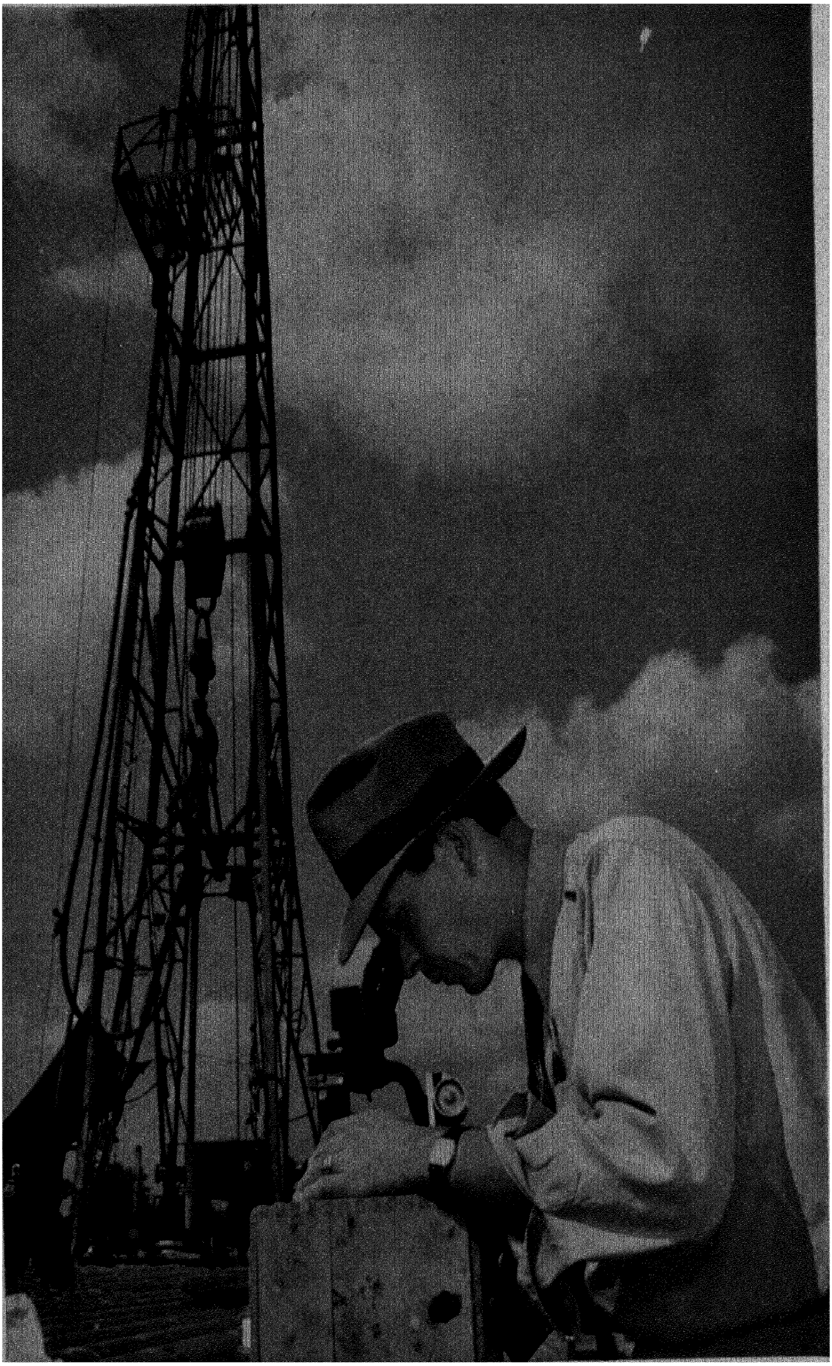
Chemistry
FOR OUR TIMES



Courtesy of Hercules Powder Co.

Chemistry

FOR OUR TIMES

ELBERT COOK WEAVER, M.A.
Instructor, Phillips Academy, Andover, Massachusetts
Formerly Chairman of Science Department
Bulkeley High School, Hartford, Connecticut

AND

LAURENCE STANDLEY FOSTER, Ph.D.
Formerly Assistant Professor of Chemistry, Brown University
Chief, Powder Metallurgy Branch, Watertown
Arsenal Laboratory, Watertown, Massachusetts

McGRAW-HILL BOOK COMPANY, INC.
New York and London

CHEMISTRY FOR OUR TIMES

PRINTED IN THE UNITED STATES OF AMERICA

II

The quality of the materials used in the manufacture of this book is governed by continued postwar shortages.

THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

AN ATOMIC age calls for a new approach to chemistry. Hence, we are presenting an entirely new elementary chemistry textbook. *Chemistry for Our Times* describes chemistry of today as it affects the citizen. In it we have interpreted advances in theoretical, physical, and organic chemistry, as far as they affect the elementary level. By keeping in close agreement with experimental facts, we have eliminated many errors that cling to chemistry textbooks by tradition. We have also tried to strike a balance between chemistry principles and applications of chemistry.

Understanding the environment, the method of science, and the applications of chemistry to the life activities of the average citizen is an important aim in this book. The workaday world of chemistry is never far away, however, and hundreds of industrial plants and laboratories were visited in order to incorporate the practical viewpoint.

This book centers about the individual pupil and his activities. It starts with his immediate environment—air and breathing, water and solutions—and then swings through the gamut of chemical actions, progressing gradually from familiar to less familiar experiences. After the principles have been established, the book concludes with a unit on the applications of those principles to human problems of food, health, and peace.

The basis of chemical progress has always been experimental evidence. This book is organized around this fundamental principle rather than theory, such as atomic structure, periodic classification, replacement activity grouping, or some other basis. All these deductions are included in their appropriate places, however.

References to books, periodical literature, visual aids, and other materials used ordinarily only by the teacher are contained in a *Teachers' Manual*, available from the publishers.

Weight-weight and weight-volume problems are postponed until pupils have sufficient practice in using balanced equations and until the need for solving problems using equations as a tool becomes evident. At first there is a thorough grounding in percentage, density, molecular volume, and other simple mathematical operations.

The questions that accompany each chapter are chiefly of the thought-stimulating type rather than tests of rote memory. The number of numerical problems is doubled by a simple device, making possible a wider range of assignments.

This book contains enough chemistry to be serviceable as a first book, in case a student decides on chemistry as a profession, yet it is not designed specifically for the training of future chemists. Thus, it is suited to either college preparatory or general chemistry classes.

In keeping with the practical approach, titles such as safety, beauty, and cleanliness will be found among the chapters. Also, more emphasis is placed upon the metals themselves than upon compounds of the metals and properties of the metallic ions. We agree with the findings of committees that have studied the matter and offer a broad, life-interest content, at the same time meeting the requirements of recognized syllabuses.

Within the last generation a new industry has sprung up in the United States. This is chemistry as big business. Because of its research program, the chemical industry is bound to develop rapidly. A shift in emphasis in popular thinking is needed in order to appreciate this fact. A new set of jobs is open; a new frontier appears for original thinkers. Moreover, products of chemical laboratories require educated consumers.

A fact about chemistry seldom appreciated is its international aspect. Ideas that have aided man's progress have come from all sections of the world. Truth is not the special heritage of the United States, Germany, China, England, or any other country. For example, although atomic (nucleonic) bombs were developed for military purposes in the United States, all the fundamental scientific discoveries on which this development was based were made in other countries. Nature yields her secrets to all persons who seek them in the proper way.

Further, the location on the earth of natural materials and ores that are useful to man is without the slightest regard to accessibility or to political boundaries. The general need for raw materials constitutes a fundamental reason for preserving international peace and for the free exchange of goods on a global basis. These thoughts are woven into the fabric of the text.

The development of this book started with suggestions and conferences with Dr. John A. Timm, now head of sciences at Simmons College, Boston, Massachusetts. To him the authors are greatly indebted. Dr. Hanor A. Webb of George Peabody College for Teachers, Nashville, Tennessee and Dr. Pauline Beery Mack, Director of the Ellen H. Richards Institute, Pennsylvania State College, State College, Pennsylvania, have also contributed valuable suggestions.

The authors wish to express their appreciation to the many industrial concerns that have cooperated in producing this book. Pictures were furnished graciously by companies in every section of the United States, and these have added greatly to the interest and understanding of the text. Many industrial people were very helpful on the manuscript itself.

Notable additions to the sections on iron and steel, aluminum, magnesium, petroleum, paper, and safety were made by technical men to whom the satisfaction of presenting an accurate picture to students and other readers is ample reward.

Thanks are due also to our colleagues on high-school and college faculties who have given many helpful suggestions.

Finally, the authors are indebted to their many students who, by their helpful questions, have guided the development of this book to meet their requirements and needs.

ELBERT COOK WEAVER
LAURENCE STANDLEY FOSTER

CONTENTS

INTRODUCTION

UNIT ONE: OUR ESSENTIAL ENVIRONMENT

UNIT TWO: CHEMISTRY'S BUSINESS OFFICE

UNIT THREE: DISPERSIONS OF MATTER

UNIT FOUR: CHEMISTRY OF THE EARTH'S CRUST

UNIT FIVE: CHEMICAL INDUSTRIES

UNIT SIX: THE METALS

UNIT SEVEN: THE CHEMISTRY OF CARBON COMPOUNDS

UNIT EIGHT: CHEMISTRY AND HUMAN PROBLEMS

UNIT NINE: ADDITIONAL TOPICS

INTRODUCTION .... CHAPTER I

CHEMISTRY AS A SCIENCE

> The Chemists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapour, soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly that may I die if I would change places with the Persian King.
>
> —JOHANN JOACHIM BECHER, 1669.

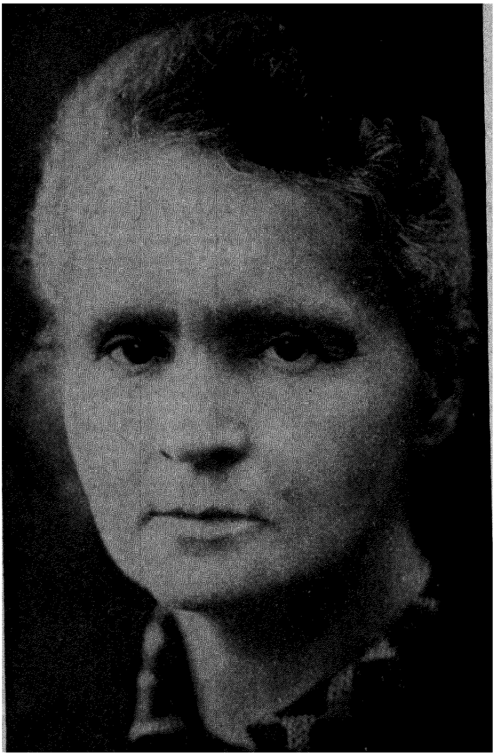
Science in Action. A quiet woman, simply dressed, is ushered into the White House at Washington. She is greeted heartily by the President and First Lady of the United States, entertained at dinner, and presented with an order for fifty thousand dollars with which to buy radium. Why should this honor come to a chemist? Why is it that neither France nor the United States could do enough to honor Marie Curie, who had spent much of her youth washing bottles in a laboratory for a bare existence while studying in a Paris university?

A knock is heard at an office door in Cambridge, Massachusetts. A student, notebook in hand, enters and approaches Prof. Theodore Richards of Harvard University. Together they go over notes and figures that represent the results of experiments. A slight error is discovered. The professor is distressed; the student more so. Why should these people be concerned about a small fraction of 1 per cent?

The scene changes to the laboratory of a large brass factory. Aproned men and women are busily engaged at different tasks. One is reading electrical meters and making notes. Another is comparing the colors of liquids in test tubes. A third is busy with a set of figures, part of a report. The chemist completes the report and carries it to the factory manager. They confer briefly. Both seem in agreement. The manager now gives orders that the copper recently received is suitable material for his company to use in making brass. Why is it that the manager can rely on the work of the chemist?

The well-known story of Marie Curie shows chemistry in service. By using radium, which she and Pierre Curie discovered, doctors have done much to check dreaded diseases. Although the chief purpose of the Curies' work was to find out, to investigate, or to discover, the knowledge they gained and gave to the world has had direct practical benefit.

Prof. Richards' work helped all chemists. His was another search into the unknown, pushing back ignorance. His determination of the atomic weights was just a little more accurate than that of any other chemist at the time. Such work as his was a big step forward. Each scientist builds on the work of others, an endless chain of progress.



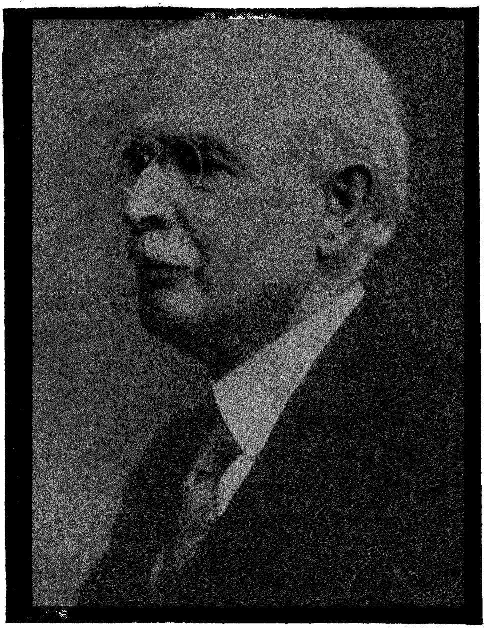
Science Service

Madame Marie Sklodowska Curie (1867–1934), the only person to receive twice the Nobel prize in chemistry, was distinguished for her discovery of radium, for her unusual skill and perseverence, and for being the mother of two distinguished daughters, one of whom has herself shared with her husband in a Nobel prize.

The chemist in industry has the task of finding out new things—such things as making threads for hosiery from coal, air, and water or making suds without soap. Another part of his job is the control of processes, checking products, and stopping waste. A paint company relies on its chemists to control the color and quality of its paints. Chemical control puts better steels in automobiles and railroad cars. Chemical control produces better gasoline to run cars and airplanes.

Benefits from Science Research. Beautiful colors for clothing, paper, and leather are now obtained from evil-smelling coal tar as a result of science research. Music and entertainment by radio in homes have been made possible by scientific research on electromagnetic waves and electrons. Lustrous fabrics of rayon have been the outcome of research on the nature of woody fibers. The rapid rise of comfortable living during the past 100 years has been the result of rapid strides in science; many advantages that we now enjoy are the fruit of scientific investigation.

A dentist injects a little novocain into the gum of a patient. A tooth now can be pulled without much pain. After a few whiffs of gas a child becomes unconscious so that tonsils can be removed or other troubles corrected. The doctor places a drop of diluted silver nitrate solution in the eyes of a newborn child, and thereby infection and loss of sight are prevented. A visiting nurse changes the food of a child who has weak legs. Soon the child gains strength, and the weak legs are straightened as vitamin D goes to work. Novocain, nitrous oxide gas, silver nitrate solution, and vitamin D are all being studied in chemical laboratories.

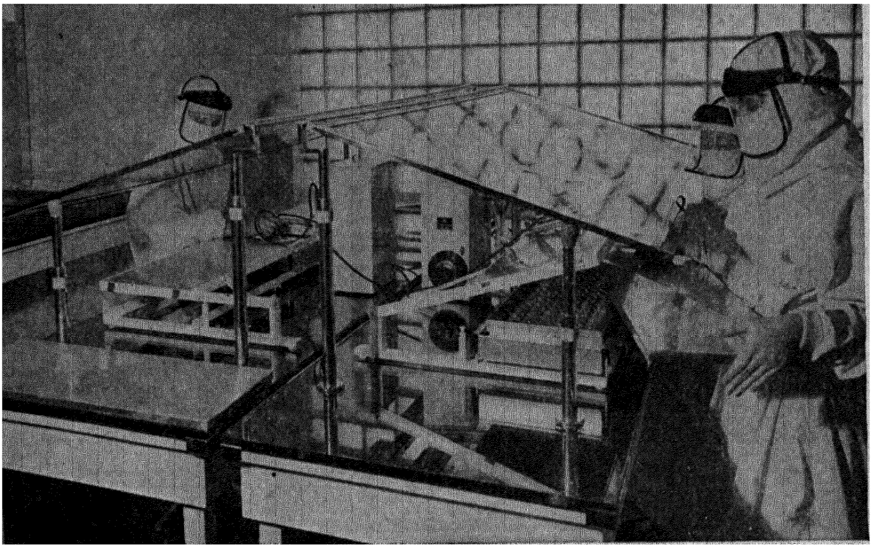


Courtesy of Journal of Chemical Education

Theodore William Richards (1868–1929) was the first American to receive the Nobel prize in chemistry. He was the top-ranking authority in the world on atomic weights of elements. In recognition of his outstanding achievements, 13 colleges awarded degrees to him.

Through chemical research suitable metals for radio tubes have been found; metals for stronger, lighter trains and trucks have been developed. Even the sea has become a commercial source of the valuable light metal, magnesium.

The Aim of the Scientist. The person who is scientifically trained seeks, first of all, to learn the truth about the deep secrets of nature. He seeks to find out the sort of material world in which people live. He discovers facts and interprets them. No prejudice or personal feeling is allowed to enter the work of a true scientist. To the engineer is left the invention of machines that make use of theories and facts discovered by the scientist, and to the artist is left the expression of the spirit of the age in terms of music, painting, or poetry.



Courtesy of Commercial Solvents Corporation and Martin's Photo Shop

FIG. 1-1.—These women are not from Mars but are workers in a penicillin factory. Much of the work in preparing this modern medicine is done under ultraviolet light in perfectly sterile air.

A story is told about a scientist and an unpracticed observer strolling through the fields. "There," remarked the observer, "goes a white sheep."

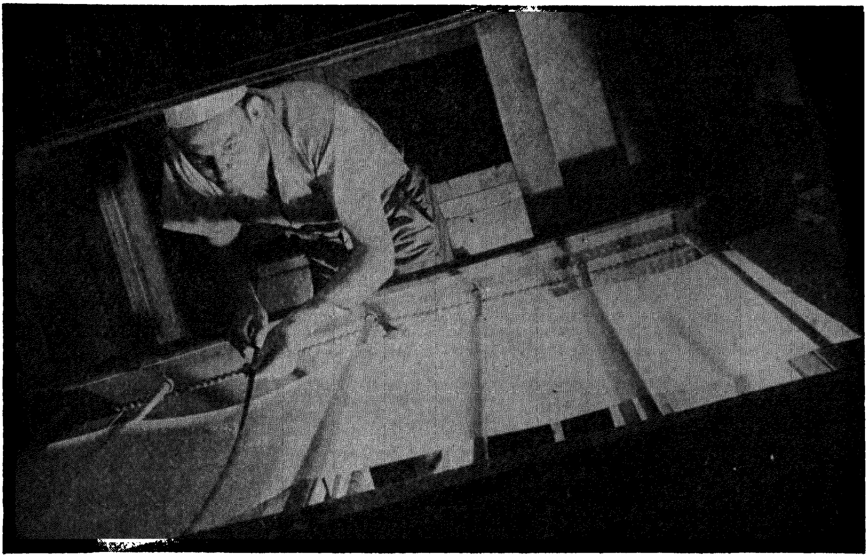
"Yes," agreed the scientist, "there goes a sheep that is white on this side."

The Scientific Method. Common to all branches of science is the method of study that is used. This ***scientific method*** of solving problems need not be limited to science alone. Indeed, many problems of business, law, and government can be solved by methods that are as scientific as those which led Pierre and Marie Curie to the discovery of radium.

Many persons are working on the problem of the cause and the cure of the disease cancer. Some workers seek a solution to this baffling problem through biology; others through chemistry. The final solution will be pieced together from the results of many different workers.

While the application of the scientific method will depend upon the situation at hand, certain general and fundamental steps are followed. The ***first*** step consists in ***collecting the facts,*** which may be done in different ways. If the methods of measurement of two scientists differ and yet the results are identical, we are more certain of the accuracy of the facts.

In the development of science, the early investigators discovered many general trends. Later and more careful work in the same field, sometimes with improved tools, has revealed facts obscured or overlooked at first. A notable example is found in the story of the discovery of argon. Lord Rayleigh, an English investigator, was checking the density of nitrogen with great accuracy. He found that the density of nitrogen prepared from air differed from the density of nitrogen prepared by heating ammonium nitrite by one-half of 1 per cent (0.5 per cent). The accuracy of his measurements permitted no difference greater than two-hundredths of 1 per cent (0.02 per cent). From these facts he later proved that the gas from air was not entirely nitrogen and that argon as well as some other gases were present in it.



Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 1-2.—One of the most significant steps in the protection of passengers against broken glass has been the development of a satisfactory and efficient safety glass for automobiles. Chemists have found an improved material for the interlayer between the sandwich safety glass. This is a modern plastic, "Butacite," which is a type of resin. The picture above shows the continuous Butacite sheeting passing through an air-cooling process.

In the city post office a postman has dumped on a table a pile of letters for the people who live in his territory. This postman's first job is to sort these letters. In this way his load of mail is organized systematically, and he saves much time in delivering the letters. Thus, by sorting and organizing the mail, the postman travels a route rather than going on a ramble. Likewise, a scientist sorts and ***organizes facts.*** This is the ***second*** step in the scientific method, ***organizing the facts.*** When the facts are studied, many will be found similar. The similar facts are classified and organized.

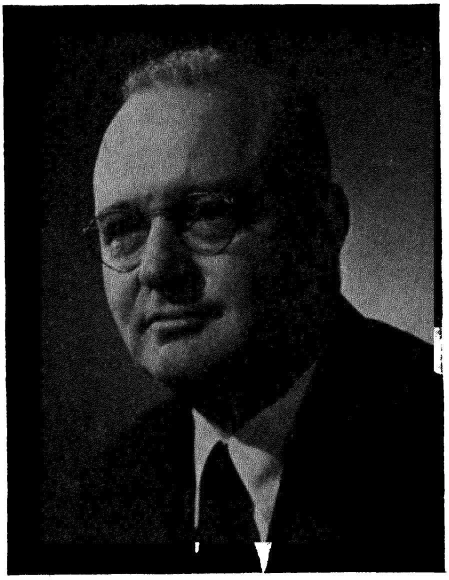
Robert Boyle (1627–1691) studied the effect of changing pressure on the volume of a given amount of gas. He found that when the temperature is unchanged (constant) and the pressure is doubled, the volume of a gas is halved; when the temperature is constant and the pressure is trebled, the volume becomes one-third of the original volume; and so on. This relationship he found to be true for all gases, pure substances and mixtures alike, provided that they were in gaseous form. Organizing the facts enabled Boyle to glean a general truth: ***The volume of a certain amount of dry gas is inversely proportional to the pressure on it, provided that the temperature is unchanged*** (Boyle's law).

After the facts had been collected and organized, Boyle came to the ***third*** step in the scientific method, ***stating the law.*** A law depends upon the facts collected and organized. A scientific law is a sentence describing the general truth that has become evident by a study of the organized facts. This statement describes the ***facts as known at the time,*** but it should not be regarded in the same sense as a civil law. If our knowledge of the facts becomes more complete, it is sometimes necessary to change the statement of the law.

Scientists ***explain a law by a theory.*** This is the ***fourth*** step in the scientific method. Of course, the theory is based on known facts, but all the details of situations become clearer as the theory points out the way. Later, it will be shown that Boyle's law was important in the growth of a theory. The theory of the nature of all gases is called the ***molecular theory*** of gases. This theory explains Boyle's law in addition to other laws dealing with gases. "A collection of facts is no more science than a pile of stones is a house." This saying illustrates the need of organizing facts and developing a theory to fit them.

Now we come to the ***fifth*** step. Suppose we study the method of numbering rooms in a certain high school. The rooms numbered 100 to 199 are on the first floor, those numbered 200 to 299 on the second floor, and on both floors 101 and 201 are near the main entrance. We may now make a good estimate of the location of a room numbered 321. We have studied the organization of the room numbering, have reached conclusions, and have used the conclusions for ***predicting new facts.*** Just so in science, keen minds study the theory, and new outcomes are suggested. Then comes the critical test of the theory. Are the new facts found to be as predicted, or are different facts discovered? In the first case, the theory is strengthened. If not, the theory is shown to need repair, and repairing it will get. This ability to predict is one of the remarkable things about science. It gives us more than satisfaction. It shows us that, by the reasoning processes of the human mind, knowledge of this universe can be obtained. A great Russian chemist, Mendeleyev, once stated in effect, "Some day you will find element *X*, which will be quite like the description I have predicted for it. The results of the study of my law and theory tell me so." Later events proved that he was right. Element *X* was discovered, and it was found to be remarkably like the description predicted (page 325).

Thomas Midgley, Jr., (1889–1944), discoverer of Freon for refrigerators and of Ethyl fluid for gasoline, wrote concerning the scientific method, "What is this scientific process? . . . To my mind the basis of the scientific process is the *reproducible experiment*. Facts are still and probably always will be determined by vote; . . . in science we require a practically unanimous vote for establishing a fact. . . . The only fundamental tool at our command for extending (our) knowledge is the reproducible experiment. This is the accepted scientific method. . . . "[1]



Courtesy of Ethyl Corporation

FIG. 1-3.—Thomas Midgley, Jr. (1889–1944) was a pioneer in the application of chemical knowledge to problems relating to automobiles. He was a leader in research and the inventor of Ethyl gasoline and of a nontoxic, nonflammable refrigerant. "Science is power."

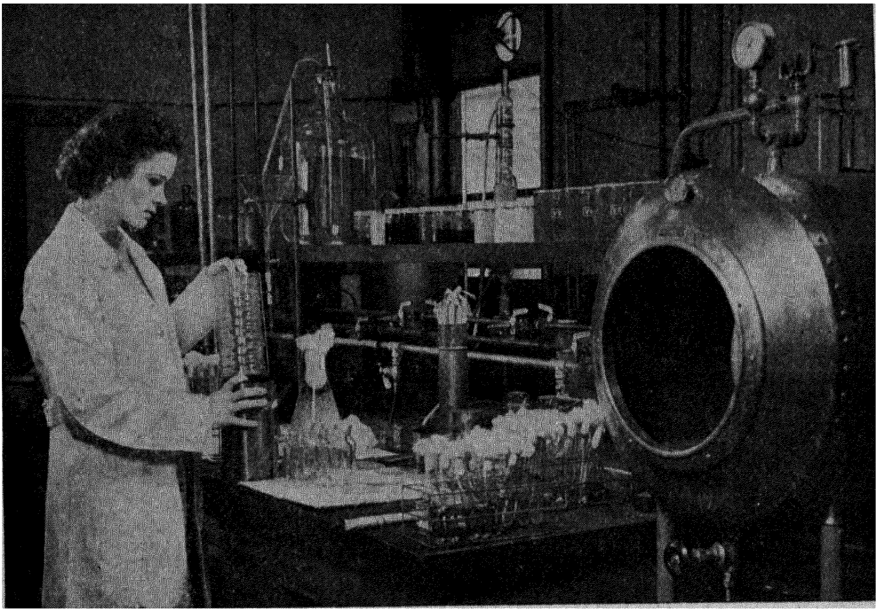
The Value of Chemistry Study. So much chemistry enters our daily lives that no really educated person can afford to be entirely ignorant of it. It can mean more to us than a dread of atomic bombs and of high explosives, more than "magic" tricks from a child's Chem-set.

The study of chemistry is necessary to the work of doctors, dentists, nurses, pharmacists, and engineers. A knowledge of some of the fundamentals of chemistry enables us to do better in almost any business. The farmer is directly concerned with chemical changes in plants and

[1] *Chemical and Engineering News*, vol. 22, p. 1756, October, 1944.

animals. In addition, there are many jobs that deal with chemistry entirely.

But what of the future housewife? Need she feel that studying chemistry is a waste of time? The modern housewife is acknowledging chemistry as one of her most efficient household aids. It helps her to cook intelligently, to give her family good food and a balanced diet, to wash clothes effectively, to understand clothing fabrics of all sorts, and to keep her home free from insects. Even in selecting cosmetics, her knowledge of chemical terms and of ingredients guides her in buying healthful and avoiding harmful products.



