogen
1910	Otto Wallach	Germany	Chemistry of the terpenes
1911	Marie Curie (born Poland)	France	Isolation of radium and polonium
1912	V. Grignard	France	Synthesis of organic compounds
	P. Sabatier	France	Catalysis in organic chemistry
1913	Alfred Werner	Switzerland	Valence and chemical constitution
1914	Theodore W. Richards	United States	Atomic weight determinations
1915	R. Willstätter	Germany	Structure of chlorophyll
1918	Fritz Haber	Germany	Catalytic synthesis of ammonia
1920	Walther Nernst	Germany	Electrochemistry, thermodynamics
1921	Frederick Soddy	England	Radioactivity and radioactive elements
1922	Francis W. Aston	England	Discovery of isotopes
1923	Fritz Pregl	Austria	Microanalysis of organic compounds
1925	Richard Zsigmondy	Germany	The chemistry of colloids, ultramicroscope
1926	The Svedberg	Sweden	The chemistry of colloids
1927	Heinrich Wieland	Germany	The chemistry of the bile acids
1928	Adolf Windaus	Germany	Cholesterol and vitamins
1929	Arthur Harden	England	Alcoholic fermentation, sugar, vitamins
	von Euler-Chelpin	Sweden	Enzymes and vitamins
1930	Hans Fischer	Germany	Production of hemin from hemoglobin
1931	Karl Bosch	Germany	Fixation of nitrogen
	Friedrich Bergius	Germany	Liquefaction of coal, sugar from wood
1932	Irving Langmuir	United States	Surface chemistry, electron theory

YEAR	WINNER	COUNTRY	CONTRIBUTION
1934	Harold C. Urey	United States	Heavy hydrogen and heavy water
1935	J. F. and I. Joliot-Curie	France	Artificial radioactivity
1936	Peter Debye	Holland	Dissociation, structure of molecules
1937	Walter N. Haworth	England	Carbohydrates
	Paul Karrer	Switzerland	Vitamins
1938	Richard Kuhn	Germany	Vitamins and paratinoids
1939	Adolf Butenandt	Germany	Sex hormones
	Leopold Ruzicka (born Jugoslavia)	Switzerland	Polymethylene, testosterone
1943	Georg von Hevesy	Hungary	Isotopes, use of x-ray analysis
1944	Otto Hahn	Germany	Nuclear fission
1945	Artturi I. Virtanen	Finland	Nitrogen cycle, cattle nutrition
1946	John H. Northrop	United States	Isolation of enzymes
	James B. Sumner	United States	
	Wendell M. Stanley	United States	Isolation of a virus
1947	Robert Robinson	England	Synthesis of alkaloids
1948	Arne Tiselius	Sweden	Biochemical work
1949	William F. Giauque	United States	Substances at extremely low temperatures
1950	Kurt Adler	Germany	Development of the dienesynthesis reaction
	Otto Diels	Germany	
1951	Glenn T. Seaborg	United States	Discovery of 6 transuranium elements
	Edwin M. McMillan	United States	
1952	A. J. P. Martin	England	Chromatography
	R. M. Synge	England	
1953	Hermann Straudinger	Germany	Giant molecules (polymers)
1954	Linus C. Pauling	United States	Nature of chemical bonds, particularly of proteins

TABLE OF SOME *pH* VALUES

Limes	1.8–2.0 *	0.1N HCl	1.0
Lemon juice	2.3	0.1N H_2SO_4	1.2
Ginger ale	2.0–4.0	0.1N $HC_2H_3O_2$ (vinegar)	2.0
Apples	3.0	0.1N H_3BO_3	5.1
Orange juice	3.3	0.1N $NaHCO_3$	8.4
Sauerkraut	3.5	0.1N $Na_2B_4O_7$	9.2
Tomatoes	4.2	0.1N NH_4OH	11.1
Carrots	5.0	0.1N Na_2CO_3	11.3
Molasses	5.0–5.4	0.1N NaOH	13.0
Cabbage	5.3		
Cow's milk	6.6		
Shrimp	7.0	* averages	
Milk of magnesia	10.5		