Courtesy of Armour Research Foundation

FIG. 1-4.—Here a worker is carrying on research in a bacteriological laboratory. Chemical training is essential for work of this sort, which helps in the conquest of disease.

How to Obtain More Information. Articles on many chemical subjects appear in the *Journal of Chemical Education, School Science and Mathematics, Chemistry, School Science Review,* and other magazines. Many commercial companies issue illustrated pamphlets describing their products and processes, often including a historical account of the industry in which they are engaged. When our curiosity is aroused, we shall want to know more about the world in which we live. This curiosity can be satisfied by the use of references such as those mentioned.

Chemistry Deals with Matter. It is fitting that we start our exploration of chemistry with a study of matter. As a guide, let us take the words of the great Chinese philosopher, Confucius (551–478 B.C.):

> The ancients who wished to illustrate the highest virtues throughout the empire first ordered well their own states. Wishing to order well their own states, they first regulated their families. Wishing to regulate their families, they first cultivated their own selves. Wishing to cultivate their own selves, they first rectified their hearts. Wishing to rectify their hearts, they first sought to be sincere in their thoughts. Wishing to be sincere in their thoughts, they first extended to the utmost their knowledge. Such extension of knowledge lay in the investigation of things. Things being investigated, their knowledge became complete. Their knowledge being complete, their thoughts were sincere. Their thoughts being sincere, their hearts were then rectified. Their hearts being rectified, their own selves were cultivated. Their own selves being cultivated, their families were regulated. Their families being regulated, their states were rightly governed. Their states being rightly governed, the whole empire was made tranquil and happy.

SUMMARY

New products, processes, drugs, and most of the knowledge of healthful living are the result of science investigation. Science study has made possible the use of machines, new means of communication, travel, and many other advantages that we may enjoy.

The scientific investigator seeks to find the actual facts about nature and to interpret them. He allows no personal prejudice to enter into his work.

The scientific method is a method of approach to problems. It involves five steps:

1. Collection of facts
2. Organization of the facts
3. Statement of a law
4. Explanation of the law by a theory
5. Prediction of new facts from the theory

The study of chemistry will give us a fund of information about materials and processes that will be useful in our everyday life.

The student of chemistry should use the public and school libraries to obtain further information on any subject in which he is particularly interested. The *Journal of Chemical Education* and other magazines contain articles on chemical subjects. Some commercial companies supply upon request pamphlets describing their products and processes.

QUESTIONS

1. State two important characteristics of a scientist.

2. The first step in most investigations is a thorough study of previous work in the field. Point out the advantage of starting an investigation in this manner.

3. List three items of equipment in your home that could not have been obtained 100 years ago.

4. List three fabrics that were unknown a century ago.

5. Point out two examples of the application of science to relieving pain.

6. State a characteristic that should be lacking among truly scientific investigators.

7. Give an important objective of the study of science.

8. List the five steps in the scientific method.

9. In Lord Rayleigh's experiment on the density of nitrogen, how many times was the experimental difference in density greater than the accuracy of his measurements?

10. Point out the value of organized classification to a lumberyard.

11. Does nature obey scientific laws, or do scientific laws describe generalities in nature?

12. Do the statements of scientific laws ever change?

13. What is a *theory?* How does a theory in science differ from an ordinary guess?

14. Point out the relationship between a fact, a law, and a theory.

15. Give an example of an abstract word; a concrete term.

16. Make a step-by-step diagram, V-shaped, of the items in Confucius' saying.

HINT: In answering a question, make a complete sentence that has meaning without referring to the question. It should not be necessary for the reader to look back to the question in order to understand the answer. For example, answers to question **1** could be:

Poor: *Interest in truth and no prejudice.*

Good: *Two important characteristics of scientists are* (1) *an interest in truth and* (2) *freedom from prejudice.*

MORE CHALLENGING QUESTIONS

17. Show how the scientific method of approach can be applied to the solution of some problem in school life.

18. Show how the scientific method of approach can be or has been applied to some problem that affects your town or city. Examples might be water supply, sewage treatment, and disposal of rubbish or garbage.

19. Write an essay on Confucius.

20. Point out examples of superstitions that have no scientific foundation.

INTRODUCTION - - - - - - - - - - - CHAPTER II

CHEMISTRY A STUDY OF MATTER

The science of chemistry is the study of all the materials of the universe; especially, it is the study of the processes by which materials can be changed into more useful ones. Fat is useful for food or fuel as we find it in nature, but it can also be made into that practical substance, soap. Coal may be burned as a fuel, or it may be changed into coke, gas, and valuable by-products. All materials, substances, stuffs can be called more accurately matter, the subject of our study.

"What is matter?" we ask. Here we must hesitate before answering this simple question.

In order to give a satisfactory definition of a word, we must describe or explain it in terms that are simpler and more fundamental than the word itself. If the word for which a meaning is sought is simple and fundamental, then it may not be easy to find a satisfactory definition. If, for example, we try to express a clear meaning of the word ***time,*** we soon discover that, the wider our experience, the more difficult it is to define.

The same problem faces the chemist who attempts to define ***matter*** and the physicist who tries to define ***energy,*** mainly because in physical sciences the ideas of matter and energy are fundamental. The definitions which we shall now give may be considered as working definitions, something like a scaffolding from which a more substantial structure can be built.

Energy comes from a Greek word meaning ***active*** and is defined as ***capacity for performing work*** or ***ability to do work. Matter*** is ***something***

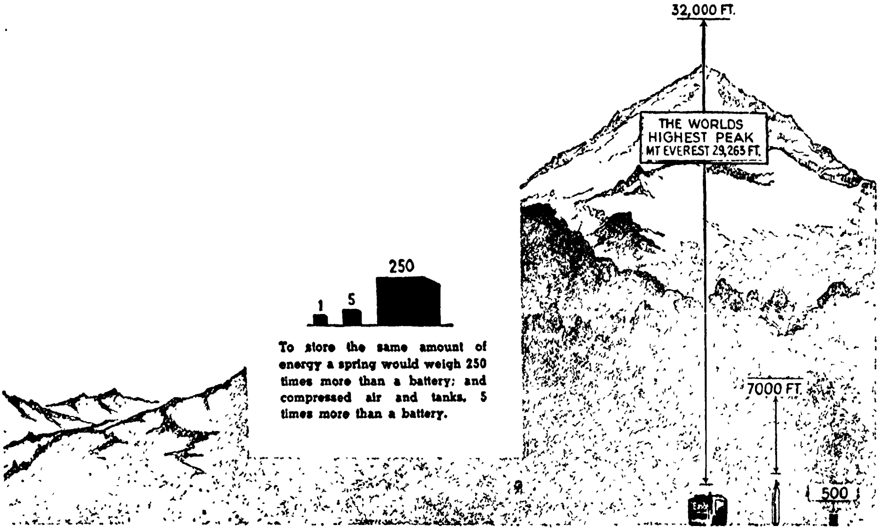
New Terms

On the first page of each chapter we shall list terms that may be new to you. If, after studying the text, the meaning of any of these is not clear, (1) consult the Glossary, (2) refer to a dictionary, or (3) ask your instructor for further explanation.

matter
energy
alchemy
metal
nonmetal
element
compound
mixture
synthesis
alloy
solid solution
chemical properties
physical properties

that has weight. Matter may be invisible; for example, air is invisible and is known to have weight. Matter may be a gas, a liquid, or a solid, and it may be dense or scattered. It has weight because of the pull of the earth on it, usually called the pull of gravity. A steam shovel weighs more than a hairpin because there is more matter, steel, in the shovel than in the hairpin. Radiations, such as light and radio waves, are not called matter. They are not subject to the pull of gravity. They are forms of energy.

Matter and Energy. Matter has mass (weight), and for ordinary purposes energy does not possess mass (weight). A piece of metal, such as a sewing needle, is matter. The needle has weight, and it has the same amount of matter whether it is hot or cold, whether it is in a high or in a low position, whether it is used as a part of an electric circuit or for sewing. When, however, the needle is hot, is at a high position, or is in an electric circuit, it has more energy than it has under the other conditions mentioned because it can do more work. The amount of energy that a needle possesses does not change the amount of material or matter in it. The explanation of the needle as a piece of steel, of how the iron for the steel was obtained from a rusty rock, and of how the "springiness" (elasticity) is produced belongs in the realm of chemistry—a study of matter. On the other hand, the explanation of how the needle may be



To store the same amount of energy a spring would weigh 250 times more than a battery; and compressed air and tanks, 5 times more than a battery.

Courtesy of Exide Battery

FIG. 2-1.—A storage battery is a reservoir of dependable power. Enough energy can be stored in a good storage battery to lift its own weight well over 32,000 ft, or over 6 miles. This tremendous power is used to perform more than 250 different jobs for modern industry.

made to float on water or of how it may be separated from a haystack belongs in the realm of physics—a study of energy.

The storage battery in the family automobile is another illustration that shows clearly the difference between matter and energy and also the different points of view of chemistry and physics. If we consider the materials of the battery plates (lead and lead oxide), the rubber case, the wooden separators, the liquid (water and sulfuric acid), and the changes in the lead, the lead oxide, and the sulfuric acid when the battery is charged or discharged, then the study of these materials is called chemistry; but if we consider the voltage and current used in charging the battery, measuring the density of the sulfuric acid and the efficiency of the battery as a source of electrical energy, then our study is called physics. (See Fig. 2-1.)

The division of physical sciences into physics, the study of energy, and chemistry, the study of matter, is for convenience. This division is an artificial one because ***chemical changes are always accompanied by energy changes.***

Courtesy of Wadsworth Antheneum

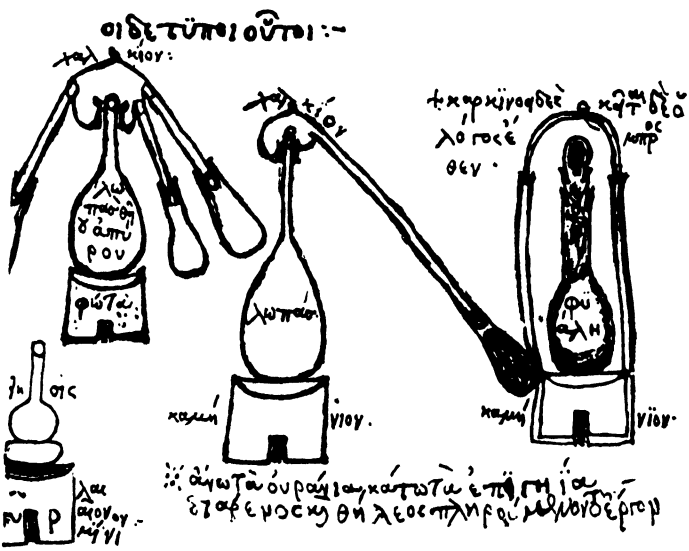
FIG. 2-2.—This wistful cat was cast in bronze in the second century B.C. in Egypt. Notice the clearness of the details that have been preserved for more than 2000 years. (From the J. P. Morgan collection.)

Primitive Man and His Knowledge of Matter. Primitive people took from their natural resources those substances which were useful to them. At first these natural materials consisted of wood, stones, animals, and plants that helped meet the fundamental needs for food, clothing, and shelter. Later, tools and weapons were sought from natural materials, also clay for pottery, and fats and oils for fuels. A great forward step in mankind's development was made when the first streak of red-colored iron oxide was used to decorate a pottery jar or to ornament a crude sketch on the walls of a cave. Later the noble metals, silver and gold, which may be found lying about on the ground if one looks in the right place, were used for ornamentation.

Still later, people discovered how to obtain useful metals from ores in which the metals are combined chemically with other substances.

Records and remains of 5000 years ago show that copper, lead, tin, mercury, zinc, and iron were obtained from ores and that useful mixtures of metals called alloys were made by melting two or more metals together. Brass (copper and zinc) and bronze (copper and tin) are examples of such early alloys. (See Fig. 2-2.) Swords and tools of fine steel were made in the ancient Syrian city of Damascus about 350 B.C. Today many primitive tribes in Africa are forgers of iron, an art they have inherited from antiquity without aid from outside civilization.

In Egypt in very early times there were many experts in practical skills. In Egyptian temples were found articles and carvings that show that the priests were skilled craftsmen. They tanned leather, made glass, pottery, and enamels, colored the surface of metals to imitate gold, and made dyes and drugs from vegetable materials. These forerunners of chemists, however, were not much concerned with the question, "What is matter?" They worked with matter and developed highly technical processes, but ideas on its composition were not brought forth until many years later.



Courtesy of General Ceramics Company

FIG. 2-3.—Byzantine chemical apparatus of the third century A.D. shows some resemblance to the apparatus of today. This equipment was used for distilling.

The Greeks. For a few centuries Greece was the cultural center of the ancient world. The Greeks, however, were not primarily workers or doers. Once a problem had been solved by thinking it through, it seemed to them unnecessary to test the solution by actual trial.

The ideas about the fundamental nature of matter that the Greeks developed came in part to them from the country that is today called

Syria and also from the Far East, India and China. Some Greek thinkers believed that all matter was made of a single fundamental material, or ***materia prima.*** Several such prime materials were suggested, and four were generally accepted: ***earth, air, fire,*** and ***water,*** the "elements" of those ancient days. (See Fig. 2-4.) Such a view seemed reasonable; for if wood is burned, earth remains in the ashes, smoke goes into the air, fire is seen, and drops of water appear for a short while at the ends of the sticks of wood.

One of the greatest of the Greek thinkers, or philosophers, was Aristotle (384–322 B.C.). He was a collector of all the information known to the ancient world. Since his writings were the only extensive source of knowledge available to many people, they were considered absolutely reliable for centuries. Many arguments were settled by the words *ipse dixit* (he himself said it); for if a statement was found in the writings of Aristotle, it was considered true without further question.

Among the teachings of Aristotle we find one that considered earth, air, fire, and water connected to the qualities of heat (hotness), coldness, wetness, and dryness. Earth was cold and dry; air, hot and wet; fire, hot and dry; and water, cold and wet. No one for 2000 years took serious exception to these descriptions, although air at times may be cold and dry and water hot or cold.

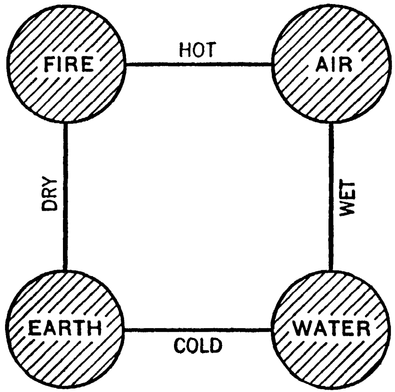


FIG. 2-4.—The ancients considered the world to be composed of just four "elements." Today we can count 92 from nature and can synthesize a few more.

QUESTIONS

1. With what does the subject of chemistry deal?

2. Define *matter; energy; substance.*

3. Give an example of changing the amount of energy in a watch; in a millpond behind a dam; in a baseball.

4. Define *chemistry; physics.*

5. List three chemical changes with which primitive man was familiar.

6. What is an *alloy?* Give an example.

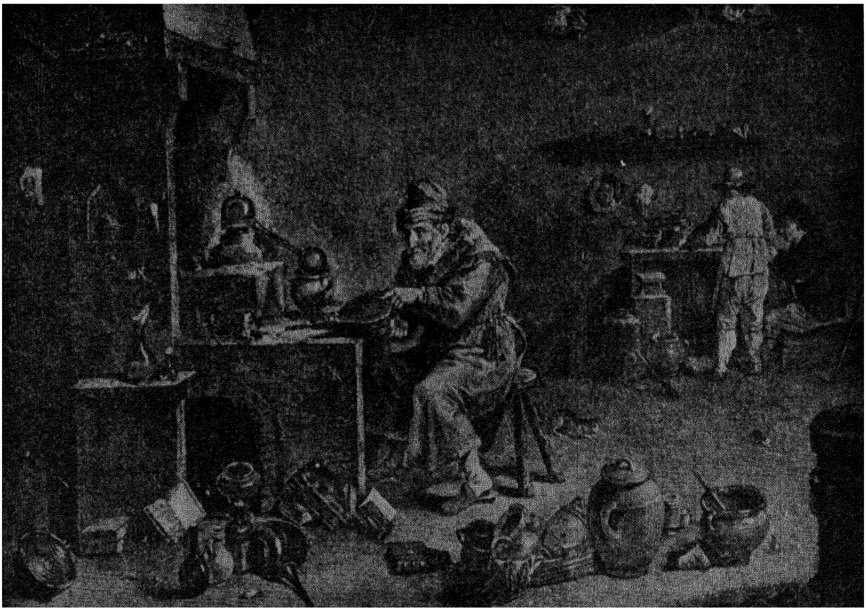
7. List five metals known in ancient times.

8. Name the most prominent person in Greek science.

9. What was the important general contribution of the early Egyptians to the progress of science? Of the early Greeks?

10. When the word *elements* is used in one of Shakespeare's plays, to what does the term refer?

The Alchemists. About 250 B.C. the city of Alexandria, Egypt, replaced Athens, Greece, as the cultural center of the ancient world. Here the famous library of 400,000 volumes was located. Here Ptolemy developed astronomy; Herophilus made the first important study of the human body, and Euclid developed geometry, with which many students have had a passing acquaintance. Here also was evolved a false logic called ***alchemy,*** practiced by ***alchemists,*** men who by a curious combination of witchcraft, magic, and experimentation tried to turn lead and other metals into gold and to find the secret of perpetual life or of renewed youth. (See Fig. 2-5.)



Courtesy of Fisher Scientific Company

FIG. 2-5.—Alchemists are the subjects of many famous paintings. These paintings are especially interesting because they reveal the same features that are found in a modern laboratory: production department, sales department, and public press (peering through the window). Note also that the apparatus is somewhat like that used today.

In other countries, too, notably China, the ideas of the alchemists had taken root independently. Is there a means of changing base metals into gold? Will anything restore youth? Is there a substance that will dissolve all others? What is the formula for immortality in this world? Such questions captivate the imagination, spur on investigation, and allure financial supporters, for would not eternal fame come to him who was able to answer even one of these questions?

Much valuable chemical information was discovered by the early alchemists, but each alchemist kept secret what he had discovered. Usually an alchemist recorded his discoveries in a mystical language full of signs and symbols so that the meaning was entirely hidden from anyone else, and after a few years even from the writer himself.

It is surprising to realize that only a century ago many people maintained alchemists as an expensive luxury, somewhat as they might maintain a stable of fine racing horses—a gamble, but one with possibilities of winning great wealth if ever the way was found of changing base metals into gold. Queen Elizabeth (1533–1603) in the time of Shakespeare took her royal lessons in alchemy from John Dee. Ponce de León (1460–1521) explored Florida in quest of the Fountain of Youth, thought by the Indians to possess rejuvenating powers. Kaiser William II of Germany (1859–1941) had dealings with alchemists. Craftiness, greed, and much ordinary "bunk" often entered into the works of the alchemists, for they had to maintain the appearance of making progress whether they were progressing or not. Otherwise, their rich patrons would withdraw support.

Alchemy, from which chemistry drew much information, was a source that we cannot always admire, although many bright spots shine out like beacons in a sea of fraud.

The Decline of Alchemy. The hold of alchemy on the imagination of the world was broken when its ideas were shown to be false. Again we find clear thinking leading the way to progress. The chief upset came when Robert Boyle (1627–1691) gave a clear definition of ***elements.*** Boyle claimed that ***elements are simple substances that cannot be broken down into anything simpler,*** are "incapable of decomposition by any means with which we are at present acquainted." His views were convincingly stated in his famous book *The Sceptical Chymist; or Chemical-Physical Doubts and Paradoxes Touching the Experiments Whereby vulgar Spargyrists are wont to Endeavour to Evince their Salt, Sulphur and Mercury to be the True Principles of Things.* He further stated that, if this definition is accepted, then the goal of the alchemists to change one element into another by chemical means is unlikely to be attained. After Boyle had published his book, the true nature of elements became known to all scientists. Boyle is often called "the father of chemistry."

Another blow to alchemy was the establishment of the law of the conservation of matter. This law claims that ***matter cannot be created or destroyed.*** Matter is eternal, never disappearing from the universe, although it may change its form. In other words, we cannot by chemical means get something for nothing or make something disappear into nothing at all. The law of conservation of matter also upset the ideas of Aristotle and lifted alchemy, an art, to chemistry, a science. The classic elements, earth, fire, air, and water, were replaced by the chemical elements of today—elements that had earned their right to their names by withstanding all chemical attempts to decompose them.

The Effect of an Idea. Technical knowledge continued to advance slowly, and 18 centuries after the Greek philosophers came another important forward step in man's conquest of matter. Before people can act intelligently they must have ideas; the world's great thinkers have ever been the source of ideas about fundamental truths. In the latter part of the sixteenth century, Francis Bacon (1561–1626) gave to the world a method for gathering more facts about matter. Bacon's directions sound simple today because they are so obvious; but at the time he lived they were quite new. He said that, if we wish to find out more about the ways of nature, we must carry on experiments; he maintained that this is the way to gather facts with which we can reason. Because of this contribution to science study, Bacon has been called the "herald of modern science." For about 150 years little was done with this thought of Bacon's but it gave good results promptly when put into practice.

QUESTIONS

11. State clearly the contribution of Francis Bacon to the progress of science.

12. Name two possible places where the early study of alchemy may have originated.

13. What were some of the aims of the alchemists?

14. Did the alchemists make any real contributions to the development of chemistry?

15. Did any alchemist succeed in making gold from lead?

16. Who is called the *herald of science?* The *father of chemistry?*

17. What definition of an element was given by Boyle?

18. State the law of conservation of matter.

19. List two factors in the decline of alchemy.

20. Did alchemy develop into chemistry, or are alchemy and chemistry two separate developments?

MORE CHALLENGING QUESTIONS

21. Distinguish matter from energy.

22. Distinguish matter from weight.

23. What factors in the problem of deep-sea diving would be considered from the standpoint of chemistry? From the standpoint of physics?

24. Point out why the possibility of changing base metals into gold seemed reasonable to the alchemists.

Elements. The entire world is composed of elements, 92 of which are known to exist naturally. No other natural elements have yet been discovered anywhere in the universe. Each consists of 100 per cent of that element, and that element only. Each one is a distinct kind of matter.

For convenience the elements may be sorted into two main groups, ***metals*** and ***nonmetals.*** We all know of copper, tin, aluminum, silver, iron, and other metals. These substances, if pure, are elements. Metals possess a bright, metallic luster and are good conductors of electricity. Sulfur, a yellow material, and phosphorus, of which the red coating on safety matchboxes is composed, are well-known nonmetals. (See Fig. 2-6.) Other common nonmetals are helium, neon, chlorine, oxygen, and carbon (diamond). Nonmetals do not have a silvery luster, and they do not conduct electricity.

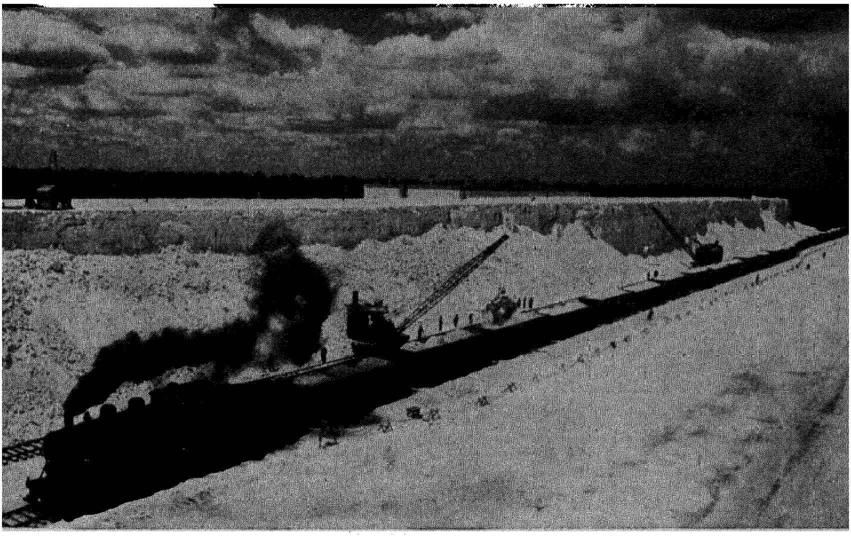

*Courtesy of Texas Gulf **Sulphur Company***

FIG. 2-6.—An enormous block of a single element, sulfur, dwarfs a railroad train and workmen. It is almost 100 per cent pure. Most of it will be made into sulfuric acid.

These 92 elements, primary substances, are foundation materials—building units—for more complicated substances. Like bricks that make up a building, they can be examined in detail, but they are essential parts of the whole. The science of chemistry is devoted to the study of the elements and their interactions.

We find out which elements are present in a given substance by ***analyzing*** it. The attitude of the chemist toward matter is somewhat like that of a small boy toward a watch; he wants to take it apart to see what makes it tick, or, more technically, to analyze it.

The elements in the outer portion of the earth, usually referred to as the "earth's crust" but including the sea and air, are estimated to be present in the percentages given in the following table.

ELEMENTS PRESENT IN THE EARTH'S CRUST

	Per Cent		Per Cent
Oxygen	49.2	Potassium	2.4
Silicon	25.7	Magnesium	1.9
Aluminum	7.5	Hydrogen	0.9
Iron	4.7	Titanium	0.6
Calcium	3.4	Chlorine	0.2
Sodium	2.6	Phosphorus	0.1
			99.2

A complete list of the elements is found in the Appendix. The 80 remaining elements taken together make up the residue of the 0.8 per cent not accounted for by the table above. The relative abundance of an element, however, does not determine its usefulness. Carbon makes up about 0.04 per cent of the whole earth, as shown in the table below, and less than 0.1 per cent of the earth's crust; yet were it not for this element it is likely that no life could have developed on the earth, since carbon is an essential element in all living matter.

H. S. Washington of the Geophysical laboratory, Washington, D.C., made the following estimate of the composition of the entire earth:

COMPOSITION OF THE WHOLE EARTH

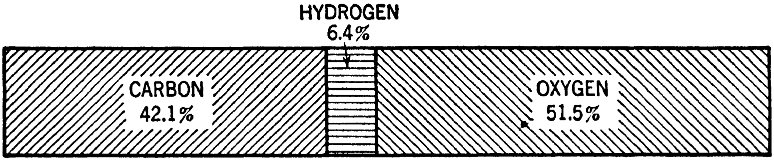
	Per Cent		Per Cent
Iron	39.76	Sodium	0.39
Oxygen	27.71	Cobalt	0.23
Silicon	14.53	Chromium	0.20
Magnesium	8.69	Potassium	0.14
Nickel	3.16	Phosphorus	0.11
Calcium	2.52	Manganese	0.07
Aluminum	1.79	Carbon	0.04
Sulfur	0.64	Titanium	0.02
			100.00

How Elements Are Found. We should not assume that all elements are found free, or uncombined, under natural conditions. A few are (although they may be part of mixtures), but most of the elements are in compounds, chemically combined with other elements. We see the bricks in a brick house joined to other bricks of the same or a different kind. Sometimes, however, we see a pile of individual bricks not part of any structure. Similarly, the elements are most often found joined with others in compounds; only occasionally do we run across an element uncombined or free. From certain rocks near Lake Superior a person may dig out chunks of fairly pure, free, or native copper, a common metallic mineral. More often, as in Montana and in South America, we find compounds containing copper combined with another element (oxygen or sulfur), forming dazzling bits of purple or soft green-colored rocks.

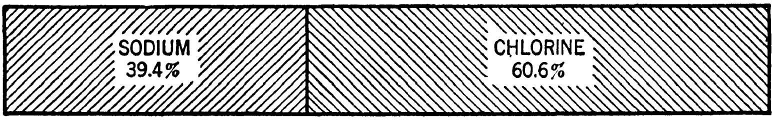
Compounds. Table sugar is a compound. As anyone knows who has spilled sugar on a hot stove, the compound decomposes when heated. A black substance, the element carbon, remains. Some of the carbon and the other elements—hydrogen and oxygen—in the sugar have been driven off by the heat into the air in the form of water vapor and flammable compounds.

As has been previously stated, elements are usually found in union with other elements. ***Substances composed of elements joined together chemically are known as compounds.***

Constant Composition of Compounds. Furthermore, chemists have discovered that the elements in a compound are not joined together in haphazard amounts. The amount of carbon in table sugar is always 42.1 per cent by weight, the same for every pure sample of sugar. This percentage by weight of the elements in a compound we cannot change by any known means. Salt, another compound, always contains 39.4 per cent of the metal sodium and 60.6 per cent of the nonmetal chlorine. (See Fig. 2-7.) In other words, the composition of a compound, if pure, always contains a definite percentage of each element. ***In a given chemical compound the elements are always present in the same proportion by weight.*** This statement is known as the ***law of constant composition.***



COMMON TABLE SUGAR, $C_{12}H_{22}O_{11}$



COMMON TABLE SALT, NaCl

FIG. 2-7.—Every compound has a definite composition by weight. Common salt contains 39.4 per cent of sodium and 60.6 per cent of chlorine; table sugar contains 42.1 per cent of carbon, 6.4 per cent hydrogen, and 51.5 per cent oxygen.

Certainly sugar is not like carbon, for sugar is comprised of white crystals, while the carbon that is left when sugar is heated is a black solid of irregular shape. Water is not like oxygen, for water is a liquid that puts out fires, while oxygen, an element in the compound water, is a gas that makes fires burn better. A compound is a distinct substance. It is like itself only; that is, it has its own properties. A given compound is the same substance regardless of its source, provided that it is pure.

How Compounds Are Made. Making a compound may be demonstrated by a simple experiment.

Let us put a thin sheet of copper foil, an element, into a jar of pale-green chlorine gas, another element. The copper glows brightly, and it may become hot enough to melt as it joins chemically with the chlorine. (See Fig. 2-8.) Bits of a brownish-white solid, the compound copper chloride, are seen around the jar. When water is added a blue color develops as the copper chloride dissolves. The color is intensified by the addition of ammonia water.

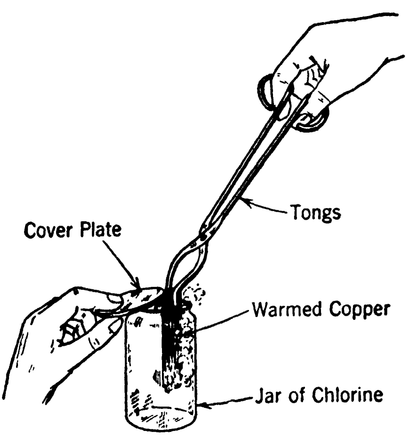


Fig. 2-8.—Copper burns in chlorine, forming copper chloride. This is an example of the direct union of two elements to form a compound.

When sulfur is rubbed on a cleaned silver coin (90 per cent silver), a black compound, silver sulfide, forms. Silvery mercury warmed in a test tube with steel-gray iodine forms red or yellow mercury iodide.

Many thousands of compounds are known. A few can be made directly from the elements by causing them to combine, as in the examples above. In the study of chemistry we may be inclined to emphasize these simple cases. However, we should not forget two facts: (1) Not all elements combine to form compounds directly. (2) Compounds are often obtained from other compounds.

The creating of new compounds, some of which may be of the greatest service to mankind, is one of the most interesting responsibilities of chemists. Sometimes, indeed, compounds that exist in nature may be prepared more cheaply in the chemical laboratory than they can be prepared from natural resources. Indigo produced in a dye factory can be sold for 12 cents a pound; but before this artificial product was put on the market, natural indigo was selling for $4 a pound. In 1897 a million acres of land in India produced a crop of indigo worth 20 million dollars. Twenty years later India's production had shrunk about 99 per cent. While this may be unfortunate temporarily from the point of view of some of India, it is a triumph for chemistry.

We call the manufactured indigo dye just mentioned ***synthetic*** indigo as compared with ***natural*** indigo. This distinction tells something about the different sources of the materials. The materials themselves are identical. We often read into the word synthetic a meaning that it does not have. Many vegetable shortenings that are sold in cans or jars at grocery stores are synthetic. Synthetic substances are made by putting together simpler substances. Synthetic is not the same as ***substitute,*** and neither word, synthetic or natural, means ***inferior.*** Often synthetic products are of greater purity than the natural products. ***Synthesis*** is a putting-together process; it is the opposite of ***analysis.***

QUESTIONS

25. Name a metal that is an element in addition to those mentioned in the text; a gaseous nonmetal that is an element.

26. Define *analysis; synthesis.*

27. What four elements are most abundant in the earth's crust?

28. What percentage of the earth's crust is composed of metals?

29. Fluorine is the most active nonmetallic element. Is it found in nature free or combined? Explain.

30. What percentage of table sugar is not carbon?

31. A few elements are mentioned in the Bible. Are these more likely to be found free or combined in nature?

32. When 32.5 pounds of zinc is heated with 16 pounds of sulfur, a compound forms. What percentage of metal does it contain?

33. Pure marble (calcium carbonate) contains 12 per cent carbon, 48 per cent oxygen. What percentage of calcium is present?

34. List some characteristics of metals; of nonmetals.

Names of Simple Compounds. Compounds contain two or more elements. Water contains two, hydrogen and oxygen. We name many compounds of two elements by stating the name of the metal or the element corresponding to the metal first. The ending of the name of the other element is changed to ***-ide.*** Water is dihydrogen ox***ide.***

What elements are present in common salt (sodium chloride)? In silver sulfide? In mercury iodide?

Many compounds that have three elements are given the ending ***-ate.*** Such compounds are composed of a metal, a nonmetal, and oxygen. An examination of the name of the compound will tell what two elements are present in addition to oxygen. Potassium nitrate contains potassium, nitrogen, and oxygen.

What elements might one expect to be present in sodium carbonate (washing soda)? In copper sulfate (blue vitriol)? In potassium chlorate?

Mixtures. Nature provides us with elements and compounds, but seldom are these elements and compounds found pure. Rocks, for example, are usually streaked with impurities; plants consist of many parts—roots, stems, flowers, leaves. Nature as we find it is seldom uniform to any great extent.

The soil under our feet is not one definite substance but is made up of several sorts of matter—clay, sand, water, and assorted bits of decayed vegetable matter called humus. Soil is a mixture composed of particles of different sorts. Such a material, made of particles unlike each other, is called a ***nonuniform*** mixture. Salad, hash, and almost all our foods are mixtures. Each substance in a mixture retains the properties that it had before it became part of the mixture. The substances mixed are not chemically combined; they are just scrambled.

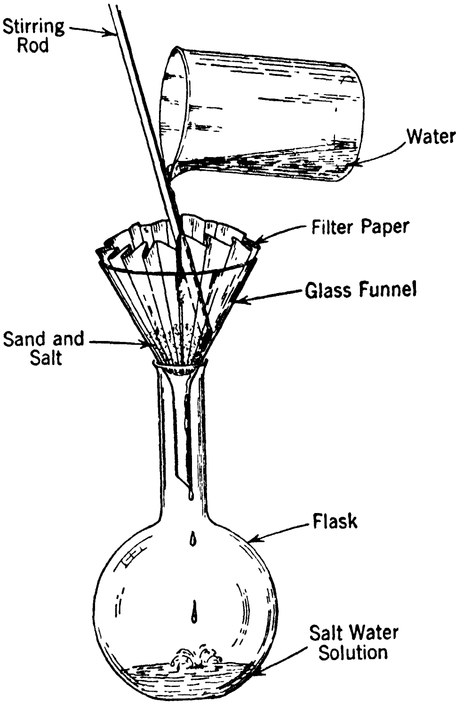


FIG. 2-9.—The properties of salt are different from the properties of sand. This enables us to separate a mixture of the two.

We can make a mixture by stirring dry sand and salt together. This mixture can be separated by placing it in a funnel in which a filter paper is inserted. (See Fig. 2-9.) When water is poured through the filter, the salt dissolves, leaving the sand on the paper. The salt may be obtained in the dry condition by evaporating the water from the filtrate. The salt and sand together form a nonuniform mixture, and the salt water is a uniform mixture. Both mixtures may have varying composition.

In addition to nonuniform mixtures, there are mixtures that are entirely the same throughout. These are called ***uniform*** mixtures.

If we stir a little sugar in water until it is dissolved, we have made a sugar solution. This solution is perfectly uniform; every drop is like every other drop, even when examined under a microscope. We can mix together 1 per cent of sugar and 99 per cent of water, 2 per cent of sugar and the rest water, and so on, up to the limit of the dissolving ability of water for sugar at the temperature at which the experiment is being performed. The uniform mixture will pass through filter paper without separation of the sugar from the water.

Mixtures, such as sugar and water, have the appearance of compounds because of their uniformity throughout. The distinguishing feature, however, is the fact that the percentage composition by weight of mixtures is not fixed. The composition of a solution may be varied by the person who makes up the solution. Brine for making pickles, sirup with canned fruit, and the contents of a bottle of a carbonated beverage are other examples of solutions that may have varying composition.

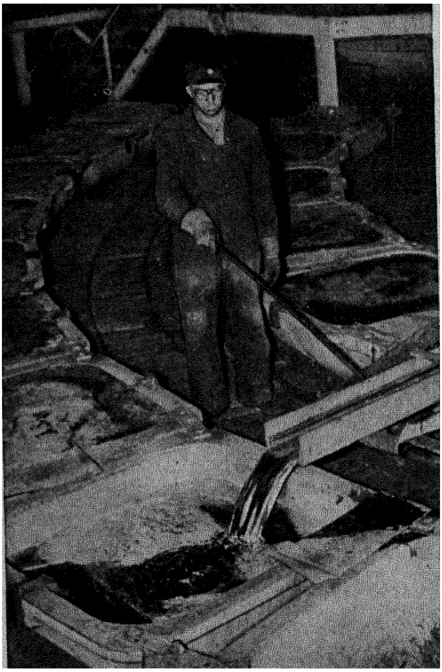
Another sort of uniform solution is interesting. When metals are melted and thus become liquid, some dissolve quite well in one another. When such a solution is cooled and hardened, frequently no separation occurs and we have a mixture of metals called a ***solid solution.*** Brass, composed of copper and zinc, is a familiar example. When these two metals are melted together and cooled, an ***alloy*** is produced that is composed of copper and zinc not chemically combined, yet with uniform color and properties throughout the piece as far as the eye or microscope can tell. The composition of brass, however, may be varied, depending upon the purpose for which the material is made. Brass, therefore, is a mixture, a solid solution, not a true compound. All the alloys used in the United States coins contain usually two, sometimes three, metals in solid solution.

What Are the Properties of Matter? Let us recall the fundamental nature of matter. It has weight. Yet when we know the weight of a bit of matter, much more remains to be told in order to give a complete description of it. For example, matter occupies space; it may exist in any of three states, solid, liquid, or gaseous; it may be colored or colorless, transparent or opaque; and it may or may not possess odor. It is said that Thomas Alva Edison (1847–1931), the famous inventor, knew more about substances than any other person. He knew the ***physical properties*** of color, odor, taste, density, solubility in water, boiling and melting temperatures, and many others that are used in describing different sorts of matter. He also knew how substances act in chemical changes. These are the ***reactions*** described under the heading of ***chemical properties.***

Classification of Matter as Solid, Liquid, or Gas. Most people know iron as a solid; yet at foundries workers are familiar with the liquid iron that is poured into molds to make iron castings. We also know that iron exists in gaseous form, for astronomers have detected this element on the sun. Water, usually liquid, quite often freezes to form solid ice and may easily be boiled to form water vapor, a gas. Water is one of the most familiar examples of a substance that may exist in all three states of matter, and it may exist in these three states simultaneously at a single temperature, 0 degrees centigrade (°C).

Not every substance is known to exist in all three states of matter, however. Mercury oxide decomposes before it can be changed into the gaseous state.

Matter can be thus classified according to physical state as solid, liquid, or gas. In spite of the fact that the state of matter is entirely dependent upon the ***conditions*** of temperature (see Fig. 2-10) or pressure, we consider that the state in which a substance exists at room temperature and atmospheric pressure is the usual one.



Courtesy of Anaconda Copper Mining Company

FIG. 2-10.—Lead, a metallic element, becomes liquid when heated and can be cast into ingot molds. Each ingot shown here weighs 4 tons.

Changes in Matter. Children grow, leaves change color, wood rots, food digests, milk sours, and many other examples show that even the complicated processes of life itself involve chemical changes. We are familiar with the fact that matter is everywhere in the process of building up or tearing down, uniting, separating, or transforming. This process of change that matter undergoes is a part of chemistry, of equal importance with the study of the composition of matter.

Two sorts of changes in matter may be noted: (1) those which are accompanied by a change in the composition of matter and (2) those in which no change in composition occurs. In the former, new substances are produced, while in the latter no new ones are formed. ***Changes in matter that are accompanied by a change in composition are called chemical changes: other changes are called physical changes.***

When water boils or ice melts, no new products are formed, since ice, water, and steam are each composed of hydrogen and oxygen in the same proportions by weight. If silver is heated to redness, no change in composition occurs: only silver remains after it has cooled. These changes are therefore physical changes. On the other hand, when sugar is heated on a hot stove, carbon is formed as well as water vapor and flammable gases. Here a change in composition has taken place. Also, when iron rusts, it combines with oxygen in the air, forming the product iron rust. Again a change in composition has taken place. These are chemical changes. A chemical change involves the disappearance of the original substances and the appearance of new substances, different in composition and in properties: the same elements are present after a chemical change, but they have been rearranged to form new substances.

It is interesting to note that changing the physical condition of temperature changes all the physical properties of a substance to a smaller or greater extent.

Conservation of Matter. Let us place a small test tube containing lead nitrate solution and another test tube containing potassium chromate solution in a flask in such a manner that the solutions do not mix while the tubes are nearly upright. (See Fig. 2-11.) Then let us set the apparatus on one pan of a balance and carefully weigh it by placing the necessary weights on the other pan. We now remove the flask and tip it so that the solutions in the two tubes run together, allowing, however, nothing to leave the apparatus. A bright-yellow, fluffy solid, lead chromate, forms in the liquid. A new substance has appeared, showing that a chemical change has taken place. When replaced on the balance

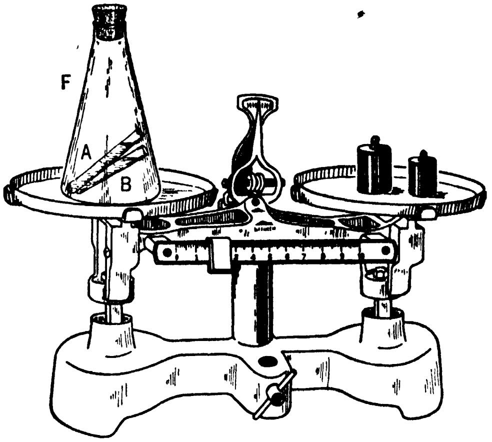
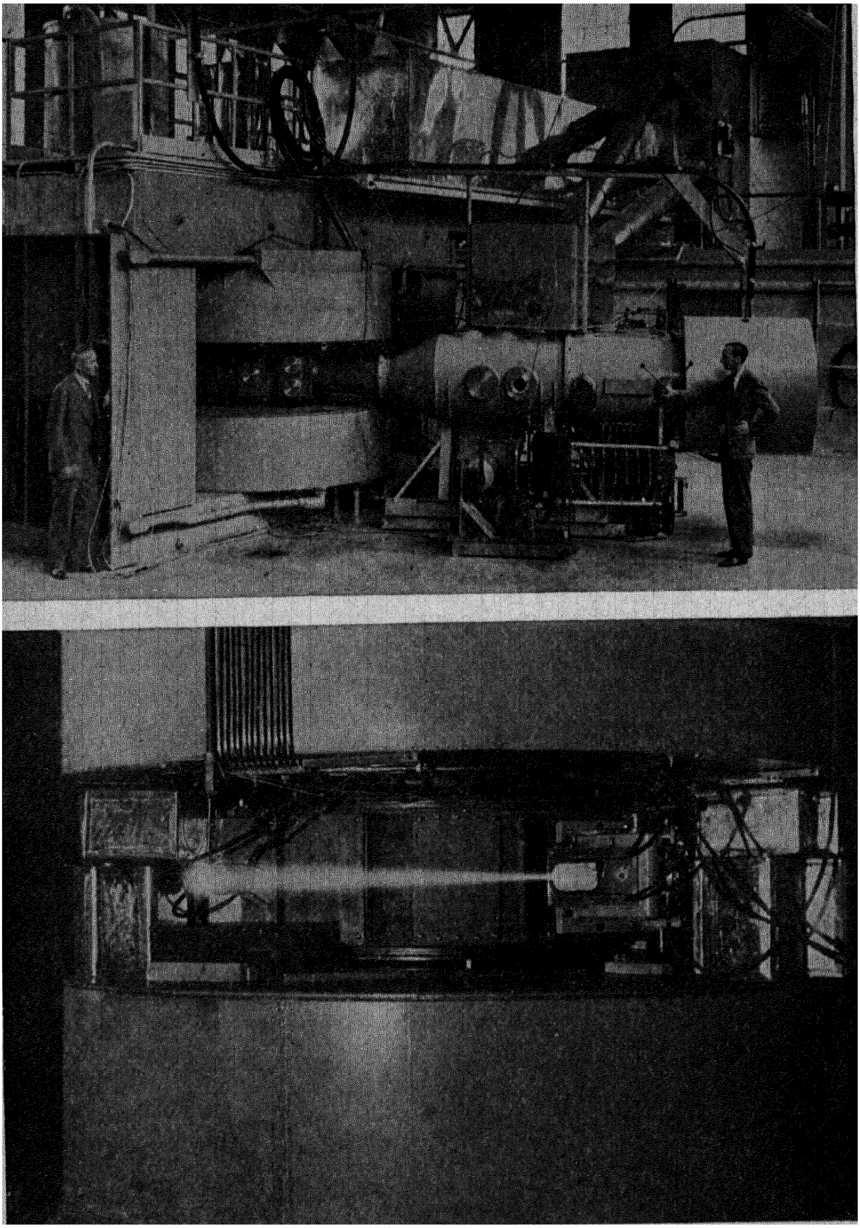


Fig. 2-11.—The weight of all the substances taking part in a chemical change is precisely the same as the weight of the products of that change.



Courtesy of University of California

FIG. 2-12.—The upper picture shows a general view of a cyclotron, an apparatus in which tiny positively charged particles are accelerated to very high velocities. The speeding particles smash into atoms and break a few of them. By examining the wreckage, scientists learn about the structure of the atom. Lower view shows the active beam of particles emerging from the machine.

pan, the apparatus is found to weigh exactly the same as previously. Nothing has been gained or lost. The weight of the substances that entered the chemical change is the same as that of the substances produced by the change.

Antoine Laurent Lavoisier (1743–1794), one of France's greatest scientists, was quick to realize the importance of the balance in chemical experiments. In his experiments he used the best balances to be found at the time in all Europe and relied on the results he obtained by their aid. Lavoisier concluded, "One may take it for granted that in every reaction there is an equal quantity of matter before and after the operation."

Since Lavoisier's time a great many chemical changes have been studied, some of them taking place entirely on the pan of a balance. The weight of the substances entering into the change and the weight of the products formed have been carefully determined. In each case a remarkable agreement exists: the total weight of the products is exactly equal to the total weight of the substances entering into the change. Although its form may be altered, ***matter cannot be created or destroyed*** in chemical reactions. This is known as the ***law of conservation of matter.***

Very careful experiments in physics and chemistry give evidence that this law may not describe the conditions on the sun and other stars where matter is believed to be destroyed to produce energy. Energy, once matter, is thrown out from the sun into space as heat, light, and other radiations. The opposite change, the creation of matter from energy, is assumed to exist somewhere in the universe, according to the observations of astronomers. When atom-smashing machines like the cyclotron are used, neither the law of conservation of matter nor the law of conservation of energy alone holds strictly true; but when they are combined under the law of conservation of mass-energy, the principle holds true exactly. Matter and energy in extreme cases may thus be connected one with the other. (See Fig. 2-12.)

Classification of Matter According to Composition. The classification of matter according to composition can be summarized by this table:

ALL MATTER

Nonuniform samples of matter	Uniform samples of matter		
MIXTURES	MIXTURES	COMPOUNDS	ELEMENTS
(Composition not definite) *Hash* Some alloys, such as *Steel*	(Composition variable) (1) Liquid solutions *Bottled soda water* (2) Solid solutions *Sterling silver* (an alloy)	(Composition fixed) Can be decomposed *Pure water*	(Simplest form of matter) Have not been decomposed by chemical means *Aluminum*

SUMMARY

Chemistry is the study of matter, especially a study of changes in the composition of matter. Matter is something that has weight (mass). Physics is the study of energy. Energy is capacity for performing work.

As early as 3000 B.C. man could obtain copper, lead, tin, mercury, zinc, and iron from their ores and mix them to form alloys. Early Egyptians were especially skilled as craftsmen. The arts of tanning leather, of coloring the surface of metals, of obtaining vegetable drugs and dyestuffs, and of making glass, pottery, and enamels were known by them. The ancient Greeks were interested in determining the nature of the fundamental substances. Aristotle conceived of only four "elements"—earth, air, fire, and water.

Alchemy, a false logic, arose in Alexandria in the third century B.C. and independently in China. Its aim was to discover a means of converting base metals into gold and to find the secret of perpetual life. Alchemy declined in the seventeenth century upon the acceptance of two discoveries:

1. Robert Boyle defined an element as a simple substance that cannot be broken down into anything simpler.
2. The law of conservation of matter stated that matter cannot be created or destroyed.

In the late sixteenth century Francis Bacon proposed experimentation to determine facts about nature.

All materials in the entire world are composed of elements. Ninety-two elements are known to exist naturally. Elements may be classified as metals and nonmetals. Most elements are found in compounds, although a few are found free.

Compounds are substances composed of two or more elements joined together chemically. The determination of the composition of compounds is aided by the process of analysis as well as by synthesis. In a given chemical compound the same elements are always present in the same proportions by weight. Compounds are distinct substances, each with its own properties. Thousands of compounds are known: some may be made by direct synthesis, that is, putting together elements or simpler compounds. The name of a compound composed of two elements ends in ***-ide,*** for example, silver sulfide, composed of silver and sulfur. Some simple compounds composed of three elements end in ***-ate,*** for example, potassium chlorate, composed of potassium, chlorine, and oxygen.

A mixture is a combination of substances in which each retains for the most part its individual properties. No chemical change takes place when a mixture forms. A nonuniform mixture is one in which are found several kinds of particles, unlike each other, for example, soil. A uniform mixture is entirely the same throughout. A solid, uniform mixture is called a solid solution. Alloys may be either uniform or nonuniform.

Physical properties of matter include color, odor, taste, solubility in water, density, and melting and boiling points. Chemical properties are the behavior in chemical reactions called chemical changes.

Chemical changes are those which are accompanied by a change in composition. New substances are formed. Relatively large amounts of energy are involved. Physical changes do not involve a difference in composition. No new substance is formed. The amount of energy required to cause a physical change to occur is small. Although its form may be altered, matter can neither be created nor destroyed, and no change in total weight occurs in a chemical change. (Law of conservation of matter.)

Matter may be classified according to physical state as solid, liquid, or gas. Matter may be classified according to composition as nonuniform mixtures, and uniform mixtures, compounds, and elements.

QUESTIONS

35. What elements are present in the following compounds: iron sulfide, calcium phosphide, sodium bromide, magnesium nitride, lead chloride?

36. Give a name to a compound composed only of (*a*) potassium and chlorine, (*b*) magnesium and bromine, (*c*) copper and chlorine, (*d*) lead and oxygen, (*e*) sodium and iodine.

37. What elements are present in each of the following compounds: potassium sulfate, copper nitrate, zinc sulfate, lead carbonate, tin oxide?

38. Define *element; compound; mixture.*

39. Classify as element, compound, or mixture, using three columns: soup, potassium chloride, zinc; bronze, lead, bread, sugar, salt, hydrogen, calcium hydroxide.

40. What facts about a substance are listed as physical properties? As chemical properties?

41. Name three states of matter. May all substances exist in all three states? Explain.

42. Give an example of a chemical change not mentioned in the text.

43. Distinguish a chemical from a physical change.

44. Are changes of ice to water, to steam, chemical or physical?

MORE CHALLENGING QUESTIONS

45. A certain ore is 50 per cent zinc oxide. Zinc oxide contains 67 per cent zinc. The process of recovery of metal from the oxide is 80 per cent efficient. What percentage of metal is obtainable when based on the weight of the original ore?

46. Carefully define: *synthetic; inferior; substitute; alternate; natural; ersatz.*

47. What elements are present in the following compounds: silver chromate, sodium zincate, potassium aluminate, calcium tungstate, lead arsenate, sodium vanadate?

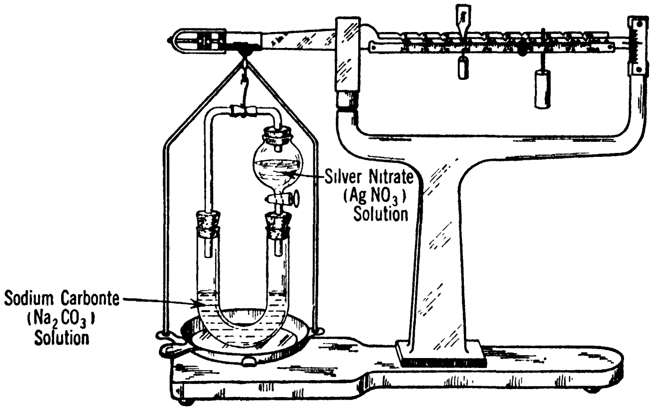
48. Classify the following as element, compound, or mixture, using three columns: a dime, sterling silver, aluminum, yeast cake, baking powder, baking soda, cake, soap, sea water, iron. Use a dictionary or the wrapper of the product, if available, for needed information.

49. When a stick of wood burns, it undergoes an extensive change. The ashes weigh much less than the original wood. Is this observation contrary to the principle of conservation of matter? Explain.

50. Classify as physical or chemical changes:

burning a candle
glowing of a tungsten filament
boiling water
decaying of fruit
glowing of a neon sign
rotting of eggs
souring of milk
tarnishing of silver
licking a postage stamp
drying of clothes
exploding a bomb
burning gasoline
flowing of water in a brook
making fudge
soaking up ink with a blotter
glowing of phosphorus
decomposing water by an electric current
making caramel candy
drying of house paint
action of sunlight on a light-intensity meter

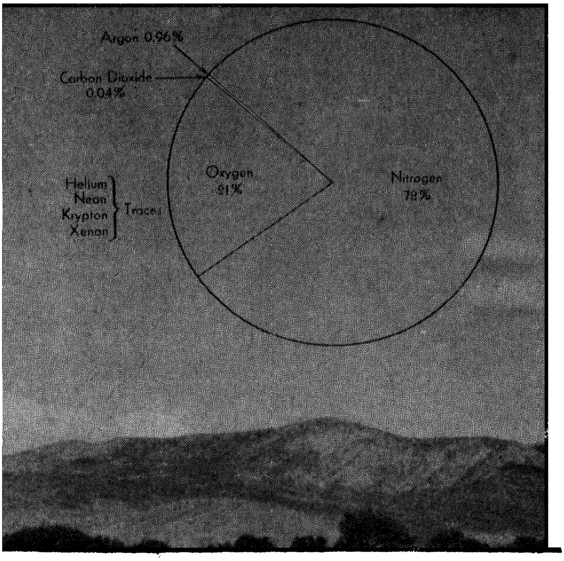
51. Figure 2-13 illustrates an apparatus that may be used for showing the principle of conservation of matter. Explain its operation.



Courtesy of Hermann Bernhardt

FIG. 2-13.—A closed system is suspended on the pan of a balance and counterpoised. The two solutions are allowed to run together and react. After the chemical change, has a change in weight taken place?