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THE CHEMICAL ELEMENTS

(Arranged According to Atomic Numbers)

AT. NO.	ELEMENT	SYM-BOL	ATOMIC WEIGHT	AT. NO.	ELEMENT	SYM-BOL	ATOMIC WEIGHT
1	Hydrogen	H	1.0080	51	Antimony	Sb	121.76
2	Helium	He	4.003	52	Tellurium	Te	127.61
3	Lithium	Li	6.940	53	Iodine	I	126.91
4	Beryllium	Be	9.013	54	Xenon	Xe	131.3
5	Boron	B	10.82	55	Cesium	Cs	132.91
6	Carbon	C	12.01	56	Barium	Ba	137.36
7	Nitrogen	N	14.008	57	Lanthanum	La	138.92
8	Oxygen	O	16.000	58	Cerium	Ce	140.13
9	Fluorine	F	19.000	59	Praseodymium	Pr	140.92
10	Neon	Ne	20.183	60	Neodymium	Nd	144.27
11	Sodium	Na	22.997	61	Promethium	Pm	(145) *
12	Magnesium	Mg	24.32	62	Samarium	Sm	150.43
13	Aluminum	Al	26.98	63	Europium	Eu	152.0
14	Silicon	Si	28.09	64	Gadolinium	Gd	156.9
15	Phosphorus	P	30.975	65	Terbium	Tb	159.2
16	Sulfur	S	32.066	66	Dysprosium	Dy	162.46
17	Chlorine	Cl	35.457	67	Holmium	Ho	164.94
18	Argon	A	39.944	68	Erbium	Er	167.2
19	Potassium	K	39.1	69	Thulium	Tm	169.4
20	Calcium	Ca	40.08	70	Ytterbium	Yb	173.04
21	Scandium	Sc	44.96	71	Lutetium	Lu	174.99
22	Titanium	Ti	47.90	72	Hafnium	Hf	178.6
23	Vanadium	V	50.95	73	Tantalum	Ta	180.88
24	Chromium	Cr	52.01	74	Wolfram	W	183.92
25	Manganese	Mn	54.93	75	Rhenium	Re	186.31
26	Iron	Fe	55.85	76	Osmium	Os	190.2
27	Cobalt	Co	58.94	77	Iridium	Ir	193.1
28	Nickel	Ni	58.69	78	Platinum	Pt	195.23
29	Copper	Cu	63.54	79	Gold	Au	197.2
30	Zinc	Zn	65.38	80	Mercury	Hg	200.61
31	Gallium	Ga	69.72	81	Thallium	Tl	204.39
32	Germanium	Ge	72.60	82	Lead	Pb	207.21
33	Arsenic	As	74.91	83	Bismuth	Bi	209.00
34	Selenium	Se	78.96	84	Polonium	Po	210
35	Bromine	Br	79.916	85	Astatine	At	(210) *
36	Krypton	Kr	83.8	86	Radon	Rn	222
37	Rubidium	Rb	85.48	87	Francium	Fr	(223) *
38	Strontium	Sr	87.63	88	Radium	Ra	226.05
39	Yttrium	Y	88.92	89	Actinium	Ac	227
40	Zirconium	Zr	91.22	90	Thorium	Th	232.12
41	Niobium	Nb	92.91	91	Protactinium	Pa	231
42	Molybdenum	Mo	95.95	92	Uranium	U	238.07
43	Technetium	Tc	(99) *	93	Neptunium	Np	(237) *
44	Ruthenium	Ru	101.7	94	Plutonium	Pu	(242) *
45	Rhodium	Rh	102.91	95	Americium	Am	(243) *
46	Palladium	Pd	106.7	96	Curium	Cm	(243) *
47	Silver	Ag	107.880	97	Berkelium	Bk	(245) *
48	Cadmium	Cd	112.41	98	Californium	Cf	(246) *
49	Indium	In	114.76	99			
50	Tin	Sn	118.70	100			

* These atomic weights are for the most stable known isotope, as given by *The Journal of the American Chemical Society* in 1952.

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