UNIT ONE

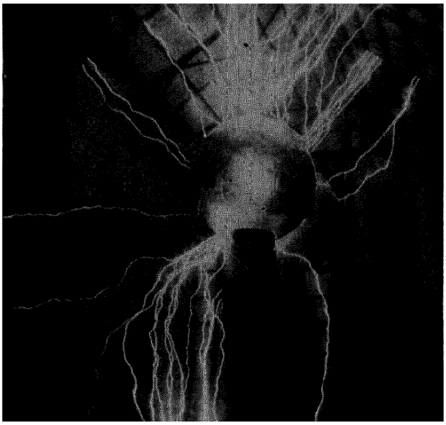


Courtesy of Caterpillar Tractor Company

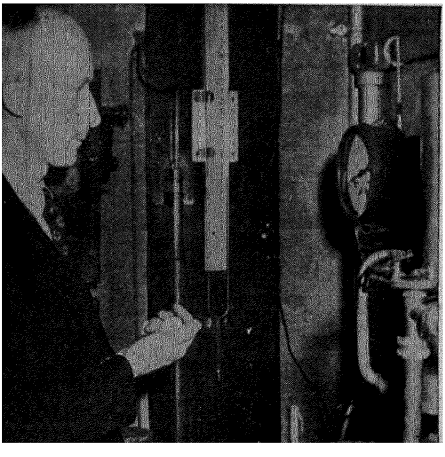
OUR ESSENTIAL ENVIRONMENT

Our environment, or surroundings, consists of air, various solids, more or less water, and living creatures. It is the purpose of this unit to describe environment from the standpoint of chemistry. Thus we may become better acquainted with the sort of planet we inhabit.

Curiosity impels scientists to find out more about our surroundings. Amazing voyages are made high into the stratosphere. Drillings, at enormous expense, reach 3 miles below the surface of the earth. Both geographical poles have been reached. The bathysphere penetrates deep under the sea. The snow cruiser trudges its path over the frozen antarctic wastes. Self-recording instruments parachute from observation balloons. Few unexplored wildernesses remain on earth. A challenge, however, still remains in the field of science. Here we know a little, but our knowledge ends abruptly. It is safe to predict that the greatest discoveries in science are yet to be made.



Many ways have been devised to study our surroundings. The above photograph shows how our electric environment is studied by putting enormous electrostatic charges on hollow metal globes. The charge is shown leaking to the metal frame of the building that surrounds the apparatus. Some of the oxygen of the air is changed into ozone by the electrical energy.



Courtesy of Port of New York Authority

A chemist of the Port of New York Authority is checking the accuracy of the analyzing instruments used to measure the concentration of poisonous carbon monoxide gas in the Holland Tunnel. If the concentration of carbon monoxide rises above a safety margin, the analyzers should operate in such a manner that a warning bell rings.

The fruits of scientific curiosity have been put to various uses. Two atomic bombs stopped a war. The sea has become an inexhaustible mine of chemical treasure. The airways have become travel routes now that strong, tough, light metals can be produced.

A generation ago no one knew the healing powers of penicillin. Two generations ago color photography was not practical. Three generations ago there was no rayon, much less nylon or vinyon, silicone ("bouncing putty"), or insulin. Almost a century ago the first coal-tar dye brightened the colors of a cotton dress. No one who sat around a campfire during the American Revolution could explain just what sort of chemical change was going on in that fire.

Whether we make a fire or cook with one, dye cotton cloth or wear dyed rayon, enjoy the healing of a sulfa drug or aspirin, we are taking advantage of a controlled chemical change. Controlled chemical change is the theme of chemistry for our times.

UNIT ONE - - - - - - - - - - - - - - - CHAPTER III

THE AIR

Living creatures as we know them exist on the earth because conditions favorable to them are present. That the mysterious spark of life may exist, warmth and light from the sun, food, air, and an orderliness in nature are necessary. Without food, but with plenty of water and air, a person may live for about 30 days. With no water whatever, but with air, a person may live a few days. But without air a person suffocates in 10 minutes or less. Air, therefore, is one of the essentials of the environment of human beings. It is thus fitting that a study of air should form the starting point of our introduction to chemistry.

Breathing. All the higher animals (including ourselves) need air. Air surrounds the animal and penetrates his body to some extent. By the breathing motions air is alternately pumped into the lungs and forced out again. The animal uses from the air part of the ***oxygen*** (about 5 per cent), a bit of the ***carbon dioxide,*** which seems to act as a stimulus to the breathing process, but none of the ***nitrogen.*** The air breathed out contains considerably more carbon dioxide and moisture than that taken into the lungs and, as a rule, is warmer.

Air is a mixture of gases. About 78 per cent by volume of dry air is nitrogen; 21 per cent by volume is oxygen; 0.9 per cent is argon and a few other argonlike gases; and 0.03 to 0.04 per cent is carbon dioxide. The air also contains water vapor in varying amounts.

We may be surprised to learn that plants breathe, also. Oxygen is taken in, and some of this gas is changed and sent out again as carbon dioxide. Plants have another process of gas exchange in which the opposite action takes place; carbon dioxide is taken in, and oxygen is given out. In sunlight this second process goes on more rapidly than the first;

New Terms

oxygen
carbon dioxide
nitrogen
stratosphere
catalyst
inert
ammonium nitrite
fixation of nitrogen
argon
helium
spectrum
radioactive
neon
krypton
xenon
radon

therefore, plants on the whole take in more carbon dioxide and breathe out more oxygen than they absorb. This process continually renews the supply of oxygen in the air and furnishes carbon for the plants to build their tissues.

If we place a quantity of water in a flask and seal it with a stopper, air remains above the water. (See Fig. 3-1*a*.) Vigorous shaking causes some of the air to disappear into the water. Such air is said to be dissolved in water. If we allow the flask to stand or heat it slightly, bubbles of air leave the water and collect on the inside of the glass below the surface of the water. (See Fig. 3-1*b*.)

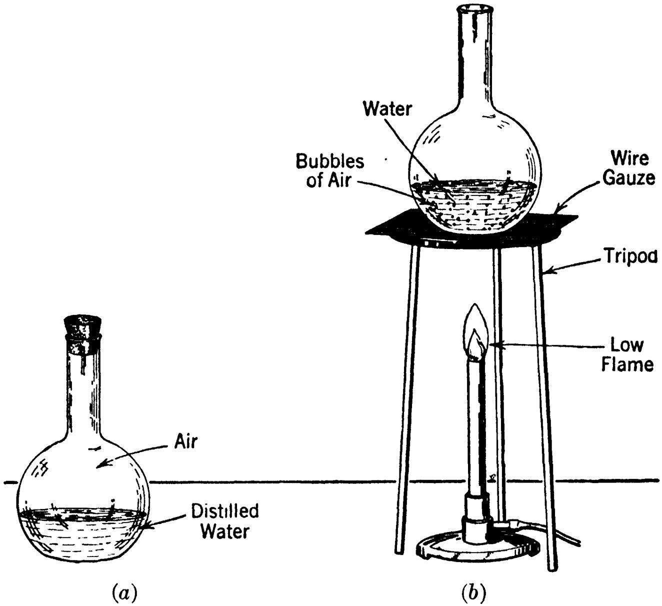


FIG. 3-1.—(*a*) Air can be dissolved in water by shaking the two together. (*b*) Dissolved air leaves water when heated.

Some of the oxygen in the air dissolves in water. Fish and other aquatic creatures use this dissolved oxygen for their breathing. Fish will die of suffocation if the water contains no dissolved oxygen.

Air Around the Earth. Air penetrates the earth to some extent. Tiny cracks in rocks allow it to penetrate deep into the underlying rock layers. It also penetrates the soil and furnishes oxygen necessary for the roots of plants. The need of plants for air is one of the reasons for plowing and harrowing the soil.

The air surrounds the earth and revolves with it. The height to which it extends upward is limited: we know that about one-half of the air is below a height of 3.6 miles (5.8 kilometers).[1] We live at the bottom of

---

[1] See Appendix for explanation of metric system of measurement.

the layer of air and in that part which has the greatest weight for a given volume—that is, in the densest part. Above 6 miles (10 km) the air is very thin (of low density), intensely cold [−55° Centigrade (C) or −67° Fahrenheit (F)], and unable to support human life. This layer of air is called the ***stratosphere.*** It has been investigated by daring explorers, especially the Piccards of Belgium and the United States and Capt. Stevens and others of the United States. As high as the stratosphere is above the earth, evidence shows that life exists even there, for bacteria and spores have been found at this great altitude. The air gets thinner and thinner as one ascends, but the composition remains nearly the same as at the surface of the earth.

Air Has Weight. Although we cannot see air, it nevertheless has weight; it is matter in gaseous form. Because it is matter and has weight, the air exerts pressure on everything in it. At sea level this pressure amounts to 14.7 pounds per square inch (lb per sq in.), but it becomes less as one rises to higher altitudes.

Air moves from places of high to places of low pressure. This accounts for the escape of air from a punctured tire, for the rush of air into a vacuum cleaner, and for the tremendous motions of the winds.

The fact that air is an actual material becomes more evident when one moves swiftly through it. A bicyclist going downhill is well aware of the backward push of the air. A hand held out from a fast-moving automobile receives a strong backward push. Engineers take account of these facts in designing streamlined airplanes, trains, and automobiles. Streamlining reduces the surfaces that obstruct the flow of air. The faster an object moves through the air, the greater becomes the pressure of the air on it and the greater the benefit gained by streamlining. This is easily understood if we assume that the air is made up of a multitude of tiny particles with spaces between them. This idea, true of all gases, will be developed later.

The Nature of Air. Air is a mixture of elements and compounds. Nitrogen, oxygen, and argon are elements found in the air in the free state, which means that they are chemically uncombined with any other element. Oxygen is also found in the air in compounds. Compounds always present in the air include water, carbon dioxide, and many others in smaller amounts.

All three states of matter are represented in atmospheric changes. Air is chiefly gaseous; but, as everyone knows, water vapor in it is quite often condensed into liquid form as rain or mist. If the weather is cold, the water condensed from the air may solidify, forming beautiful crystals of snow or occasionally hail.

There are always particles of dust, other solids, in the air. Dust tints sunsets, hinders cleanliness, and pollutes city air. Soot and ashes from fires, fragments from volcanoes and meteors (shooting stars), and other bits of solid material are found in dust. In fact, several tons of solid material fall on the earth as dust each day. Ways have been found to measure the amount of dust in the air. Information gained from these measurements has been valuable in protecting workmen in shops where dangerous dusts may be present in the surrounding atmosphere. In an ordinary room near the ceiling a quart-bottle sample of air may contain as many as 5 billion dust particles.

This air in which we live is a vast storehouse of oxygen and nitrogen, serving as a reservoir of these gases. Tons of various gases are removed from the atmosphere daily by burning, breathing, and manufacturing processes. Also, tons of different gases and solids are daily put into the air. Yet the total amount of air is so great that these changes are on the whole of very little account. Also, the winds keep the air well stirred so that no local change is effective for a long period of time.

Composition of Air. It has been stated that air is a mixture and not a compound. We may well ask, "What proof is there that air is a mixture?" Air, purified of dust, moisture, and carbon dioxide, is made up as follows:

COMPOSITION OF AIR

	By weight, %	By volume, %
Nitrogen	75.5	78.06
Oxygen	23.2	20.99
Argon and other inert gases	1.3	0.94

Proofs That Air Is a Mixture. 1. The composition of air, although always consisting of essentially the same elements, does vary a little from time to time; that is, the most accurate experiments show differences which must be due to slight variations in the composition. A true compound always has exactly the same composition by weight.

2. Air can be made into a liquid. A liquid compound has one boiling point at a fixed pressure. Liquid air, however, does not have one definite boiling point, since liquid nitrogen boils off first at a lower temperature range than liquid oxygen.

3. When a compound is dissolved in water and then taken out again, its composition is not changed. This certainly is true of table salt (a compound, sodium chloride), which contains 60.7 per cent chlorine and 39.3 per cent sodium regardless of how many times it has been dissolved in water. Air, on the other hand, dissolved in water and then recovered shows a greatly increased percentage of oxygen because oxygen is more

soluble in water than nitrogen. The "air" bubbles that collect on the side of a drinking glass left standing contain 35 per cent oxygen by volume, 14 per cent richer in oxygen than the air in the room (21 per cent). Such a condition is possible because air is a mixture and not a compound.

4. If air is allowed to penetrate (diffuse) through a porous porcelain tube, the lighter gases in the air pass through more rapidly and the composition is changed. If a compound is treated the same way, no change of composition takes place.

QUESTIONS

1. What exchange of gases takes place in animal breathing?

2. From what original source in the body does the carbon in exhaled carbon dioxide come? The oxygen?

3. What is the effect on marine life of a coating of oil over water?

4. List three characteristics of air 6 miles above the earth's surface.

5. Give evidence that air is matter.

6. Name the two most abundant elements in the air.

7. In what state of matter are the elements in the air? Are they free or chemically combined with each other? Are they pure or mixed?

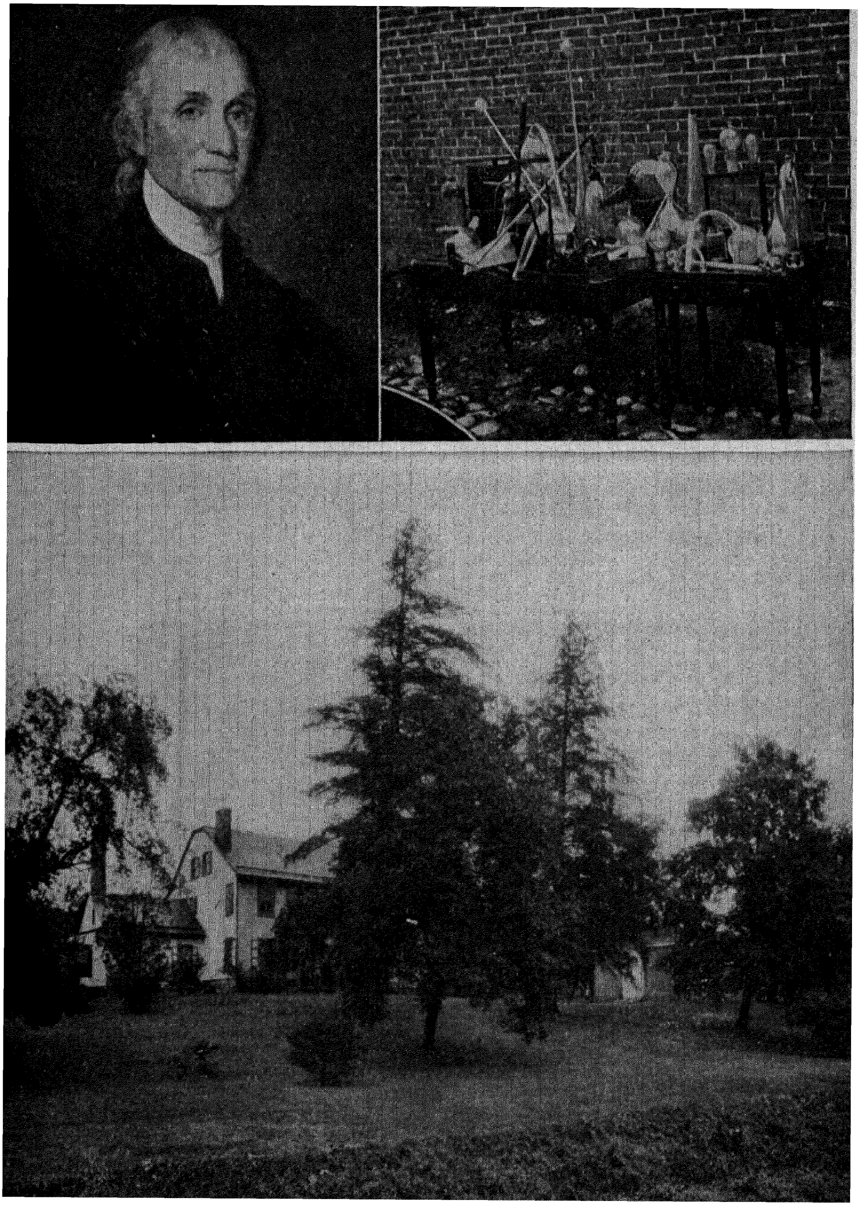
8. How many cubic feet of oxygen is contained in 100 cubic feet of air? In a room 20 by 10 by 10 feet?

9. How many pounds of nitrogen is contained in 100 pounds of air?

10. Prove conclusively that air is a mixture.

Oxygen. Oxygen is the most important element in the air. Our bodies, to a large extent, are composed of compounds of oxygen. In the natural world oxygen takes part in burning, rusting of metals, and decay of vegetation.

Even a thousand years ago the Chinese recognized an active part of the air and called it "yin." The writings of Leonardo da Vinci (1452–1519), the famous Italian artist, mention the presence of two gases in the air. The amount of the active portion of the air and its part in burning, rusting, fermentation, and breathing were discussed at some length by Mayow (1643–1679) in 1669. While Mayow did not prepare a sample of oxygen, we believe that 62 years later Hales (1677–1761) made the gas by heating saltpeter. Hales, however, did not recognize that the gas he had prepared was also found in the air. During the years 1771 and 1772, a Swedish druggist of great experimental ability, Karl Wilhelm Scheele (1742–1786), made oxygen from at least seven different substances.



Courtesy of Walter Taggart and Frank C. Whitmore

FIG. 3-2.—Joseph Priestley (1733–1804) lived in Northumberland, Pennsylvania, during the latter part of his life. He is noted for his pioneer investigations of the process of burning. The portrait of Priestley above to the left was painted by the well-known artist, Gilbert Stuart. To the right above is some of Priestley's laboratory apparatus. Below is Priestley's residence, now preserved by the Pennsylvania State College, and a memorial built by the American Chemical Society.

Joseph Priestley, Chemical Experimenter. Although oxygen was suspected, predicted, described, and even prepared by several investigators in advance of his time, the discovery of oxygen is usually credited to Joseph Priestley (1733–1804), a clergyman of Birmingham, England. (See Fig. 3-2.) He not only prepared and described the gas but also published an account of his experiments. His most famous experiment took place on Aug. 1, 1774. He inverted a test tube filled with mercury oxide, a red powder, over a pan of mercury, with the mouth of the tube below the level of the mercury in the pan in such a fashion that the red powder floated above the mercury. Then he heated the mercury oxide with the sun's rays, focusing them by a large burning glass. In this process a gas was released, leaving a heavy silver-white metallic liquid. When Priestley put a burning candle in the gas, he noticed that the flame burned with increased brilliance. He caught a mouse in his laboratory and confined the animal within a jar of oxygen. The mouse did not suffocate but scampered about excitedly. Then Priestley tried breathing some of the gas himself. "The feeling of it to my lungs was not sensibly different from that of common air; but I fancied that my breath felt peculiarly light and easy for some time afterwards," he reported. Priestley's choice of mercuric oxide was fortunate, for mercuric oxide is one of the few oxides that decompose when heated at the temperature of an ordinary gas burner.

Priestley's life outside the laboratory was tempestuous, for he was a man of radical views. He sympathized with the French Revolution, and his religious views were not popular. A mob rose against him and burned his house and laboratory on July 14, 1791. The clergyman barely escaped with his life. In his later years, he came to America and lived with some of his children in Northumberland, Pennsylvania. (See Fig. 3-2.) He died there in 1804. Because of his contribution to science, the American Chemical Society purchased his house and made it into a museum.

Oxygen for Sale. Oxygen of commerce is prepared chiefly from liquid air, but sometimes it is made by passing an electric current through water. In many high-school laboratories this element is produced by heating some compound rich in oxygen that decomposes readily. Potassium chlorate is frequently used. This colorless crystalline compound contains 39.2 per cent oxygen; when it is heated, oxygen is released as a gas and solid potassium chloride, another colorless crystalline compound, remains.

The apparatus used in this experiment is a flask or a hard glass test tube mounted in such a manner that it can be heated by a Bunsen burner. (See Fig. 3-3.) Usually some manganese dioxide, a material that takes no part in the chemical reaction but that hastens the decomposition of potassium chlorate, is added to the potassium chlorate within the vessel being heated. Such a helper in a chemical change is called a ***catalyst.*** The gas escapes from the generator (apparatus in which a gas is liberated) through a rubber tube, and it is collected by displacing the water in an inverted jar of water that rests in a pan of water. Such an arrangement for collecting gases is sometimes called a pneumatic sink or pneumatic trough.

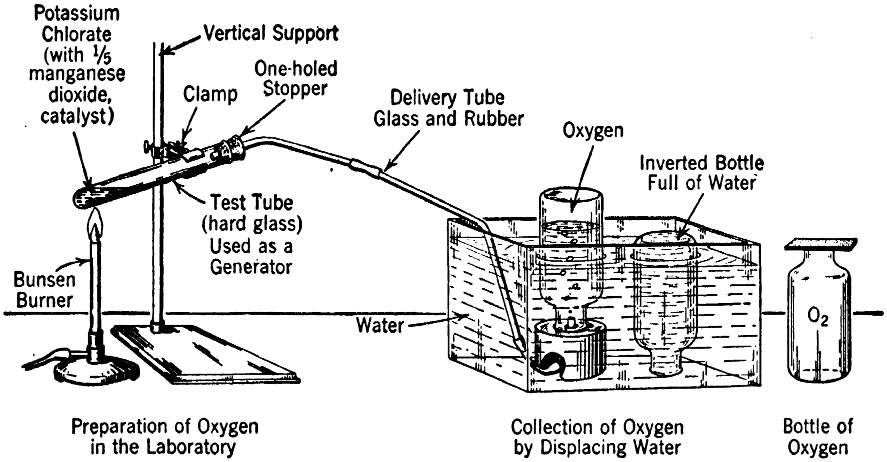
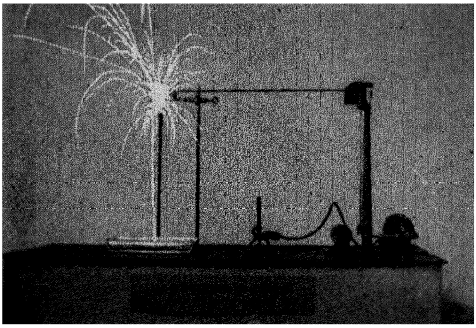


FIG. 3-3.—An apparatus for preparing oxygen in the laboratory by heating potassium chlorate, with manganese dioxide as a catalyst, until the chlorate decomposes. Note that the oxygen is liberated in the generator which is heated, that the gas is conducted from the generator by the delivery tube, and that it is collected in jars by displacing water in the pneumatic trough.

Properties of Oxygen. Oxygen is a colorless gas, quite like air in appearance. When pure, it has no odor or taste. Twenty-five quart bottles of water would absorb 1 quart (qt) of oxygen gas. We say, therefore, oxygen dissolves about 4 volumes in 100 volumes of water. A liter volume at 0°C and a pressure of 1 atmosphere (atm) [760 millimeters



Courtesy of Journal of Chemical Education

FIG. 3-4.—Iron burning in oxygen.

(mm)][1] weighs 1.429 grams, compared with 1.29 grams for a liter of air. Substances burn better in pure oxygen than in air, but the oxygen itself does not catch fire. At a very low temperature (−190°C) oxygen can be changed to a pale-blue, magnetic liquid that is sometimes used as an explosive.

Let us place successively in jars of oxygen (1) a wooden splinter with a glowing spark on the end, (2) sulfur burning in a metal spoon that has a long wire handle (deflagrating spoon), (3) glowing charcoal suspended on a stout wire, (4) phosphorus burning in a deflagrating spoon, and (5) fine iron wire with a gob of burning sulfur on the lower end. In each case the burning is noticeably more brilliant than in air, dazzingly bright in the case of phosphorus. The iron burns with bright sparks. (See Fig. 3-4.)

QUESTIONS

11. Who is given credit for discovering oxygen? When was it discovered?

12. What products are formed when mercury oxide is heated? Is a chemical or a physical change illustrated? By what properties can we recognize the products?

13. What products are formed when potassium chlorate is heated? What properties do each of the products exhibit?

14. List five physical properties of oxygen.

15. What is the relationship of oxygen to burning?

16. Is water present in liquid oxygen?

17. When 100 pounds of potassium chlorate is heated, what weight of oxygen may be released?

18. Under the same conditions, how many times heavier is a liter of oxygen than a liter of air?

19. How much does 1 liter of oxygen weigh at 0 degrees centigrade and 760 millimeters? 100 liters of oxygen?

20. If pure liquid oxygen is confined and allowed to warm up and explode the container, what becomes of the liquid oxygen?

MORE CHALLENGING QUESTIONS

21. What weight of potassium chloride is left when 200 pounds of potassium chlorate is heated?

22. What weight of oxygen can be made by heating 600 grams of potassium chlorate?

---

[1] These conditions of measurement, called standard conditions and abbreviated STP, may be assumed unless other conditions are given.

23. What volume (liters) of oxygen does 142.9 grams occupy (STP)?

24. List four general properties of compounds, and opposite them list the contrasting properties of mixtures.

25. What percentage increase in oxygen, based on original percentage of oxygen in air, is effected by dissolving air in water and then recovering it?

Nitrogen. Nitrogen was discovered in 1772 by a Scottish professor of botany named Rutherford and independently in the same year by Scheele, the experimenter who is credited with the discovery of oxygen, also. Rutherford prepared nitrogen by enclosing some air in a jar that was inverted over water and then burning carbon within the jar. The carbon dioxide formed was removed by dissolving it in the water, leaving chiefly fairly pure nitrogen.

Four-fifths of the air by volume is nitrogen. Over each square mile of the earth's surface are 20 million tons of gaseous nitrogen. We may say safely that we have an ample supply of nitrogen as a raw material for chemical manufacturing.

Properties and Some Uses of Nitrogen. Nitrogen is made commercially, along with oxygen, by boiling liquid air. Cylinders containing gaseous nitrogen at 2000 lb per sq in. pressure are available.

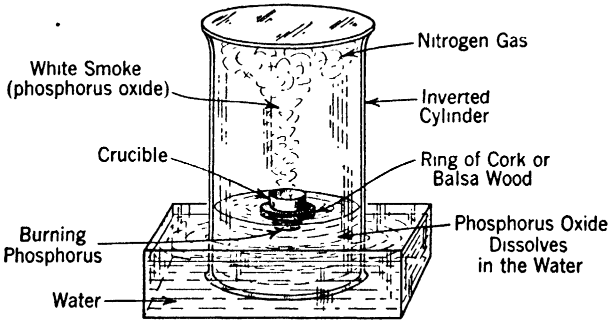


FIG. 3-5.—Impure nitrogen may be prepared by burning phosphorus within a jar inverted in water. The phosphorus oxide formed dissolves in the water and leaves impure nitrogen in the jar.

Nitrogen is a little lighter (1.25 grams per liter) than an equal volume of air. It dissolves in water to a less extent than oxygen. It is seldom used in the laboratory (see Fig. 3-5) except to supply an inert (inactive) atmosphere, but if needed it can be made by heating ammonium nitrite (a compound of nitrogen, hydrogen, and oxygen). (See Fig. 3-6.) This compound decomposes easily, releasing 43.75 per cent of its weight as nitrogen and also forming water.

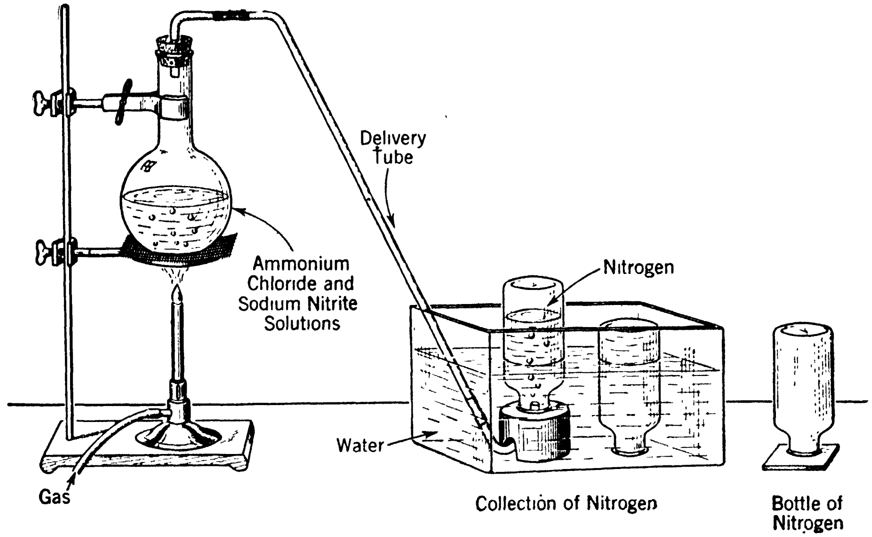


FIG. 3-6.—Ammonium nitrite, an unstable compound, can be prepared when needed by warming a mixture of ammonium chloride and sodium nitrite solutions. When these are warmed, nitrogen gas is liberated and collected by the displacement of water.

Nitrogen as it occurs in the atmosphere is an inactive element; that is, it is difficult to cause the nitrogen of the air to combine chemically with other elements. Compounds of nitrogen are rich in stored energy and are very reactive (reaction takes place at a rapid rate). Practically all explosives are nitrogen compounds. Always difficult to get into combination with other elements, nitrogen gas readily re-forms. Because of its inertness, that is, lack of chemical activity, nitrogen in the free state is used to fill electric light bulbs and the space above the mercury in high-grade thermometers.

Nitrogen from the air is a raw material of importance in many chemical processes. Processes in which atmospheric nitrogen enters chemical combinations are referred to as ***fixation of nitrogen.*** Later references to food, fertilizers, dyes, and explosives will show the importance of nitrogen compounds.

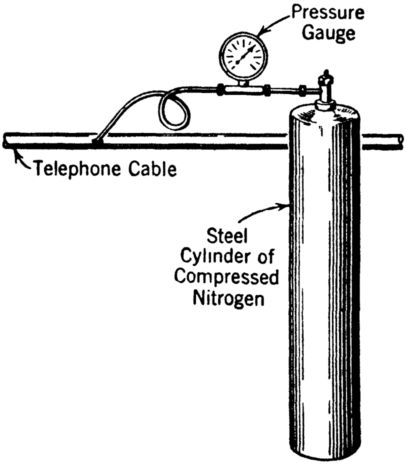


FIG. 3-7.—One use of nitrogen. What properties of nitrogen make it suitable for keeping moisture out of telephone cables? Would oxygen serve as well? How does the lineman know when the cable sheath becomes broken?

QUESTIONS

26. Who discovered nitrogen and at what date?

27. How many cubic feet of nitrogen, approximately, are contained in 100 cubic feet of air?

28. List five physical properties of nitrogen.

29. What adjective describes the chemical activity of nitrogen?

30. Define *inert.*

31. When ammonium nitrite is carefully warmed, what two products are formed?

32. What is meant by the term *fixation of nitrogen?*

33. Hot magnesium joins nitrogen chemically. What compound is formed?

34. List two uses of free nitrogen.

35. List three classes of compounds that are nitrogen-containing.

The Inert Gases. The story of the inert gases starts in London, England, with some experiments performed by Henry Cavendish (1731–1810), a nobleman who had a scientific hobby. He was an eccentric bachelor, shy, rich, and very cautious in the presence of ladies. Cavendish experimented with an L-shaped piece of bent glass tubing. Two wires were placed within the tube, extending to the top of the bend where their ends were a small distance apart, and were connected with a source of electricity. The lower open ends of the tube were placed in goblets that contained water. (See Fig. 3-8.) Gases or a mixture of gases could be placed within the glass tube.

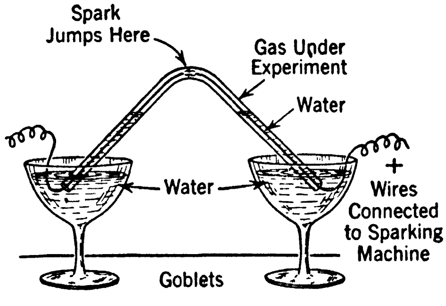


FIG. 3-8.—Cavendish used an apparatus similar to the one shown here.

When Cavendish placed air in such a tube and caused a spark to jump across the ends of the wires within the tubing, nitrogen of the air joined oxygen and formed nitrogen dioxide. The nitrogen dioxide then dissolved in the water contained in the goblets, and water rose in the tube to take the place of the gas used up in the experiment. After continued sparking, all the oxygen of the air was used up, and no further action took place. Cavendish then added more oxygen and continued the experiment, but he found after several trials that always a small part of the air would not combine with oxygen when a spark was passed through the mixture. He writes: " . . . If there be any part of the . . . air [oxygen] of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid [or oxide], we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole."

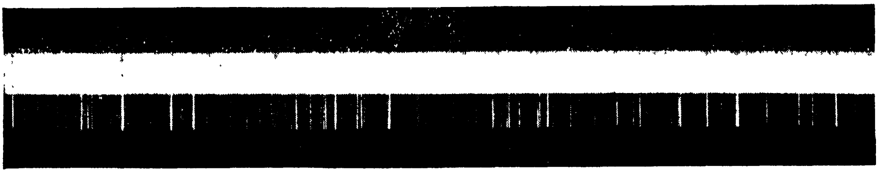
About a century later that small part of the air became important. John William Strutt (1842–1919), who later became Lord Rayleigh, was performing experiments to find very accurately the density of nitrogen gas. To his surprise he found that nitrogen prepared by heating ammonium nitrite differed in density by 1 part in 200 from nitrogen prepared by removing all the oxygen from dry air. He could not solve this problem alone and discussed the question with Sir James Dewar, a fellow professor at the Royal Institution. Dewar suggested that the two samples could not be exactly alike and that possibly some other gas, hitherto undiscovered, might be present in the air. Together these men looked up the report that Cavendish had made years before, and both read the words quoted above. Then they saw clearly that the search was a challenge. The very air we breathe had become a frontier. Only the two most obvious elements had been found in it. They enlisted the aid of Sir William Ramsay (1852–1916), a chemistry professor at University College, London, and five more elements were found eventually among the gases in the air.

Argon. Ramsay took an enclosed sample of dry air and passed it over hot copper until all the oxygen was removed by combining with copper to form copper oxide. Then he passed the remaining oxygen-free gas over hot magnesium until all the nitrogen was removed by combining with the magnesium to form magnesium nitride. The remainder, small in volume, was chiefly argon.

Argon is found in air 0.94 per cent by volume and a little over 1 per cent by weight. This colorless, odorless, and tasteless gas is a little more dense than either nitrogen or oxygen, a fact that accounts for the small difference noticed by Rayleigh. The outstanding characteristic of argon is its complete chemical inactivity. It has not been made to combine with any other element, a fact that is very important in the development of a chemical theory that we shall study later. Argon's name, well deserved, comes from a Greek word meaning "lazy." We obtain the gas as a by-product of liquefying air. Oxygen and nitrogen are made into a liquid, and the part of the air that resists being changed into a liquid is chiefly argon.

Because argon will not combine chemically with any other substance, even a red-hot metal, and because the gas is now readily available, it is used to fill electric light bulbs to prevent too rapid evaporation of the hot filament. In fact, most incandescent light bulbs between the 50- and 1000-watt sizes are now filled with this gas at about atmospheric pressure. Just as the nitrogen-filled electric light bulb was better than the older evacuated type from which the air was removed as completely as possible, so the argon-filled bulb is an improvement over the nitrogen-filled bulb. Argon is also used inside the fluorescent tubes. Argon is shipped compressed in steel cylinders, much more expensive than similar cylinders of oxygen or nitrogen.

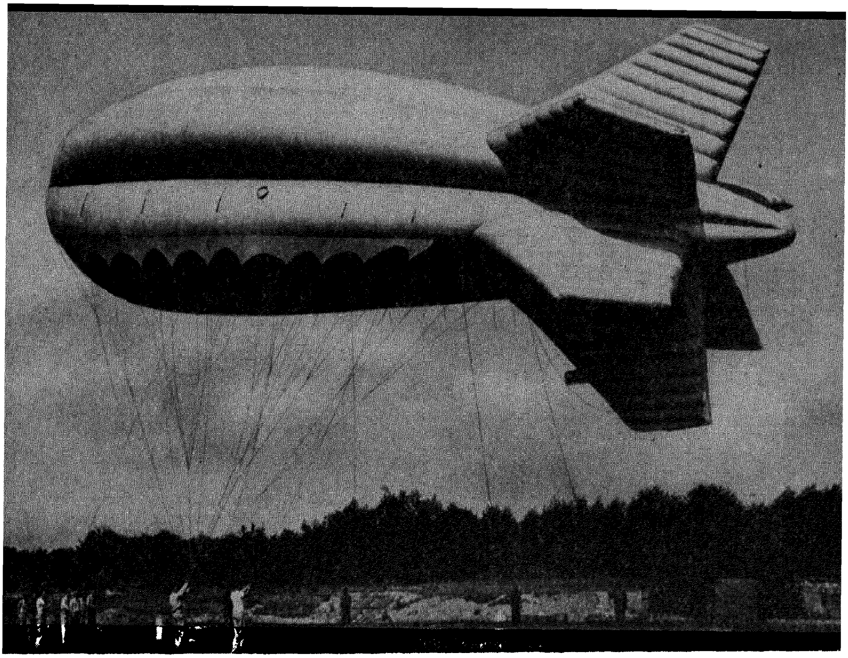
Inert Helium, the Sun Element. In 1868 Prof. Janssen studied the sun by observing it through an instrument called the spectroscope, in which the light of the sun is spread out into a "rainbow," or ***spectrum.*** In this spectrum the presence of an element in the sun's atmosphere is indicated by a set of black lines, the position of which is definite for that element. This had been proved by observing in the laboratory the light emitted or absorbed by the various elements, by means of the spectroscope. (See Fig. 3-9.) As he was investigating the ruddy gaseous layer surrounding the sun, known as the chromosphere, he discovered a black line in the yellow portion of the spectrum that belonged to no element then known upon the earth. This element was called ***helium,*** or the sun element. In 1890 the American chemist Hillebrand found that a gas which he thought to be nitrogen was liberated when samples of certain rocklike substances obtained from the earth, called minerals, were immersed in dilute acid. After hearing of Hillebrand's experiments, Ramsay promptly bought all those minerals which he could obtain. From them, in 1894, he found the gas helium, the second inert gas to be discovered. It gave the same line in the spectroscope that Prof. Janssen had observed.



Courtesy of E. Harold Coburn

FIG. 3-9.—The sun's spectrum (light with dark bands) is compared here with the spectrum of iron made by a spark between two spikes (bright lines). Notice that the position of the lines coincides. This proves that iron is on the sun.

A year later helium was also found in the air, but in an exceedingly small amount. It is a gas that comes from certain minerals that contain ***radioactive*** elements. These elements give out radiations of both matter and energy. More will be said about such minerals in a later chapter (page 641). Some natural gases, particularly in Texas, contain helium. Helium is next to the lightest gas, the first being hydrogen. Like argon, it shows no chemical activity whatever. Helium is the most difficult of all gases to liquefy, because for liquefaction to take place it must be



Courtesy of Goodyear News Service

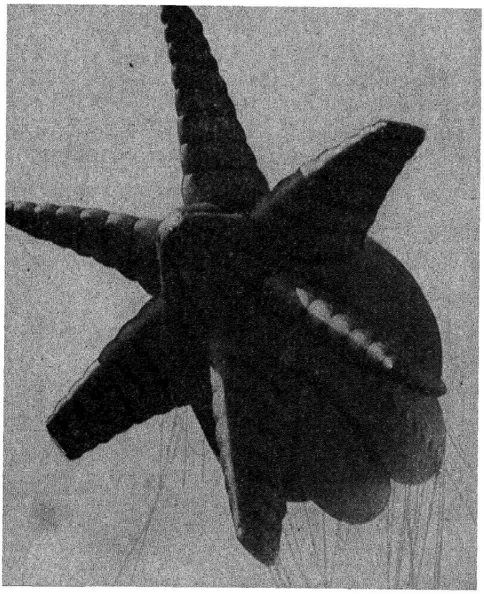


FIG. 3-10.—Here are side and rear views of a six-lobe six-fin Strato Sentinel barrage balloon for high altitude protection against bombing attacks. This balloon has 68,000 cu ft helium capacity and can ascend to 15,000 ft.

cooled to an exceedingly low temperature, −268°C. Helium is also the least soluble gas. It boils at −268.9°C at atmospheric pressure. Solidified helium melts at −272.3°C at a pressure of 26 atmospheres (atm).

Helium is present in many natural gases in the United States, and these have proved to be ample sources of this gas for filling airships. (See Fig. 3-10.) The gas from certain wells near Fort Worth, Texas, contains 0.97 per cent helium. Helium is obtained by liquefying all the other elements of a natural gas and in this way separating them from the helium, which is the most difficult to liquefy. In 1925 a plant in Texas was able to isolate helium at a cost of 3 cents per cubic foot. With improved methods of separating it, helium now costs about 2 cents per cubic foot.

In addition to being used as a lifting gas in balloons in place of hydrogen, helium mixed with oxygen is used to make an artificial atmosphere for deep-sea divers. Helium is less soluble in the blood than is nitrogen. The use of the helium-containing mixture for respiration lessens the likelihood of painful "bends," due to bubbles in the veins and arteries, experienced by men who have to work in caissons and elsewhere under great pressure. Nonflammable helium-hydrogen mixtures (20 to 80 parts by volume) are used in some balloons.

Neon, Krypton, Xenon, and Radon. After argon and helium had been discovered in the air, interest in finding new elements was awakened. Ramsay immediately continued the search. Exceedingly skillful methods of analysis were devised, and in 1898 the discovery of three new elements, krypton, xenon, and neon, was announced. Another gaseous inert element, radon, was later discovered to be liberated when radium disintegrates. All these gases, like argon and helium, do not act chemically on any other element. Radon has been used in the treatment of the disease cancer, but krypton and xenon do not exist in sufficient amounts in the air to make use of them. Neon, however, forces itself upon our attention. This is because at a low pressure in a closed tube it conducts electricity well and gives forth an attractive red glow. Hence,

TYPICAL ANALYSIS OF A NATURAL GAS
FROM A WELL NEAR FORT WORTH, TEXAS

Substance	Formula	Per Cent
Methane	CH_4	56.85
Nitrogen	N_2	31.13
Ethane and other hydrocarbons	C_2H_6	10.30
Helium	He	0.93
Oxygen	O_2	0.54
Carbon dioxide	CO_2	0.25

it is used for advertising signs, for filling spark-plug testers, and for filling a type of glow lamp frequently used for pilot lights because the power demand is as low as ½ watt.

SUMMARY

Breathing is a process by which living creatures obtain oxygen. Animals absorb oxygen and breathe out carbon dioxide. Plants in sunlight absorb carbon dioxide and give out oxygen—a type of breathing. Marine life uses oxygen and carbon dioxide dissolved in water.

Air is matter. It has weight, exerts pressure, and dissolves slightly in water. Air surrounds and to some extent penetrates the earth. It consists of a large reservoir of chemical raw material. Although many changes go on in it, the composition is almost constant; by volume, 21 per cent oxygen and 78 per cent nitrogen, and by weight mainly 23 per cent oxygen and 76 per cent nitrogen, together with 1 per cent of other gases. The following are proofs that air is a mixture and not a compound:

1. The composition of air varies slightly. A compound does not vary in composition.
2. Liquid air boils at several temperatures. A compound has a constant boiling point at a given pressure.
3. Dissolving air in water increases the percentage of oxygen because the oxygen is more soluble in water than the nitrogen. Dissolving a true compound in water has no effect on the composition of the compound (provided that the compound does not react with water).
4. Air passed through a porous porcelain tube shows a change in composition. A true compound so treated shows no change in composition unless it decomposes.

Oxygen is found free in air and combined in water; it is also found combined in many other oxides and in other types of compounds. It is the most abundant element. Credit for its discovery is usually given to Joseph Priestley, an English clergyman, who prepared and identified the gas in 1774 by heating mercuric oxide and thus obtaining mercury and oxygen. The gas is commercially prepared by passing an electric current through water and thus obtaining hydrogen and oxygen or by allowing liquid air to evaporate, whereupon the nitrogen escapes, leaving liquid oxygen. In the laboratory, oxygen is prepared by heating potassium chlorate and thus obtaining potassium chloride and oxygen. Oxygen is colorless, odorless, tasteless, a little more dense than air, and slightly soluble in water. It can be liquefied. Ordinary burning is the combining of oxygen with some other element; ordinary burning goes on more rapidly in pure oxygen than in air, forming oxides in either case.

Nitrogen was discovered by Rutherford in 1772 and independently by Scheele at about the same time. It is found free in air and is combined in many living tissues. It is found in relatively few other compounds in nature. Nitrogen is prepared commercially by boiling liquid air and collecting the gas that escapes first. In the laboratory it can be obtained by removing oxygen from air by means of hot phosphorus, or purer samples can be obtained by the careful heating of ammonium nitrite. Nitrogen is colorless, odorless, tasteless, a little less dense than air, and very slightly soluble in water. The gas does not burn, nor will ordinary burning go on in nitrogen. At elevated temperatures nitrogen combines with a few very active elements, forming nitrides of these elements. Magnesium is such an element.

The inert gases comprise less than 1 per cent of the air. Each has its history of discovery, but in general their discovery came as a result of very careful work. They are all colorless, odorless, tasteless, and insoluble in water and do not burn or support burning. In fact, they form no ordinary chemical compounds. The uses of the inert gases depend upon their inactivity. Argon and neon are used in electric light bulbs and signs. Helium is used as a lifting gas in airships because it is very light and nonflammable. Krypton and xenon are found in only very tiny amounts.

QUESTIONS

36. Name the five inert gases of the air.

37. Name one property that is common to all the inert gases.

38. How many cubic feet of argon are contained in 100 cubic feet of air?

39. Name a use of argon; of neon; of helium.

40. Compare hydrogen with helium as a lifting gas for balloons.

41. What advantage is secured when liquid oxygen is used for an explosive in a coal mine?

UNIT ONE - - - - - - - - - - - - - - - CHAPTER IV

BURNING, BREATHING, RUSTING

"Sir, last Christmastide four of my sturdy men dragged an immense yule log into the fireplace in my great room. For five days and nights this log burned while the household made merry celebrating Christmas. Afterward one of the kitchen servants cleaned out the fireplace, carrying off the ashes, scarcely more than a basketful. There is no doubt in my mind, sir, that things lose weight when they burn."

"I agree with you, my lord, that the reports which come to us from this Frenchman Lavoisier seem unreasonable. How can one be expected to believe that which goes against reason? Any child can see that burning makes for loss of weight. Surely charcoal weighs less than wood. This fellow Lavoisier, who claims that substances gain weight when they burn, is a little queer."

In this manner was the news of the experiments carried on by Lavoisier in Paris received by the people of about 175 years ago. Many warm arguments were taking place in Europe at that time. The political disagreements were extensive, but the scientific wrangle centered chiefly about the question, "What is burning?" The saddlebags of the postriders and the mail pouches of·the stagecoaches carried letters between noted people who argued this point. Some thought that burning was a process by which weight was lost, but a few ventured the opposite view that weight was gained. Many supporters of the first idea clung to the fantastic theory that a fiery principle ***phlogiston*** escaped in the flame, leaving a ***calx,*** or ash; substances that burned leaving very little ash, like wood, were thought to be composed of nearly pure phlogiston. This theory, founded by Stahl and Becher in Germany (about 1690), soon led to absurd ideas. Yet these ideas were believed by learned poeple. Even Priestley, who did such fine work with oxygen and certainly understood something about the nature of burning, died (1804) still believing this

---

New Terms

physical properties
chemical properties
spontaneous
ignition
oxide
photosynthesis
effervescent
sublimation
reduce

older but incorrect phlogiston theory. One writer summarizes the transition in thinking about burning as follows:[1]

> This alchemistic notion that combustible substances contained the ponderable principle phlogiston, which on rapid escape caused the appearance of fire, was doomed by the discovery of various pure gases. In 1775 Black discovered carbon dioxide (CO_2) and showed that it was present in small amounts in the air. Between 1767 and 1777 Priestley and Scheele discovered several new gases, each having properties different from air, and laid the foundation for modern gas chemistry, incidentally providing Lavoisier with material to disprove the phlogiston theory and enabling him to substitute therefor the oxygen theory of combustion, which has since been amply verified.

The argument about "What is burning?" was settled conclusively by Lavoisier. Not only did this famous French experimenter reason correctly, but unlike his less scientific opponents he secured facts to support his reasoning. Lavoisier obtained such excellent results because he made use of accurate balances and weights. (See Fig. 4-1.) He weighed, reweighed, organized his data, and formed conclusions from the results. In 1772 he wrote:

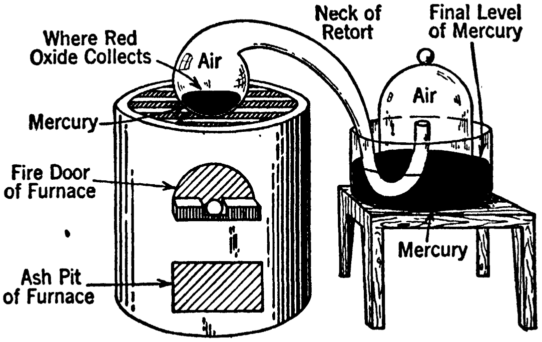


FIG. 4-1.—With this apparatus, Antoine Laurent Lavoisier performed his classic experiments on burning.

> About eight days ago I discovered that sulfur in burning, far from losing weight, rather gains it; that is to say that from a pound of sulfur may be obtained *more* than a pound of vitriolic acid, allowance being made for the moisture of the air. It is the same in the case of phosphorus. The gain in weight comes from the prodigious quantity of air . . .

Two years later Lavoisier experimented with tin and mercury, heating each with air in a *closed* vessel. Both these metals he found to unite with a portion of the air, about one-fifth. The "air" that remained after oxygen had been removed would not allow substances to burn in it.

---

[1] FIOCH, E. F., *Scientific Monthly*, Vol. 52, pp. 216, 349, March, 1941.

The metals took on a new appearance, since they had combined with the oxygen of the air, and in every case he found that they had gained weight. By these experiments the old theory was overthrown and a chemical revolution started.

A political upheaval, the French Revolution, was in progress at the time when Lavoisier was conducting his famous experiments. Unfortunately, Lavoisier had made many enemies through his activities in public life as a member of the board of Farmers-General. He was brought before the Revolutionary Tribunal and accused of putting water in tobacco intended for soldiers' use. For this unproved and supposedly serious crime he was sentenced to be beheaded with these infamous words: "The Republic does not need scholars. Justice must take its course."

Prof. C. S. Minot has said of this event:

> Compared with the growth of science, the shiftings of government are minor events. . . . Until it is clearly realized that the gravest crime of the French Revolution was, not the execution of the King, but the execution of Lavoisier, there is no right measure of values: for Lavoisier was one of the three or four greatest men France has produced.

How to Make a Fire. If we wish to make a fire, we procure something to burn and a match. The substances to be burned, fuel, may be a solid (coal, wood, coke, or charcoal), a liquid (kerosene or alcohol), or a gas (natural gas, bottled fuel gas, or the gas supplied by city gas companies). One characteristic is common to these fuels: they are all capable of combining with oxygen. Rock (except coal) is not selected as a fuel because it does not combine with oxygen.

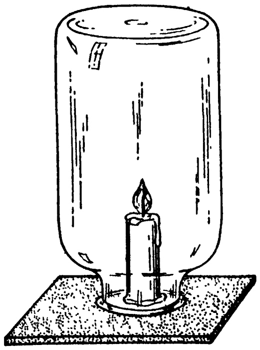
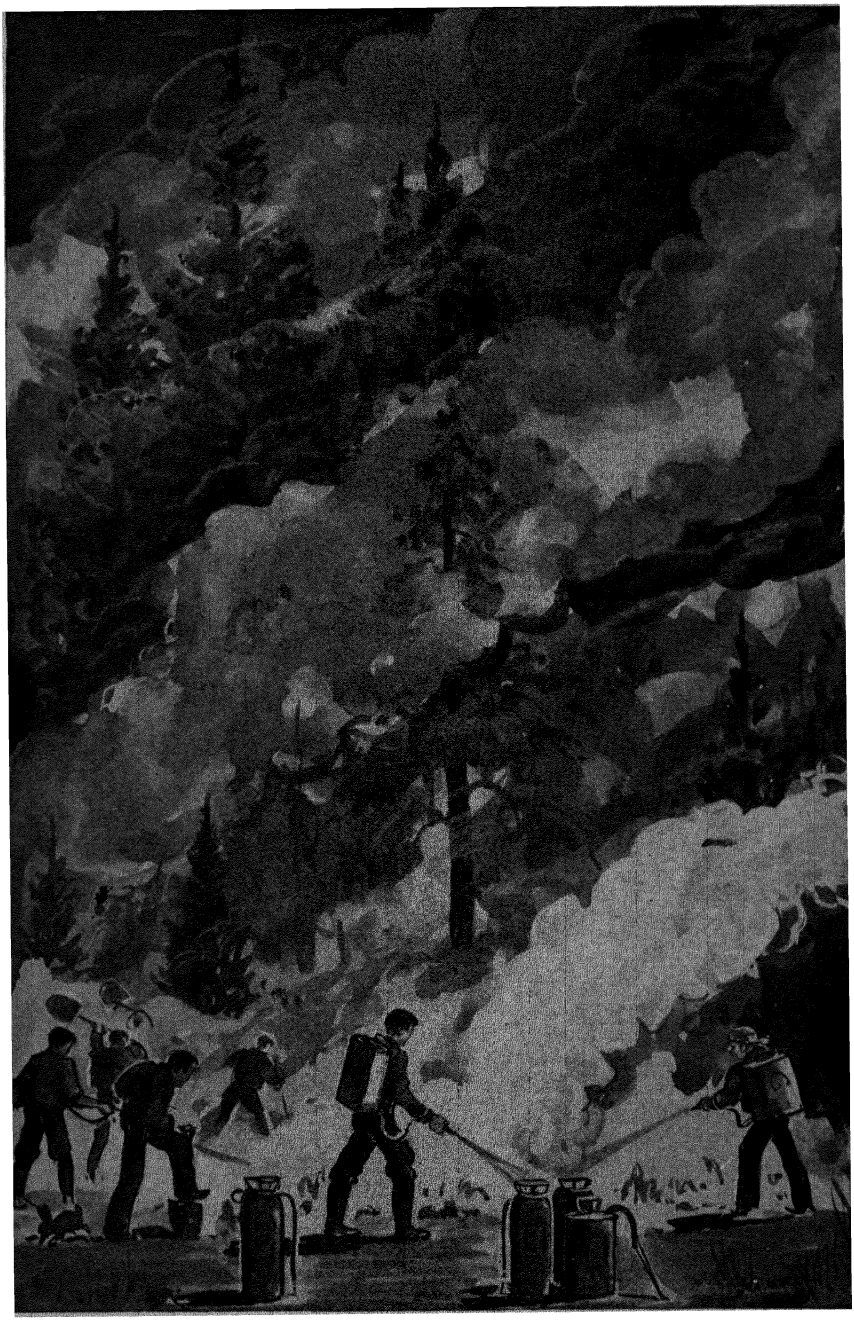


Fig. 4-2.—If a burning candle is placed in an inverted closed jar of air, it is soon extinguished because the supply of oxygen is consumed.

The match is used because, when lighted and applied to the fuel, it raises the temperature of the substance high enough to cause it to burn. Flammable substances will burn when they become warm enough; we say that they have reached their igniting or ***kindling temperature.*** The kindling temperature is not the same for every substance or for every condition of the same substance. However, some substances can, in general, be classified as having low kindling temperatures—paper, leaves, hay, match heads—and these are used to start fires.

Who has not heard of kindling wood? Why will a large stick not serve as well to start a fire? Let us try an experiment.

Suppose we apply a lighted match to a large stick of wood; it produces a scorched spot but does not ignite the wood. We then try wood shavings made by the



Courtesy of Travelers Insurance Company

FIG. 4-3.—Notice that three methods of fighting a forest fire are illustrated here.

same conditions; they catch fire quickly. The difference is explained by the fact that a solid stick conducts heat away from the burning match much better than do shavings. So we may say that the time required for a substance to reach its kindling temperature depends upon its ability to conduct heat.

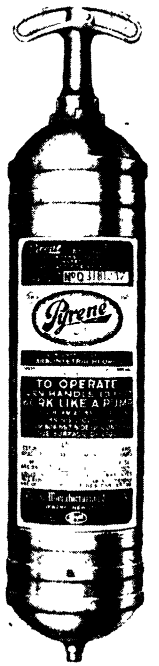
We have said that to make a fire we must raise the temperature of fuel to the kindling point, but one more condition is required if a substance is to burn. Oxygen or air containing oxygen must be present in adequate amount. If a piece of lighted paper is placed under an inverted drinking glass, it goes out before all the paper is consumed because the supply of oxygen in the glass is soon used up. (See Fig. 4-2.)

If any one of the three conditions—fuel, temperature above the kindling point, and oxygen—is lacking, the common chemical change called burning cannot take place.

How to Put Out a Fire. The fire siren sounds. The firemen arrive quickly at the burning building and pump water on it. A temperature race is on! If the firemen can cool the building below the kindling point by sufficient cold water, the building is saved. If the heat of the fire can keep the building above the kindling temperature in spite of the efforts to cool it, the building is doomed. If a substance is kept cool enough, it will not burn.

After a skating party we join friends around an open fire. Its welcome warmth is inviting. One of the girls, busily talking while standing too close to the flame, finds to her horror that her clothing has caught fire. Quickly she rolls on the ground. Sweaters and blankets are thrown over the burning garments. The fire goes out for lack of oxygen. The fire is smothered, we say.

Other ways to smother a fire are sometimes used. Sand or dirt may be thrown on the fire. Water also helps, although the chief purpose of using water is to lower the temperature of the burning substance. A heavy gas that does not burn can be directed over the fire to act as a gaseous blanket, shutting out the air. (See Fig. 4-3.) Carbon dioxide serves well for this purpose but is hazardous because it suffocates people and animals. A liquid that turns to a heavy vapor in the heat of the fire may also be used. Carbon tetrachloride (CCl_4; tetra means "four") is such a liquid.



Courtesy of Pyrene Manufacturing Company

FIG. 4-4.—This fire extinguisher contains carbon tetrachloride. The operator uses the handle as a pump and directs a stream of liquid at the base of the flames. The evaporating liquid smothers the flame with a dense gas.

This is the chief substance contained in one kind of fire extinguisher (see Fig. 4-4) in which the liquid is pumped onto the fire. Since the vapor formed is injurious to human beings, ventilation after use is important.

To put out the fire in a gas burner we remove the fuel, that is, shut off the gas. Removing the fuel is sometimes accomplished by dynamiting, as is done in the cases of oil-well fires and fires involving flimsy beach buildings in a high wind. Setting "backfires" and trenching to stop a forest fire are ways to remove the fuel.

Some Properties of Oxygen and Air. A bottle of air and a bottle of oxygen are alike in many ways. Both oxygen and air are gases at ordinary temperatures, without color or odor. One liter of air weighs 1.29 grams, while a liter of oxygen weighs 1.43 grams. Oxygen dissolves in water only a little better than air.

These facts about oxygen and air describe their ***physical properties.*** They do not describe any change involving chemical action. Their ***chemical*** nature or ***properties*** can be investigated by testing to find out the chemical changes they undergo under certain conditions.

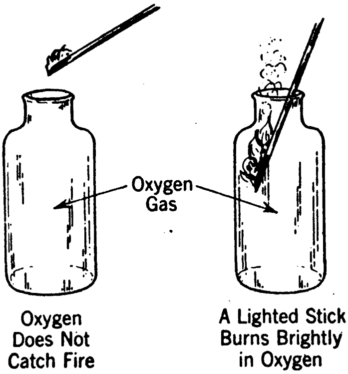


Fig. 4-5.—A test for oxygen.

One of the simplest tests for oxygen is to place a burning splinter in the gas. (See Fig. 4-5.) We then discover that the splinter burns much better in oxygen than in air. In fact, even a tiny spark will glow so brightly in oxygen that soon the splinter will catch fire. In this way we can ***test*** to distinguish oxygen from air or many other gases.

Breathing Is Like Burning. In a hospital or dentist's office one may notice cylinders of oxygen; the strong steel bottles hold the gas compressed until it is ready to be used. When a patient "takes gas," the oxygen is mixed with nitrous oxide (N_2O). When a person is ill with certain lung difficulties, the air used for breathing is enriched with pure oxygen; thereby the lungs are well supplied with this gas so that a sufficient amount of it dissolves in the blood.

Let us consider what happens to the oxygen after it is dissolved in the blood. The blood carries the oxygen to the tissues where it is needed. Here the oxygen combines with the food material in the same manner as oxygen combines with fuel in burning, but at a much slower rate; energy for action and heat in the body are released, at the same time producing waste products, which are carried off by the blood on its way back to the lungs for another load of oxygen. This process goes on whether we are sick or well. If breathing is carried on with difficulty, as at high altitudes or in closed spaces as in submarine work, the oxygen of the air may be supplemented by oxygen from tanks.

In a similar manner, oxygen from cylinders is used to make fires burn better. Frequently we see the oxyacetylene flame used in welding metals. The torch that produces this intensely hot flame develops enough heat to melt steel even under water. When the steel is hot enough, it will burn with a brilliant shower of sparks as pure oxygen is supplied.

QUESTIONS

1. When sulfur burns, what change in weight, if any, takes place?

2. When tin burns, what change in weight, if any, takes place?

3. The wood in an ordinary chair is good fuel, and it is surrounded by air. What condition for burning is lacking?

4. Define *kindling temperature.*

5. A burning candle is covered by an inverted bottle. What happens? Explain the answer.

6. A crumpled newspaper burns more quickly than a stack of folded newspapers. Explain.

7. Describe the action of carbon tetrachloride when it is used to extinguish a fire.

8. A very shallow layer of kerosene is placed in a dish. A lighted match is placed so that it is only partly submerged. The match continues to burn. The dish is now tilted quickly so that the kerosene covers the match. What happens? Explain this experiment.

9. What is an oxygen tent?

10. Compare the relative amounts of carbon dioxide and oxygen in the blood of the arteries and in the blood of the veins.

What Are the Products of Burning? Ordinary burning consists in joining a fuel with oxygen, producing simple chemical products. The physical result of the chemical change is the liberating of heat and light energy. We buy fuel oil, coal, coke, or gasoline because of the heat energy they will produce when burned. This part of the story is interesting to the chemist, but chemists also deal with substances formed by the process of burning.

We are now ready to illustrate chemical changes by a shorthand method called an equation. We need not be concerned for the present about the small numbers before the formulas or subscripts (written beneath) in the formulas. Their meaning will be brought out later. For the present it is good practice to write the names of the substances below the chemical formulas.

When an element combines with oxygen, the substance formed is called an ***oxide*** of that element. Examples are:

$$\underset{\text{Carbon}}{C} + \underset{\text{and oxygen}}{O_2} \xrightarrow[\text{form}]{} \underset{\text{carbon dioxide (di = two)}}{CO_2}$$

$$\underset{\text{Sulfur}}{S} + \underset{\text{and oxygen}}{O_2} \xrightarrow[\text{form}]{} \underset{\text{sulfur dioxide}}{SO_2}$$

$$\underset{\text{Phosphorus}}{4P} + \underset{\text{and oxygen}}{5O_2} \xrightarrow[\text{form}]{} \underset{\text{phosphorus pentoxide (pent = five)}}{2P_2O_5}$$

$$\underset{\text{Hydrogen}}{2H_2} + \underset{\text{and oxygen}}{O_2} \xrightarrow[\text{form}]{} \underset{\text{hydrogen oxide (water)}}{2H_2O}$$

Many metals readily unite with oxygen. Examples are:

$$\underset{\text{Aluminum}}{4Al} + \underset{\text{and oxygen}}{3O_2} \xrightarrow[\text{form}]{} \underset{\text{aluminum oxide}}{2Al_2O_3}$$

$$\underset{\text{Zinc}}{2Zn} + \underset{\text{and oxygen}}{O_2} \xrightarrow[\text{form}]{} \underset{\text{zinc oxide}}{2ZnO}$$

$$\underset{\text{Iron}}{3Fe} + \underset{\text{and oxygen}}{2O_2} \xrightarrow[\text{form}]{} \underset{\text{iron oxide}}{Fe_3O_4}$$

$$\underset{\text{Copper}}{2Cu} + \underset{\text{and oxygen}}{O_2} \xrightarrow[\text{form}]{} \underset{\text{copper oxide}}{2CuO}$$

In general:

$$\text{Element} + \text{oxygen} \xrightarrow[\text{form}]{} \text{element oxide}$$

Carbon dioxide and sulfur dioxide are gases under ordinary conditions, and hydrogen oxide (water) is a liquid. The heat developed in the process of burning, however, changes water to a vapor or gas. Phosphorus pentoxide and all the oxides of metals listed above are solids.

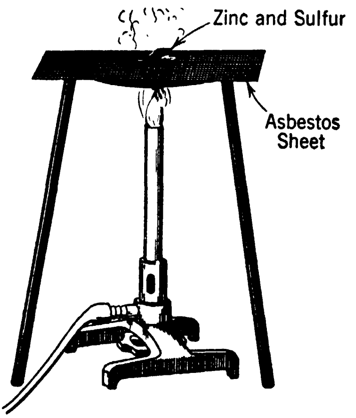


FIG. 4-6.—When a mixture of small amounts of powdered zinc and sulfur are heated, a lively burning results; the zinc joins the sulfur, forming zinc sulfide.

$$Zn + S \rightarrow ZnS$$

Some fuels, for example oil and natural gas, are chiefly carbon combined with hydrogen; these burn to form carbon dioxide and water. Other fuels, such as wood, fat, and alcohol, have oxygen in combination in the substances; this oxygen present in the compound means that less is needed from the air than would be required otherwise for complete burning.

Now we have the explanation of why a piece of wood actually gains weight when it burns. The ashes are largely the part of the wood that for the most part did not burn. The substances formed that weigh more than the original wood are the gases, and they usually pass off into the air or up the chimney. Small wonder that they were overlooked by the pompous country gentleman who is represented as speaking at the beginning of this chapter.

We are also ready to give an explanation of how metals tarnish or corrode. Iron rusts chiefly by combining with oxygen, forming a brown flaky scale, principally iron oxide. Moisture helps the process. Zinc and aluminum when joining with oxygen form white oxides, while copper forms two oxides, one black and the other red.

Joining with oxygen is a common chemical change. Ordinary house paint hardens because linseed oil adds oxygen; rubber becomes hard and brittle when it has joined with oxygen; lacquers on cars become dull by this sort of corrosion; fresh-cut fruit darkens because of oxidation; and blood clots in part because the scab of oxidized blood temporarily closes the wound.

Other elements behave like oxygen in that they unite with the same elements as oxygen. It is possible to have burning that resembles ordinary burning go on in a chemical laboratory without using oxygen. Note how similar in action to oxygen are the elements chlorine and sulfur. (See Fig. 4-6.)

$$\underset{\text{Carbon}}{C} \;\underset{\text{and}}{+}\; \underset{\text{sulfur}}{2S} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{carbon disulfide}}{CS_2}$$

$$\underset{\text{Phosphorus}}{4P} \;\underset{\text{and}}{+}\; \underset{\text{sulfur}}{3S} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{phosphorus sulfide}}{P_4S_3}$$

$$\underset{\text{Hydrogen}}{H_2} \;\underset{\text{and}}{+}\; \underset{\text{sulfur}}{S} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{hydrogen sulfide}}{H_2S}$$

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

$$\underset{\text{Copper}}{2Cu} \;\underset{\text{and}}{+}\; \underset{\text{sulfur}}{S} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{copper sulfide}}{Cu_2S}$$

$$\underset{\text{Silver}}{2Ag} \;\underset{\text{and}}{+}\; \underset{\text{sulfur}}{S} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{silver sulfide}}{Ag_2S}$$

$$\underset{\text{Sulfur}}{2S} \;\underset{\text{and}}{+}\; \underset{\text{chlorine}}{Cl_2} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{sulfur chloride}}{S_2Cl_2}$$

$$\underset{\text{Phosphorus}}{2P} \;\underset{\text{and}}{+}\; \underset{\text{chlorine}}{3Cl_2} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{phosphorus chloride}}{2PCl_3}$$

$$\underset{\text{Hydrogen}}{H_2} \;\underset{\text{and}}{+}\; \underset{\text{chlorine}}{Cl_2} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{hydrogen chloride}}{2HCl}$$

$$\underset{\text{Sodium}}{2Na} \;\underset{\text{and}}{+}\; \underset{\text{chlorine}}{Cl_2} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{sodium chloride}}{2NaCl}$$

$$\underset{\text{Copper}}{Cu} \;\underset{\text{and}}{+}\; \underset{\text{chlorine}}{Cl_2} \;\underset{\text{form}}{\longrightarrow}\; \underset{\text{copper chloride}}{CuCl_2}$$

In one of the above cases, that of the union of hydrogen with chlorine, both the uniting substances are gases. They burn together with a pale, weird flame, which gives off a feeble, flickering light. A mixture of chlorine and hydrogen when illuminated with sunlight explodes with great violence.

Special Cases of Burning. Many fuels contain both hydrogen and carbon. When they burn, water vapor and carbon dioxide are formed, provided that enough air is present. If the supply of air is insufficient or the flame cools, the burning is incomplete. Instead of carbon dioxide, carbon monoxide or even black carbon (soot) may be formed. There is always some incomplete burning inside the cylinder of a running automobile engine. The flame of burning gasoline vapor and air strikes the water-jacketed or air-cooled metal wall of the cylinder. Poisonous carbon monoxide is always present (3 to 12 per cent) in the exhaust gas of an automobile engine. As little as 0.04 per cent of carbon monoxide (CO) is definitely poisonous to breathe. In fact, harm may come from but a few parts per million (ppm) of this deadly gas.

If burning is still more hampered, water and carbon are formed. The carbon is formed as smoke or soot, black and dirty, a waste of fuel. A candle flame is sooty if cooled by a draft.

The following equations represent different degrees of burning:

Complete burning:

$$\underset{\text{Methane and}}{CH_4 +} \quad \underset{\text{oxygen (abundant)}}{2O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{carbon dioxide and}}{CO_2} \quad \underset{\text{water}}{+ 2H_2O}$$

Partial burning:

$$\underset{\text{Methane and}}{2CH_4 +} \quad \underset{\text{oxygen (limited)}}{3O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{carbon monoxide and}}{2CO} \quad \underset{\text{water}}{+ 4H_2O}$$

Burning with difficulty:

$$\underset{\text{Methane and}}{CH_4 +} \quad \underset{\text{oxygen (scarce)}}{O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{carbon}}{C} \quad \underset{\text{and water}}{+ 2H_2O}$$

Here are some examples of substances, already oxides, that can be made into higher or more complete oxides:

$$\underset{\text{Carbon monoxide}}{2CO} \quad \underset{\text{and oxygen}}{+ O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{carbon dioxide}}{2CO_2}$$

$$\underset{\text{Sulfur dioxide}}{2SO_2} \quad \underset{\text{and oxygen}}{+ O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{sulfur trioxide (tri = three)}}{2SO_3}$$

$$\underset{\text{Cuprous oxide}}{2Cu_2O} \quad \underset{\text{and oxygen}}{+ O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{cupric oxide}}{4CuO}$$

$$\underset{\text{Ferrous oxide}}{4FeO} \quad \underset{\text{and oxygen}}{+ O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{ferric oxide}}{2Fe_2O_3}$$

Chlorine has a similar action. For example:

$$\underset{\text{Ferrous chloride}}{2FeCl_2} \quad \underset{\text{and chlorine}}{+ Cl_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{ferric chloride}}{2FeCl_3}$$

$$\underset{\text{Phosphorus trichloride}}{PCl_3} \quad \underset{\text{and chlorine}}{+ Cl_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{phosphorus pentachloride}}{PCl_5}$$

Each chemical change represented here is one of the simplest sorts of chemical action, that of joining together. Each product is a distinct and separate substance having its own properties.

All the chemical changes given previously in this chapter can be performed in the laboratory. Some, indeed, require a high temperature and some are aided by the presence of a catalyst, but all will form the products shown, provided that the conditions are correct. On the other hand, the reverse actions usually do not work.

$$\underset{\text{Carbon and oxygen}}{C + O_2} \quad \underset{\text{form}}{\longrightarrow} \quad \underset{\text{carbon dioxide}}{CO_2}$$

represents a reaction. The reverse,

$$\underset{\text{carbon dioxide}}{CO_2} \quad \underset{\text{forms}}{\longrightarrow} \quad \underset{\text{carbon and oxygen}}{C + O_2}$$

does not work under any ordinary set of conditions. We should not assume chemical actions beyond the reach of our chemical experience.

QUESTIONS

11. Define *oxide.*

12. What is burning?

13. Complete these chemical statements (*do not write in this book*):
tin + oxygen → ; sulfur + oxygen → ; selenium + oxygen →
lead + oxygen → .

14. Name the elements present in each of the following compounds: carbon dioxide, sulfur dioxide, ferric oxide. What element is common to them all?

15. What element is present in all oxides?

16. Explain how the law of conservation of matter applies to the burning of a piece of wood.

17. Some freshly cut fruit, such as bananas, darken rapidly when exposed to air. Suggest one possible cause for the change.

18. Does a change in weight take place when a metal corrodes?

19. What evidence do we have of similarity between the chemical actions of oxygen and of sulfur?

20. When 1 ton of coke, 95 per cent carbon, burns, approximately 2.5 tons of gaseous products go up the chimney. Explain the increase in weight.

MORE CHALLENGING QUESTIONS

21. Why does soot accumulate in a chimney?

22. A hand-fed boiler sends smoke up the chimney chiefly when fresh fuel is supplied to the fire. Explain.

23. Calculate the weight of unchanged gas that went up the chimney in question 20.

24. Describe how Lavoisier applied the scientific method in his studies of the process of burning.

25. Investigate the Stahl-Becher theory of phlogiston, and explain it convincingly.

26. What products are formed when kerosene burns?

27. For what reason does the flame on a lighted candle go out when
(*a*) The wick is pinched with the fingers?
(*b*) A person blows on it?
(*c*) The candle is suddenly dropped?
(*d*) The candle is thrown?
(*e*) The wick is inserted between the nearly closed jaws of a monkey wrench?

The Rate of Burning. *1. Effect of Temperature.* Experiments show that, the hotter a fuel, the better it burns. Many chemical actions take place more easily when the substances reacting are warm rather than when they are cold. In fact, many reactions that proceed nicely at high temperatures apparently do not take place at all at ordinary temperatures. An automobile engine is designed so that the pipe carrying the mixture of fuel and air to the engine passes over the pipe carrying the hot exhaust gases from the engine. This arrangement preheats the gasoline vapor, making more efficient use of the fuel. Throwing cold fuel on top of a hot fire is a wasteful process, although it is often the only practicable way to feed a fire. A temperature rise, then, increases the rate at which fires burn or, in general, increases the rate of oxide formation.

2. Effect of Surface. A crumpled newspaper burns better than a flat one; shavings burn better than a log of wood. A "fuzz stick" (see Fig. 4-7) is used to start a fire. Finely divided iron burns in air, as evidenced by the sparks seen when a knife is sharpened on a grinding wheel.

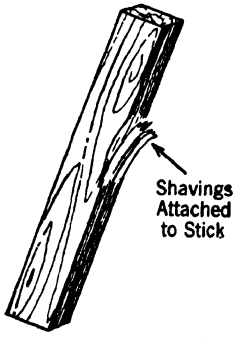


FIG. 4-7.—Fuzz stick.

Chemical action takes place between ***particles*** of reacting substances. Just as two boxers who are close together have a better chance to "mix it up" than when they are far apart, so it follows that, the more closely or intimately mixed the different particles are, the better the chance for chemical action. If pure oxygen is used in place of air for burning, the chance of the fuel and the oxygen coming together is increased fivefold. Pure oxygen is seldom used for ordinary fires because of the expense of gas. Another method, however, is commonly used if rapid burning and a very hot fire are desired, namely, that in which the fuel is powdered and sprayed into the air. Powdered coal packs and burns slowly, and an open vessel of oil burns poorly. But if particles of coal or droplets of oil are mixed well with air and carried along by an air or steam jet and thrown into a firebox, then burning takes place so quickly that it is almost explosive.

We can illustrate this reaction by opening up a firecracker, spreading the black gunpowder out on a metal pan, and carefully applying a lighted match to the powder. The resulting flash shows that the carbon and sulfur in the gunpowder have united with oxygen, but in this case compacted oxygen comes from a compound, potassium nitrate, which readily gives up that element.

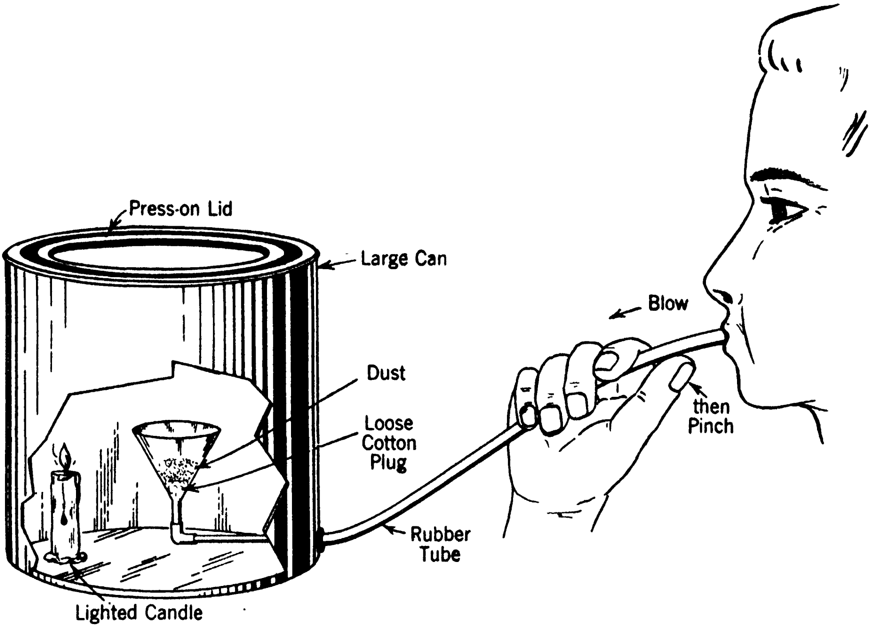


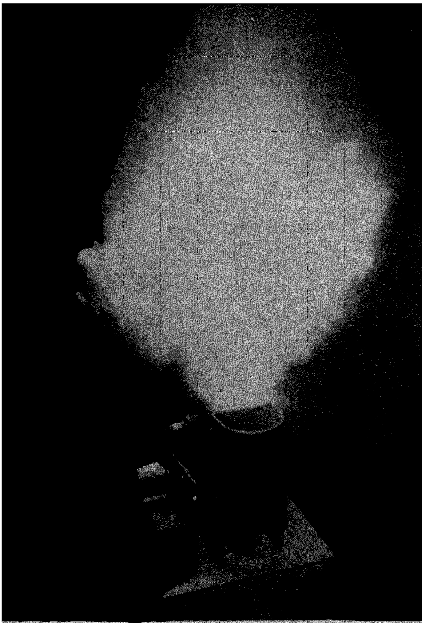
FIG. 4-8.—A homemade dust explosion apparatus produces impressive results.

Iron in Form of	Burning
Spikes	None
Steel wool	Slowly if heated strongly
Dust	Well if blown into air and ignited
"Pyrophoric"* iron (atom-fine dust)	Catches fire by itself

* Pyrophoric iron may be made by heating ferrous oxalate carefully. Beware of the carbon monoxide produced at the same time.

The effect on burning of the amount of surface exposed to the air is well illustrated by the oxidation of iron. As we know, a common nail or spike will rust (oxidize slowly), but we cannot light it with a match and make it burn. Fine steel wool, on the other hand, burns a bit in air if heated in the flame of a Bunsen burner, and the shredded metal burns brilliantly if heated and plunged into pure oxygen. If the iron is powdered, it burns readily when warm enough, as is the case when fireworks "sparklers" are burned. Still further, if the iron is in a very finely divided condition, as it is when it is made by heating ferrous oxalate, it catches on fire when sprinkled into the air. We may observe that the nail is the best conductor of heat in the group and that the fine dust, separated by air spaces, is the poorest.

Dust Explosions. Sometimes the large amount of surface of a fuel exposed to air is the cause of a serious disaster. Dust of flour, starch, paper, or other substances that will burn readily may become suspended in the air of a mill. While the mixture does not burn under ordinary conditions for lack of a kindling temperature, a lighted match or cigarette or any spark will set the entire mass to burning. What was once dust floating in air in a twinkling becomes a raging inferno of heated gas; we say that a dust explosion has taken place. Thousands of dollars' worth of property are destroyed and lives are lost each year in such explosions. Dust from spices, cork, hard rubber, and even dry milk has been reported as causing dust explosions.



Courtesy of The Travelers Insurance Company

FIG. 4-9.—Will the dust in a factory explode? Insurance companies find out by using this apparatus. Once a hazard is discovered, measures are taken to avoid an explosion.

We can make a laboratory-size dust explosion by using some flammable dust and a "press-on" covered can, funnel, rubber tubing, and candle arranged as shown in the diagram. (See Fig. 4-8.) Using a teaspoon, let us put the dust in the funnel, then light the candle, press the cover on, give a sharp puff through the rubber tubing to distribute the dust inside the can, and (important) immediately pinch the tube to prevent backfire. A miniature dust explosion should occur instantly. Lycopodium powder works well in this experiment, although starch, wood dust, and other powders might be tried. An electric sparking device may be substituted for the candle.

3. ***Effect of Catalysts.*** All of us have at some time attended a party that "fell flat." Perhaps the right person did not come. Some persons seem to ensure the success of a social event: they may not do anything in particular, but by merely being present they "make things go." In like manner some chemical actions "do not go well" unless another substance is present. This substance merely by its presence seems to control the rate at which the chemical change proceeds. Strangely enough, the substance is not changed in nature or amount and may be recovered unchanged after the chemical action. For example, dry phosphorus burns hardly at all, but if the phosphorus is moist the burning will proceed easily. Also, extremely dry ammonia and hydrogen chloride are reported not to react, but when only slightly moist they form a white cloud of ammonium chloride. Apparently in many cases a little moisture acts as a helper of burning.

Let us illustrate the action of a catalyst by a competitive experiment. Two pupils are given test tubes containing identical weights of potassium chlorate, but one has a little manganese dioxide mixed in with the potassium chlorate. At a given signal both pupils begin to heat their tubes at the same rate and to test by inserting glowing splinters into the tubes to see which produces oxygen sooner. The pupil in whose tube the catalyst (manganese dioxide) is placed wins the contest easily, but the other will also get just as much oxygen although a longer time and higher temperature are required.

Many other helpers might be mentioned. For example, sulfur dioxide unites with oxygen in the presence of platinum; and platinum causes a mixture of hydrogen and oxygen to explode. The chemists call these helpers—substances that change the rate of chemical actions—***catalysts.*** A large measure of the success of the present-day chemist depends upon his finding suitable catalysts to act as regulators for his chemical reactions. A rubber tire contains catalysts that aid its curing and others (antioxidants) that delay its hardening. Prepared house paint has a "drier," a catalyst that helps it harden. A black substance, manganese dioxide, speeds the decomposition of potassium chlorate when the latter is heated to release oxygen. The same catalyst will make hydrogen peroxide solution decompose rapidly. This solution sold at drugstores usually contains an inhibitor (acetanilide), a sort of negative catalyst, to prevent decomposition.

QUESTIONS

28. Certain types of stokers feed coal to a fire slowly from below the fire bed. What advantage has this method of supplying fuel?

29. A certain type of stove has coal supplied to it from a hopper that is placed directly above the center of the fire. What advantage has this method of supplying fuel?

30. Describe and explain the burning of fireworks "sparklers."

31. Why does a nail not catch fire in the flame of a burning match?

32. Suggest a way to make sawdust burn well.

33. When oil is sprayed into the firebox of a boiler by a steam jet, what becomes of the steam?

34. Describe the conditions that cause a dust explosion.

35. What can be done in a starch factory to avoid a dust explosion?

36. Define and give an example of a *catalyst.*

37. Manganese dioxide hastens the decomposition of potassium chlorate. Does manganese dioxide hasten other decompositions?

MORE CHALLENGING QUESTIONS

38. What conditions are needed to produce spontaneous ignition?

39. The term *flammable* is now preferred to the word *inflammable,* both having the same meaning. What advantage has the first-mentioned term?

40. Oily rags used about a garage do not catch fire as easily as rags used by painters. Compare the rate of oxidation of motor crankcase oil with that of linseed oil.

41. How does a flowing stream of water purify itself?

42. Do "fireproof" buildings ever burn?

Spontaneous Ignition, Commonly Called Spontaneous Combustion. Burning may go on rapidly or slowly, as we found when we considered the three factors—temperature, amount of surface, and the presence of a catalyst—that influence the rate of this process. The burning of a match is quite rapid; the explosion of a firecracker is still more rapid. The combining of a substance with oxygen, on the other hand, may be exceedingly slow. The rusting of iron, the decay of wood, the "drying" of paint are all examples of slow oxidation. Even when they are cold, coal and sulfur both join slowly with oxygen.

Some painters who were working on a house used cloths to wipe off excess paint. When the job was finished, they threw the cloths together in a metal can, as was proper, although spreading them out would have been a better way to avoid fire. The cloths were soaked with paint, which is mixed with linseed oil, the oil from flaxseed (linen seed). This oil has the ability to unite slowly with oxygen, liberating heat. If the heat energy is not conducted away by air currents, thus cooling the cloths, the rise in temperature will hasten the rate of oxidation. Faster oxidation means heat generated at a still faster rate. The cloths mentioned above became warmer and warmer until finally the temperature was reached at which they began to burn actively. They had reached their kindling temperature by their own slow but rapidly accelerating oxidation and had begun to burn of their own accord. This process is called ***spontaneous ignition.*** Moist hay, coal, and other substances sometimes set themselves afire this way. In order to prevent spontaneous ignition, ventilating shafts are put in piles of coal, in the holds of ships carrying grain, and in other closed spaces where flammable materials are kept, to allow the hot air to escape before the temperature rises to dangerously high values.

We can illustrate spontaneous ignition by wetting some paper with a solution of phosphorus in carbon disulfide and allowing the carbon disulfide to evaporate. This leaves the phosphorus in finely divided condition. Oxidation will be rapid, and the paper soon catches fire. (See Fig. 4-10.)

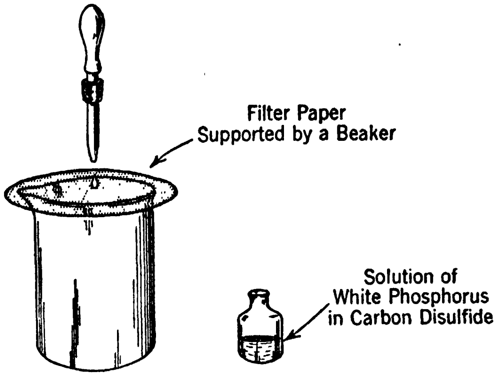


FIG. 4-10.—Spontaneous ignition of phosphorus in air.

Fireproof Substances. If a building is to be absolutely fireproof, the construction materials must consist of fireproof substances, such as bricks, concrete, plaster, glass, and asbestos. These substances do not burn because they cannot; they already hold in combination all the oxygen that they can. Structural steel is also used; it is fireproof, but for a different reason. Unlike brick, the iron can combine with oxygen; but a girder exposes so little surface compared with the total amount of iron particles in it that oxidation takes place at a very slow rate. Also, heat is conducted away rapidly by the girder. Of course, we know from experience which materials are fireproof and which are not, but we may expect to find out from our study of chemistry the reason why some substances burn and others do not.

The Great Scavenger. The earth is a much pleasanter place in which to live because of decay. Were it not for this process, the earth's surface would be littered with dead plants and animals. By the help of oxygen this dead matter is changed into soil and other products, which in turn furnish nutriment for living matter.

After a stream has traveled for several miles over rocks and waterfalls, it purifies itself of waste matter that may have been put into it. The problem of waste matter disposal needs attention in many communities. Some people take great liberties with nature by turning rivers and lakes into open sewers. A farsighted city located on a river or lake first treats its sewage before discharging it into the water. The great harm that waste matter does in a stream is to consume the life-giving oxygen. If no fish or plants can live in the stream because of lack of dissolved oxygen in the water, then the stream becomes foul. Harmful bacteria that may cause disease can be killed by spraying sewage or drinking water into the air and sunshine. This enables the oxygen of the air to destroy the bacteria. Of course, the effect of spraying is to increase the available surface for the action of the oxygen. For the same reason a storm on inland or coastal waters has a sanitary effect.

Thus we see the element oxygen playing two parts on the stage of life. Its role as a necessary, humble, life-giving servant, healer of the sick, and preventer of disease is one that we all appreciate. Oxygen also plays the part of the villain when out of control, destroying our homes and forests with its terrible chemical action, burning.

Plant-life–Animal-life Balance. The woody part of plants consists chiefly of compounds containing three elements—carbon, hydrogen, and oxygen. These elements must be obtained by the plant from its surroundings, the soil and the air. The soil furnishes water, the air carbon dioxide. With sunlight, the leaves of a plant are able to carry on changes in these materials, converting them into starches, sugars, and woody tissues—wonderful changes that no person has yet been able to duplicate

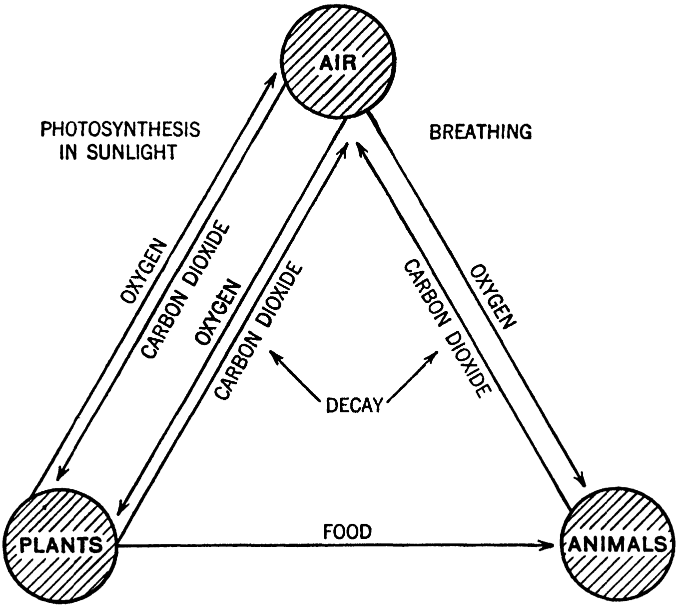


FIG. 4-11.—Carbon dioxide-oxygen cycle.

in the best chemical laboratory. ***Photosynthesis,*** as this process is called, essential for animal life on the earth, uses the carbon dioxide from the air and restores oxygen to it. A green coloring matter, chlorophyll, in the leaf is the catalyst.

We have seen that carbon dioxide may be formed by burning in air anything containing carbon. This gas also enters the air from the natural processes of decay, breathing, and fermentation. It is apparent, therefore, that the same carbon does duty again and again, going through the plant-animal cycle from time to time. It is also apparent that energy from the sun is necessary to keep carbon, essential to both plant and animal life, moving in this cycle. Possibly all the oxygen in the air is there as a result of photosynthesis. (See Fig. 4-11.)

Making Carbon Dioxide. At certain places on the earth gas wells send forth enormous supplies of carbon dioxide gas. An old well, cistern, cave, or similar cavity where decay is going on may have a layer of this gas near the bottom where it is being produced faster than it diffuses into the air above. One instance of this is a certain Italian cave, where any small animal, such as a dog, becomes suffocated in the lower layer of gas, whereas a larger animal or adult human being may wade through it unharmed.

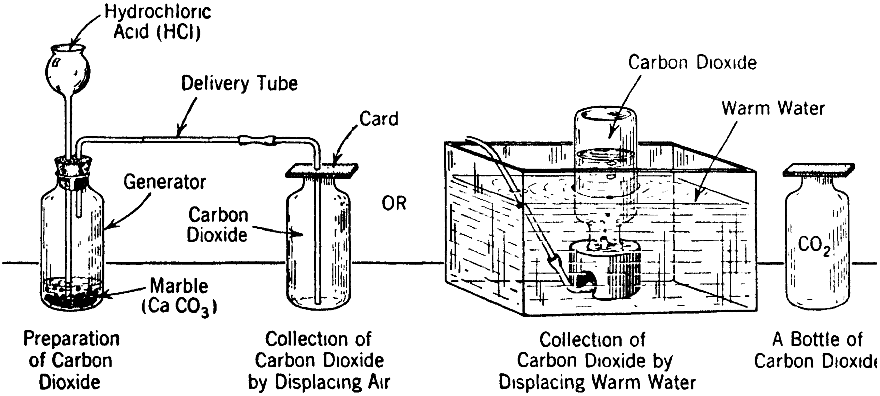
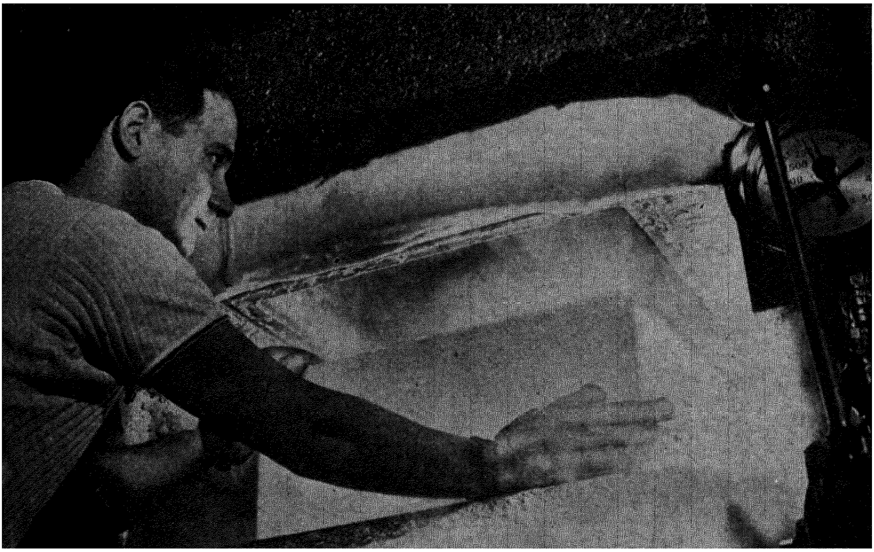


FIG. 4-12.—Carbon dioxide is prepared in the laboratory by the use of a carbonate and an acid—in this case, marble and hydrochloric acid.

Carbon dioxide was discovered and shown to be a distinct gas by a Scotch chemist, Joseph Black (1728–1799), in 1775. All complete burning of carbon or its compounds in air produces carbon dioxide, $C + O_2 \rightarrow CO_2$. This reaction and the process of fermentation are both used industrially as a source of this gas. Commercial sources of carbon dioxide also include some natural gas and carbonates and bicarbonates, which are heated to obtain the gas.

We generate carbon dioxide in the home when we make bread. The yeast plant acts on the sugar to produce this gas, which in turn makes bubbles in the dough to leaven (lighten) it. The porous nature of most baked foods is due to bubbles of this gas. All baking powders make carbon dioxide when added to water or heated. ***Effervescent*** tablets or powders, sometimes used medicinally, generate carbon dioxide in a manner similar to the action of baking powders.

In the laboratory it is customary to select the method for making a gas that proceeds at a moderate rate, is convenient, and uses cheap and readily obtainable materials. These conditions for making carbon dioxide are all met by putting acid on marble in a gas generator bottle. (See Fig. 4-12.) Marble is almost pure calcium carbonate ($CaCO_3$), the source of the carbon dioxide in this case. Hydrochloric acid (HCl), a compound of hydrogen and chlorine in water solution, is added through a funnel or safety tube, and the gas escapes through the delivery tube into a vessel made ready to receive it. The action is thought to go on in two steps, the carbonic acid first formed being quite unstable and therefore decomposing at room temperature.



Courtesy of Pure Carbonic, Incorporated

FIG. 4-13.—Every 7 minutes a 220-pound block of solid carbon dioxide drops out of this huge machine. Solid carbon dioxide has extensive use as a refrigerant because it sublimes.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2CO_3$$

Calcium carbonate + hydrochloric acid → calcium chloride + carbonic acid

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Carbonic acid decomposes to form water and carbon dioxide

This action is quite general; any strong acid and any carbonate will give similar results.

If carbon dioxide is present in large amounts in the air, there is usually a lack of oxygen. For example, in Chungking, China, in 1941, 4000 Chinese died in an air-raid shelter, not from bombs, but from suffocation and panic caused by lack of sufficient oxygen in the air.

Properties and Uses of Carbon Dioxide. The gas carbon dioxide, since we breathe it out through our nostrils, obviously has no odor, color, or marked taste. One liter weighs 1.98 grams, compared with 1.29 grams for a liter of air. Water dissolves a moderately large volume of carbon dioxide, especially when the water is cold and the gas under pressure.

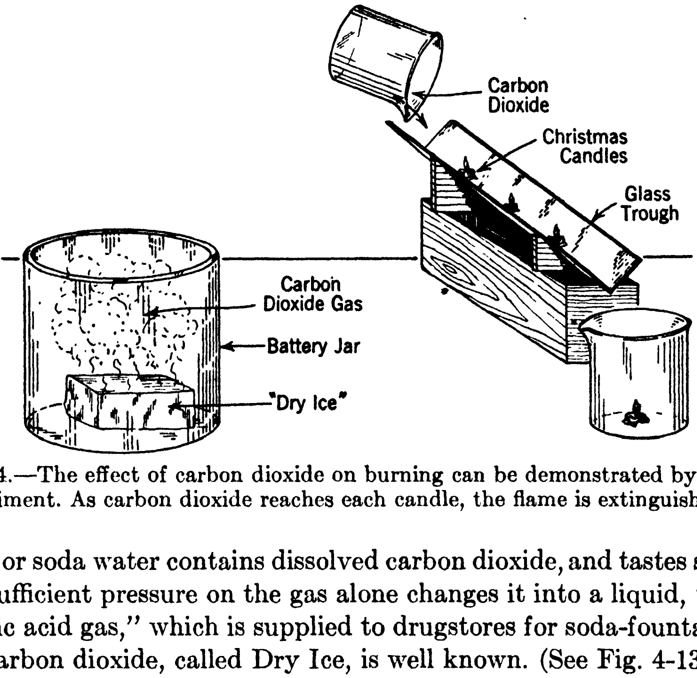


FIG. 4-14.—The effect of carbon dioxide on burning can be demonstrated by this experiment. As carbon dioxide reaches each candle, the flame is extinguished.

Seltzer or soda water contains dissolved carbon dioxide, and tastes slightly sour. Sufficient pressure on the gas alone changes it into a liquid, "liquid carbonic acid gas," which is supplied to drugstores for soda-fountain use. Solid carbon dioxide, called Dry Ice, is well known. (See Fig. 4-13.) This substance may be formed by rapid expansion of the compressed gas from a small opening. It is useful for refrigeration purposes because of its low temperature, about −78°C, and the fact that it evaporates into a gas at room conditions of temperature and pressure without going through a liquid state, a process known as ***sublimation.***

Dry Ice generators make effective fire-fighting devices. One notices a funnel or cone-shaped end on the hose leading from the cylinder of liquid carbon dioxide on this type of fire-fighting equipment. (See Fig. 4-15.) The funnel-shaped opening directs the shower of carbon dioxide snow formed when the valve is opened. Since ordinary burning will not occur in carbon dioxide, nor will the gas catch fire and burn, this dense, cold gas makes an effective substance to use to put out fires.

The turnover type of fire extinguisher contains a bottle of acid that when inverted mixes with a bicarbonate solution, generating carbon dioxide gas.

$$H_2SO_4 + 2NaHCO_3 \rightarrow Na_2SO_4 + 2H_2O + 2CO_2\uparrow$$

(See Fig. 4-16.)

Other types of fire extinguishers generate the gas by a similar action but enclose it in a stiff foam. This is a much more effective way to use the gas, especially for fighting oil fires. (See Fig. 4-17.) Still another sort of fire extinguisher contains a capsule of compressed liquid carbon dioxide similar to that used for inflating life rafts. When the capsule is broken by inverting the extinguisher and striking it against a hard surface, the gas forces itself and water, which is also in the extinguisher, out the nozzle.

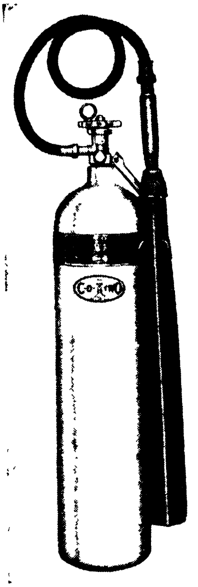

Courtesy Pyrene Manufacturing Company

FIG. 4-15.—This fire extinguisher contains liquid carbon dioxide. When the valve is opened, the escaping liquid evaporates, forming carbon dioxide snow, thus showering the fire with a very cold blanket of nonflammable gas.

Liquid carbon dioxide is used extensively as an explosive in mining coal.

Sparkling beverages containing carbonic acid are great thirst quenchers. Soda water in all its tasteful flavors is sweetened carbonic acid solution. The beverage is prepared by the addition of a little flavored sirup to a carbon dioxide-water mixture under pressure.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Taken into the mouth where the temperature is warm, the carbonic acid decomposes into water and carbon dioxide again, the gas bubbles causing a sensation on the tongue that "tastes like your foot's asleep." Beverages like homemade root beer have carbon dioxide produced in them by fermentation.

Carbon dioxide reaches our lungs and is discharged as a waste product of the body after it is separated from the blood. Experiments show that some carbon dioxide dissolved in the blood is essential for normal breathing. In cases of attempts to revive a person after gas poisoning, Prof. Henderson of Yale University found that 3 per cent carbon dioxide mixed with oxygen is more effective than pure oxygen. The carbon dioxide stimulates the "breathing centers" in the brain.

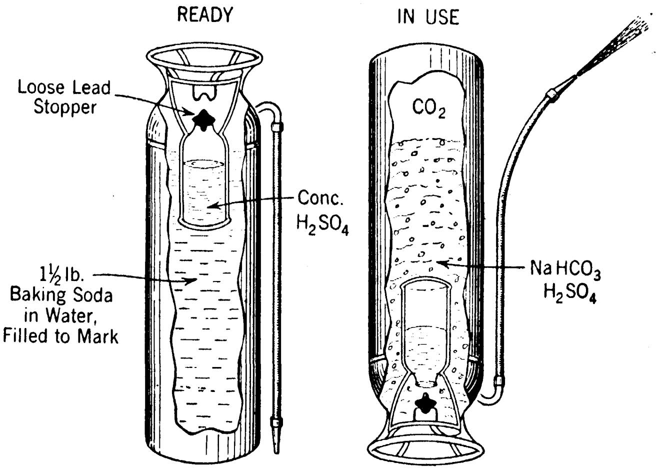
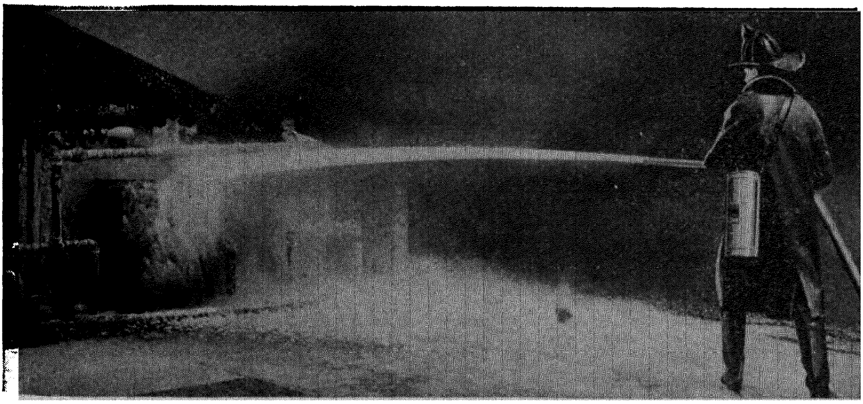


FIG. 4-16.—When the extinguisher is inverted, the contents of the acid bottle mixes with the bicarbonate solution. Carbon dioxide is formed under pressure, and the contents of the extinguisher is forced out of the nozzle.

Courtesy of Pyrene Manufacturing Company



Courtesy of Pyrene Manufacturing Company

FIG. 4-17.—A typical industrial fire involving flammable liquids is short lived when a foam-type carbon dioxide extinguisher is used. A stream of water would be useless for such a fire.

One way in which an engineer tests his steam boilers for operating efficiency is to measure the percentage of carbon dioxide in the gas that goes up the chimney. Frequently a "stack CO_2 recorder" is part of the equipment of a large boiler. (See graph, Fig. 4-18.) One type of recorder depends for its success on one of the important properties of carbon dioxide—its ability to combine with a solution of a hydroxide. Probably the carbonic acid is first formed.

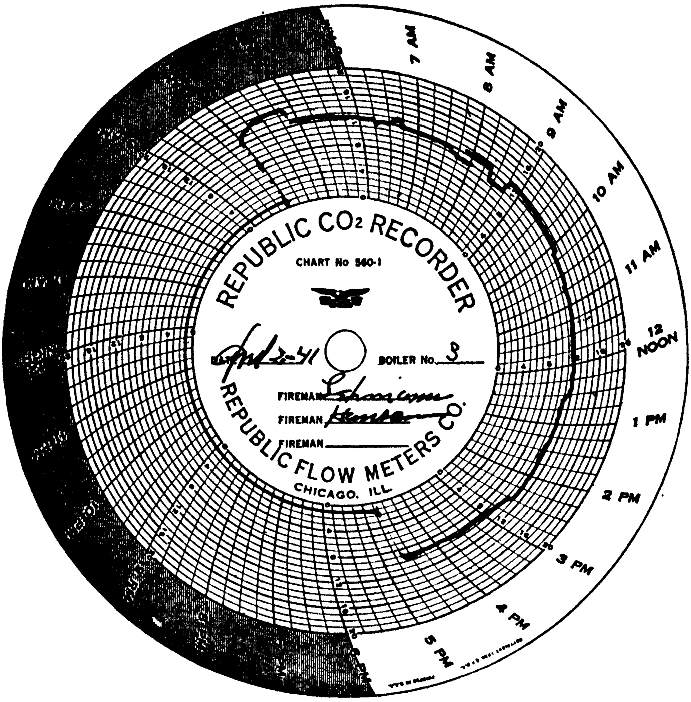


FIG. 4-18.—At what time did the fireman start the boiler for heating the school building? At what time was the oil fire shut off? The record on the stack carbon dioxide recorder tells the story. It also indicates how effectively the fuel was burned.

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Then the acid acts on the hydroxide.

$$\underset{\text{Carbonic acid}}{H_2CO_3} + \underset{\text{sodium hydroxide (lye)}}{2NaOH} \rightarrow \underset{\text{sodium carbonate}}{Na_2CO_3} + \underset{\text{water}}{2H_2O}$$

When a solution of calcium hydroxide is used for this action, the calcium carbonate that is produced is insoluble in water. It is seen as a white powder in the liquid, giving an appearance of milkiness. Small, solid, insoluble particles formed in this manner are called a ***precipitate.*** When their density is greater than that of the liquid, they usually settle to the bottom of the container.

$$\underset{\text{Carbonic acid}}{H_2CO_3} + \underset{\substack{\text{calcium hydroxide}\\\text{(limewater)}}}{Ca(OH)_2} \rightarrow \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{water}}{H_2O}$$

Since no other gas acts in just this way, this action is used as a ***test*** to identify the gas carbon dioxide. (See Fig. 4-19.)

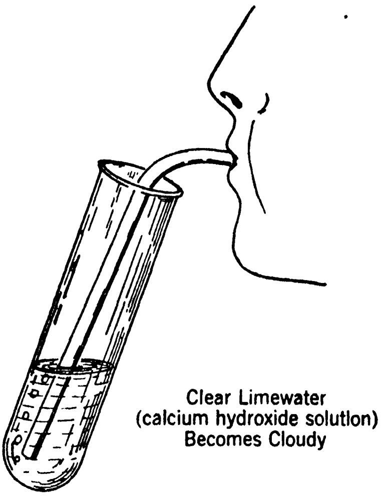


FIG. 4-19.—The presence of carbon dioxide can be proved by the milky precipitate it forms in lime water.

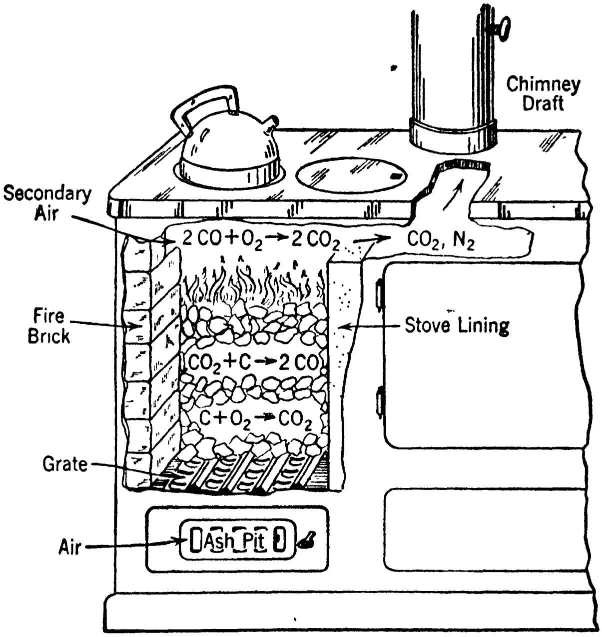


FIG. 4-20.—A number of chemical changes go on in an ordinary coal fire. When the stove is operating properly, the dangerous carbon monoxide is completely burned.

The Household Stove. Another chemical action of carbon dioxide is illustrated by the changes that take place in the firebox of a household stove that burns charcoal, coal, or coke—all considered to be pure carbon in this discussion. (See Fig. 4-20.) Air enters the stove through the bottom door. The oxygen unites with the hot carbon in the lower part of the fire.

$$C + O_2 \rightarrow CO_2$$

As the carbon dioxide formed rises, it meets more hot carbon, which shares the oxygen with it, forming carbon monoxide.

$$CO_2 + C \rightarrow 2CO$$

In this action we say that the carbon dioxide was ***reduced,*** that is, had oxygen taken from it. Carbon monoxide reaches the top of the bed of coals, where it receives more air through the upper door and burns with the blue flame seen playing over a coal fire, again forming carbon dioxide.

$$2CO + O_2 \rightarrow 2CO_2$$

Compared with oxygen, carbon dioxide often exhibits an opposite character.

Oxygen aids burning.	Carbon dioxide stops burning.
Oxygen aids breathing.	Carbon dioxide suffocates.
Oxygen combines with burning substances.	Carbon dioxide is a product of burning

SUMMARY

In ordinary burning a flammable substance unites with oxygen of the air, a change that gives out light and heat; the products formed are oxides. This process was not always understood correctly. The phlogiston theory (about 1700) gave an incorrect explanation that was disproved by careful experimentation on burning carried out by Antoine Laurent Lavoisier, a great French scientist.

The requirements for burning are

1. A flammable fuel
2. An adequate supply of air or oxygen
3. Temperature up to the kindling or ignition point

Methods of extinguishing a fire include removal of any one of the three conditions necessary for burning. More specifically, we may

1. Cool the burning material below its kindling point
2. Shut off the air or oxygen
3. Remove the fuel

Physical properties: Oxygen is colorless, tasteless, odorless, and slightly soluble in water and has a density of 1.29 grams per liter at standard conditions.

Chemical properties: Oxygen aids burning and does not catch fire, and it forms oxides when it combines with both metals and nonmetals.

Oxygen is identified by the fact that a glowing wooden splinter will burst into flame in the gas.

Oxygen is used to aid breathing under difficulties such as in sickness, in submarine work, and at high altitudes. It is also used to produce intensely hot fires as in the oxyacetylene torch. The gas comes to the market compressed in strong steel cylinders.

When an element joins oxygen, an oxide is formed. The oxide weighs more than the original element, but the weight of the element plus the weight of the oxygen used just equals the weight of the oxide formed. The elements sulfur and chlorine both act chemically in supporting burning in a manner similar to oxygen, but they form sulfides and chlorides, respectively, as products of burning.

Incomplete burning of carbon or its compounds may produce carbon monoxide, a very poisonous gas. Hence attention to the exhaust fumes from a running motor and to other sources of this deadly gas is advisable from a health standpoint. Oxidation may be complete or partial, depending upon the conditions of burning.

Increased temperature hastens the rate of burning, and the closer the contact between the fuel and air the more rapid the burning. A dust explosion is an extreme case of rapid burning. Conditions necessary for a dust explosion include the distribution of a flammable dust in the air of a closed space and a means of igniting the mixture. An extremely rapid oxidation takes place.

Substances acting as catalysts hasten the rate of combining with oxygen. Their action is specific to a given situation. An example of the use of a catalyst is the adding of manganese dioxide to hasten the decomposition of potassium chlorate in the preparation of oxygen.

Spontaneous ignition is sometimes called spontaneous combustion. To undergo spontaneous ignition, a substance must be capable of slow oxidation, and the heat resulting from the oxidation must accumulate. The rising temperature increases the rate of oxidation, and this in turn increases the temperature until the kindling temperature is reached.

Oxygen enters in the natural processes of decay and fermentation of waste materials. Oxygen purifies natural water, and it is used for burning and breathing.

Carbon dioxide is found in the air (about 0.03 per cent) and in places where decay and fermentation are occurring. Some natural gas wells are rich in this gas. A little of the gas is needed to stimulate the breathing of animals, and plants use the gas extensively in photosynthesis. Impure carbon dioxide is made by burning carbon or carbon compounds. It can also be collected from tanks in which fermentation is proceeding and from certain natural gas wells.

In the laboratory, carbon dioxide is prepared by the action of an acid on a carbonate or a bicarbonate. Marble, consisting chiefly of calcium carbonate, is usually used as the source of the gas. The gas may be collected by displacement of either water or air.

Physical properties: Carbon dioxide is colorless, odorless, almost tasteless, moderately soluble in water, and more soluble with increased pressure. Its density (1.98 grams per liter) is greater than that of air, and it is rather readily changed to a liquid or to a solid (Dry Ice).

Chemical properties: Carbon dioxide not only does not burn, but also it extinguishes ordinary fires. It combines with water, forming carbonic acid, and it forms a carbonate with any soluble hydroxide. The test to identify the gas is made by passing some of it into limewater (calcium hydroxide solution). If a white precipitate forms, the presence of carbon dioxide is shown.

Carbon dioxide is used in carbonated beverages because it is moderately soluble and forms a weak acid with water. It is used extensively as in fire extinguishers and as a refrigerant, especially in the form of Dry Ice.

QUESTIONS

43. Suggest a practical way to find out whether carbon dioxide is present in a well; in a silo.

44. Explain the holes in baked cake dough.

45. List five natural sources of carbon dioxide.

46. Tell how to make impure carbon dioxide from paper.

47. Describe a laboratory method of preparing carbon dioxide from marble. Include a labeled sketch of the apparatus.

48. Complete these statements of chemical changes (*do not write in this book*):
(*a*) Magnesium carbonate + hydrochloric acid →
(*b*) Strontium carbonate + hydrochloric acid →
(*c*) Barium carbonate + hydrochloric acid →
(*d*) Sodium carbonate + hydrochloric acid →

49. List at least four physical properties of carbon dioxide.

50. Dry Ice is sometimes placed inside closed automobiles crossing the desert. Point out a possible danger from refrigerating a car in this manner.

51. Point out a use of carbon dioxide in connection with rubber life rafts.

52. Complete these statements of chemical changes (*do not write in this book*):
(*a*) Carbonic acid + sodium hydroxide →
(*b*) Carbonic acid + potassium hydroxide →
(*c*) Carbonic acid + calcium hydroxide →
(*d*) Carbonic acid + barium hydroxide →

MORE CHALLENGING QUESTIONS

53. Distinguish carbon dioxide from oxygen by practical laboratory testing.

54. Compare the methods of storing and distributing ice cream using mechanical refrigeration and Dry Ice with methods of doing the same job without these conveniences.

55. Give a description of conditions that can cause a parlor stove to become a death-dealing device.

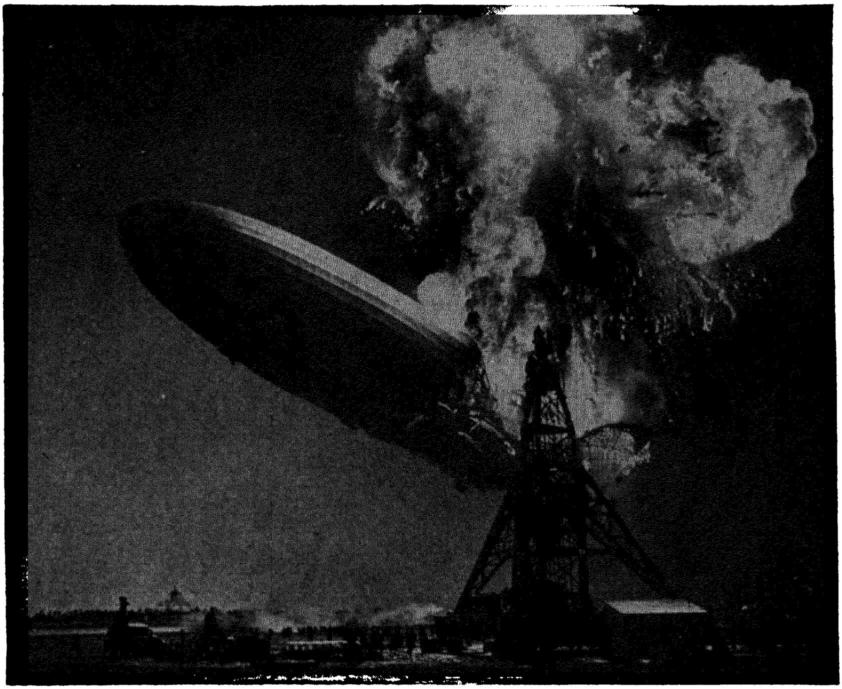
56. Make a labeled diagram of a furnace burning coal, pointing out all chemical changes occurring.

57. A stack CO_2 recorder shows an abnormally high amount of the gas. What are the cause and remedy of this condition? If the CO_2 indicator shows too low a percentage of the gas under full load, why is fuel being wasted?

UNIT ONE ---------------- CHAPTER V

HYDROGEN, THE LIGHTEST GAS

On May 6, 1937, the dirigible *Hindenburg*, pride of Germany's aircraft, was nosing her way toward a mooring mast at Lakehurst, New Jersey. Suddenly the hydrogen-filled bag, which buoyed the ship up, burst into an inferno of blazing gas. (See Fig. 5-1.) The intense heat from



International News Service

FIG. 5-1.—One of the greatest disasters in air history took place in 1937. Many lives were lost in this tragedy. The burning of hydrogen from the gas cells of the Hindenburg is clearly shown here.

New Terms

decomposition
electrolysis
reducing agent
reduction
oxidized
oxidizing agent
deuterium
heavy hydrogen
kinetic
molecule

the fire melted much of the metal framework as the ship fell to the ground, a complete disaster. The cause of this tragedy is thought to have been a spark due to static electricity resulting from friction. Afterward a small local rainstorm occurred; the burned hydrogen formed steam, and the steam condensed to water which soon followed the framework of the ship to the ground.

Early History of Hydrogen. Hydrogen was discovered in 1766 by Henry Cavendish, a wealthy Englishman who studied science as an all-absorbing hobby. He called the gas "inflammable air." The name hydrogen, meaning "water producer," was given to the gas by Lavoisier (see page 54) in 1783, when he proved that water is the only product formed by burning hydrogen.

Soon its lightness was noticed, and hydrogen-filled balloons were making ascents over Paris. Pilatre de Rozier (1754–1785), who made the first notable flight in 1783, also tried breathing the gas. (See Fig. 5-2.) No immediate effect was noticed until an additional experiment was tried. The experimenter filled his lungs with hydrogen. On exhaling, he applied a lighted torch to his breath. The result was startling. Not only did his exhaled breath burn, giving the effect of a human torch, but the hydrogen mixed with air exploded in his mouth, throat, and lungs. "I thought that my teeth would jar loose from their sockets," he writes, after barely surviving the explosion.

FIG. 5-2.—Pilatre de Rozier's famous balloon flights are commemorated on this French postage stamp.

Where Is Hydrogen Found? The element hydrogen is seldom found free. Free hydrogen does occur among the gases coming from certain gas wells, but only to a small extent. Although this gas exists so rarely in the free state on earth, astronomers report that free hydrogen is abundant in the exceedingly hot gases on the sun and other stars.

Compounds of hydrogen, on the other hand, are abundant. For example, all living tissues contain compounds of hydrogen. Also, water, fats, oils of every sort, starch, sugar, alcohol, acids, wood, cotton, paper, gasoline, and natural gas all contain hydrogen in combination, that is, in compounds.

In many manufacturing processes hydrogen is a product. Water gas, coal gas, and producer gas are three commonly manufactured fuel gases that contain hydrogen. Water gas, a mixture of hydrogen and carbon monoxide, contains about 48 per cent hydrogen, coal gas almost 50 per cent, and producer gas 14 per cent by volume. Many processes involve electrolysis, or the passage of an electric current through a solution, and hydrogen is usually a product. When, for example, a storage battery is charged, bubbles of hydrogen come up through the liquid (sulfuric acid solution) inside the battery. When these bubbles mix with air, they may explode if ignited. Electroplating and other processes in industry, such as the electrolysis of salt water, may evolve hydrogen.

Decomposing Water into Its Elements. Water is such a common compound that for many centuries it was thought an element. Water is ***stable;*** that is, it is extremely difficult to decompose by heating. When steam in a closed vessel is heated to the extremely high temperature of 2000°C, about 1 per cent of the water decomposes into hydrogen and oxygen. As the mixture cools the two elements rejoin to form water. Heating to a high temperature, therefore, is not a satisfactory way to decompose water, but it is readily decomposed by means of electrical energy.

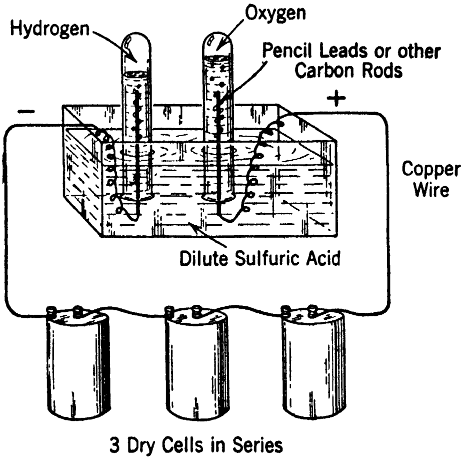
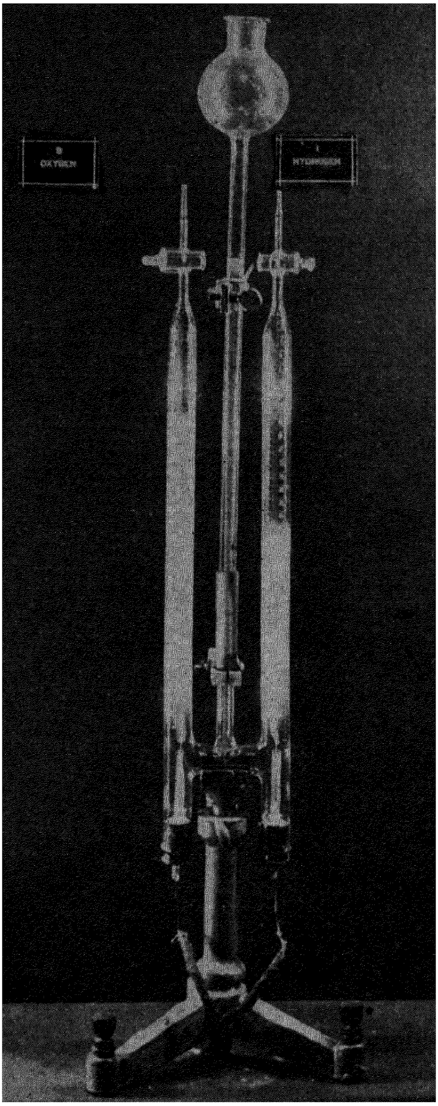


FIG. 5-3.—The electrolysis of water can be carried out with a relatively simple apparatus. Two metal strips, preferably platinum, are inserted in separate test tubes that are inverted in a vessel of dilute acid. When the metal strips, or electrodes, are connected to a battery, decomposition proceeds readily.

Pure water is a poor conductor of electricity. The addition of sulfuric acid or sodium hydroxide (lye) to water improves its conducting ability. A suitable apparatus in which we can carry out this important experiment consists of two connected vertical tubes. (See Figs. 5-3, 5-4.) Each tube is equipped with a metal plate at the bottom, one providing a surface for the electrical energy to enter the solution and the other for the electricity to leave. A stopcock at the top of each tube is convenient for removing the gases collected. When we turn the current on, bubbles of gas arise from the two plates, or electrodes, and collect at the top of the tubes. After the chemical change has gone on for a short while, we notice that gas is collecting faster in one tube than in the other. Let us stop the current after



Courtesy of Buffalo Museum of Science

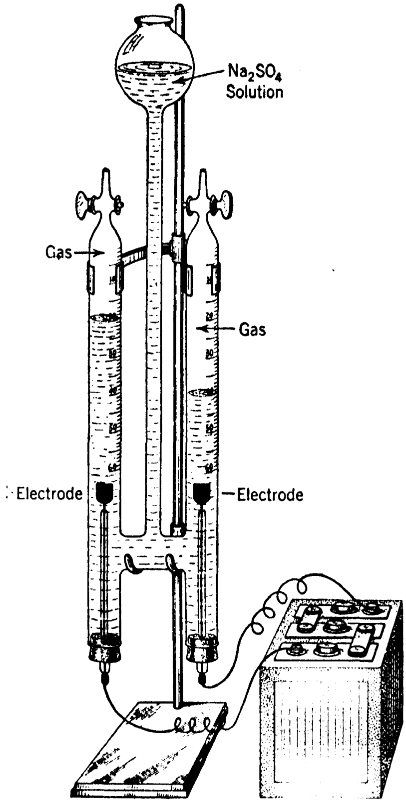


FIG. 5-4.—Hoffman's apparatus for electrolysis of water. Water yields two volumes of hydrogen and one of oxygen when sulfuric acid is added and an electric current is passed through the solution.

a few minutes and measure the amount of gas found in each tube. We find, for example, that 18.4 ml has collected in one tube while a little less than 9.2 ml has collected in the other.[1]

What are these gases? Both are colorless like air. The larger volume of gas catches fire when a lighted match is applied; this will serve for the present as a

---

[1] The volumes of hydrogen to oxygen gas are not exactly in the ratio 2:1 because of the differences in solubility of the gases in water.

test for hydrogen. The smaller volume of gas makes a glowing splinter catch fire; it is oxygen.

This chemical change can be summed up in the statement that

Water forms hydrogen (18.2 ml) and oxygen (9.2 ml)

or, in general, that

Water forms hydrogen (2 parts by volume) and oxygen (1 part by volume)

Still more concisely:

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

This experiment is called the ***decomposition*** of water. Since it is a chemical change brought about by electrical energy, it is also called the ***electrolysis*** of water.

How to Prepare Hydrogen. Hydrogen gas is readily liberated from its compounds. Let us conduct some experiments in its preparation.

1. ***From Water.*** *a.* We have just seen (above) that passing an electric current through water that contains some sulfuric acid liberates hydrogen as well as oxygen. This experiment is identical with the preparation of oxygen by this method. The volume of hydrogen formed is twice that of the oxygen.

The change that takes place may be represented by the statement

$$\underset{\text{Water}}{2H_2O} \xrightarrow{\text{(sulfuric acid)}} \underset{\text{hydrogen}}{2H_2\uparrow} + \underset{\text{oxygen}}{O_2\uparrow}$$

b. Active metals—calcium, sodium, or potassium—replace hydrogen from cold water, forming the hydroxides of the metals at the same time.

Chips of metallic calcium are allowed to sink in a bottle of water. (See Fig. 5-5.) The bottle is immediately covered with a glass plate and inverted, mouth downward, in a tank of water. The glass plate is then removed. The liberated hydrogen rises through the water to the top of the bottle, and the slightly soluble calcium hydroxide [$Ca(OH)_2$], or slaked lime, may be seen as a white suspension in the water.

$$\underset{\text{Calcium}}{Ca} + \underset{\text{water}}{2HOH} \rightarrow \underset{\text{calcium hydroxide}}{Ca(OH)_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

Apparently more rapid action takes place when sodium is used instead of calcium, so that a different experimental method (technique) is used. A piece of sodium the size of a small pea is cut from a larger chunk with a dry knife. The soft, bright, silvery metal is placed in a wire-screen cage at the end of a long wire handle and cautiously but quickly lowered under an inverted bottle full of water, which is resting in a pan of water. (See Fig. 5-6.) CAUTION: The experimenter should be protected by goggles and by working at arm's length, for the action is rapid, and the resulting solution of hot sodium hydroxide (NaOH) is corrosive to the flesh.

$$\underset{\text{Sodium}}{2Na} + \underset{\text{water}}{2HOH} \rightarrow \underset{\text{sodium hydroxide}}{2NaOH} + \underset{\text{hydrogen}}{H_2\uparrow}$$

Even more vigorous action takes place when a tiny chip of metallic potassium is dropped into a large pan of water. In this case the hydrogen is formed at a temperature above its kindling point; thus the gas will catch fire and burn as fast as it is produced if the action takes place in the open air. The caustic potash solution —potassium hydroxide (KOH)—formed at the same time is also dangerous. The experiment, therefore, must be performed with extreme care, only small bits of potassium being used at one time.

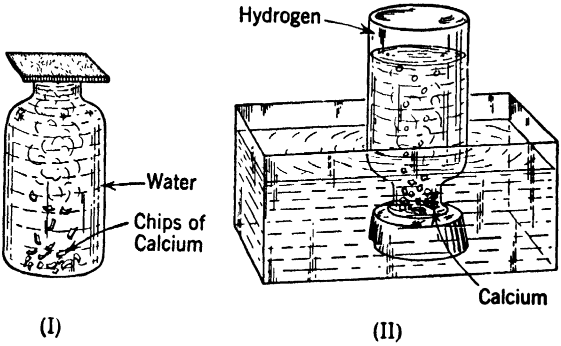


FIG. 5-5.—Active calcium replaces part of the hydrogen in water, liberating the gas.

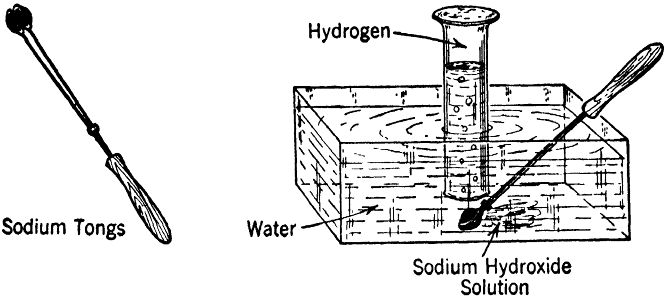


FIG. 5-6.—Extreme care must be used when sodium is placed in water. The energy of the reaction may cause steam to spatter the chemicals. The use of sodium tongs, shown above, keeps the experimenter somewhat removed from this danger.

This last experiment is not practical for a laboratory preparation of hydrogen; but, if considered with the other two experiments, it shows the relative activity of the metals used. We may arrange these metals in a list on the basis of the vigor of their action with water.

Most active..........................	Potassium	K
	Calcium	Ca
Less active..........................	Sodium	Na

Other experiments show that the problem of determining the relative activity of a metal is not quite so simple, for surface tarnish may interfere.

c. Steam produces hydrogen when it is passed over hot coke, iron, or zinc. In the first case the hydrogen is mixed with carbon monoxide, a gas that might interfere with the laboratory use of hydrogen but that usually does not interfere with its commercial use.

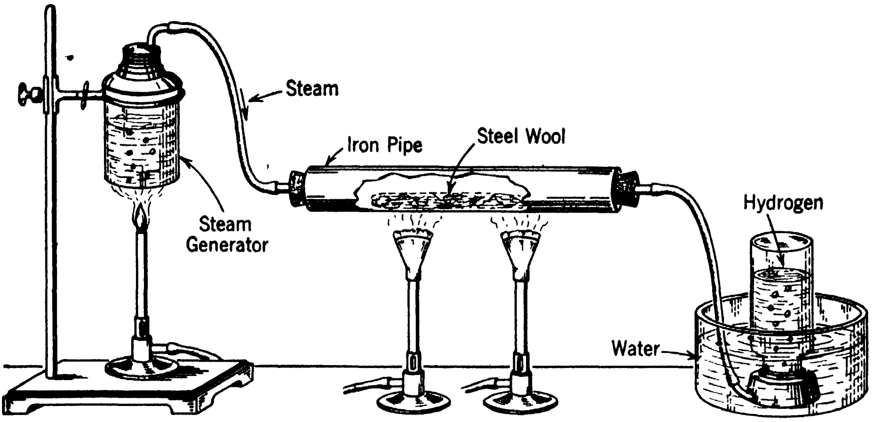


FIG. 5-7.—Heated iron will replace the hydrogen in steam. A convenient method of performing this experiment is shown above. Any unchanged steam passes through the tube and is condensed in the water over which hydrogen is collected.

$$\underset{\text{steam}}{H_2O} + \underset{\text{coke}}{C} \rightarrow \underbrace{\underset{\text{carbon monoxide}}{CO} + \underset{\text{hydrogen}}{H_2}}_{\text{water gas}}$$

For several reasons, this experiment is not easily adapted to demonstration on a small scale, but there is no trouble in using a ton of hot coke in a generator to prepare water gas on a large scale.

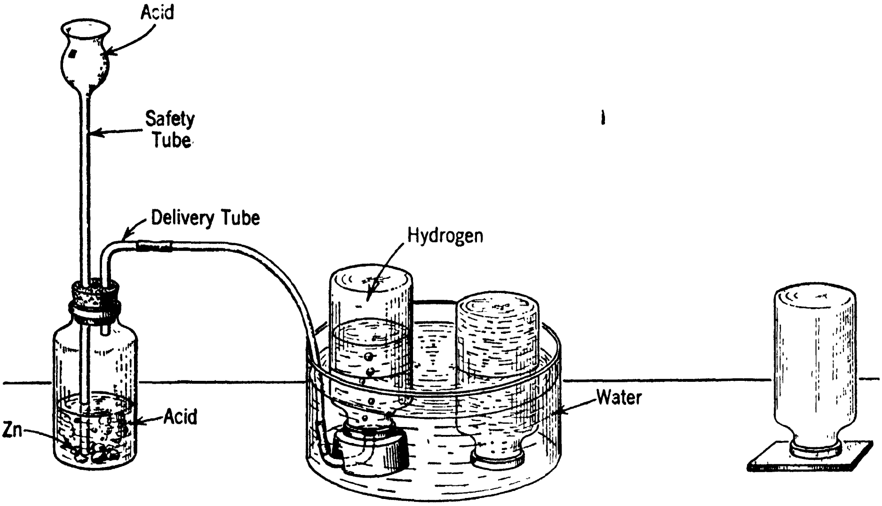
To pass steam over iron, an iron pipe is stuffed loosely with steel wool and placed in position to be heated. The steam is then passed into one end, and a mixture of hydrogen and steam emerges from the other. The steam is condensed by passing the products through water, and the hydrogen is collected as shown in the figure. (See Fig. 5-7.)

$$\underset{\text{iron}}{3Fe} + \underset{\text{steam}}{4H_2O} \rightleftarrows \underset{\text{magnetic iron oxide}}{Fe_3O_4} + \underset{\text{hydrogen}}{4H_2}$$

After a while the iron in the pipe becomes changed into magnetic iron oxide. It is interesting to note that the process can be reversed by passing hydrogen through the tube containing heated iron oxide. Then the iron oxide changes back to iron and the hydrogen to steam. Such a chemical action is called ***reversible.***

2. From Acids. All strong acids contain hydrogen that can readily be replaced by a metal. A plumber "cuts" muriatic acid (hydrochloric acid) by adding bits of scrap zinc. The resulting solution of zinc chloride is useful as a flux in soldering metals together.

Hydrogen is usually prepared by the replacement method in the laboratory. If we wish to examine the gas formed, we use a generator similar to that shown for the preparation of carbon dioxide (see Fig. 5-8) and collect the hydrogen by displacing water. The chemical action that takes place is represented by the equations



Hydrogen Generator

Collection of Hydrogen by Displacing Water

A Bottle of Hydrogen

FIG. 5-8.—The common method of preparing hydrogen. A moderately active metal, such as zinc, is used to replace the hydrogen in a dilute acid. The gas is collected in the same manner as is oxygen.

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

Zinc + hydrochloric acid solution → hydrogen gas + zinc chloride (left in solution)

With dilute sulfuric acid the statement is

$$Zn + H_2SO_4 \rightarrow H_2\uparrow + ZnSO_4$$

Zinc + sulfuric acid (solution) → hydrogen gas + zinc sulfate (left in solution)

An action of this kind is rather general. Aluminum, magnesium, or tin may be used instead of zinc. Each metal produces hydrogen at a different rate. Dilute sulfuric acid, phosphoric acid, or acetic acid may also be used in place of hydrochloric (muriatic) acid. Aluminum and tin do not liberate hydrogen from nitric acid because of a protective oxide coating. Copper and the precious metals are not active enough to ***replace*** the hydrogen from acids.

By comparing the activity of metals in acids, as we did in the case of potassium, calcium, and sodium in water, we can list all the metals in the order of their activity. (See Fig. 5-9.) It is customary to place the most active metal first and the least active last and to include hydrogen in the list. Any metal above hydrogen will replace it from an acid, but any metal below hydrogen will not. Likewise, any metal above will replace one below it from a compound of the less active metal. For example, an iron nail placed in a solution of copper sulfate soon forms a pink coating of copper on the nail.

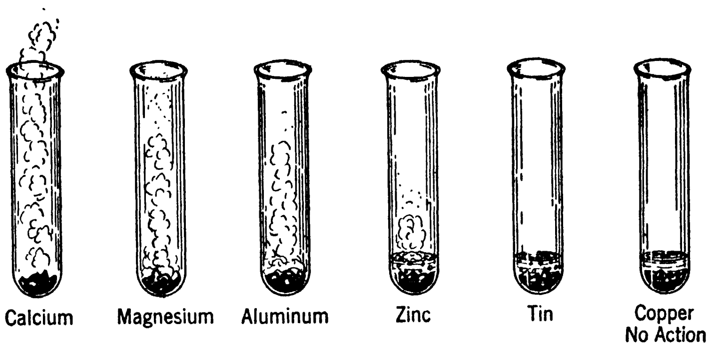


FIG. 5-9.—The metal that dissolves in the acid first is the most active chemically (provided all other conditions are equal).

$$\underset{\text{Nail}}{Fe} + \underset{\text{copper sulfate solution}}{CuSO_4} \rightarrow \underset{\text{iron sulfate solution}}{FeSO_4} + \underset{\text{copper}}{Cu}$$

Yet a solution of Epsom salts (magnesium sulfate) can be carried in a zinc pail without any chemical change taking place. We notice, of course, that zinc is below magnesium in our list; and since it is thus a less active metal than magnesium, we expect no chemical action to take place.

THE REPLACEMENT SERIES OF METALS*

K	Potassium
Ca	Calcium
Na	Sodium
Mg	Magnesium
Al	Aluminum
Zn	Zinc
Fe	Iron
Ni	Nickel
Sn	Tin
Pb	Lead
H	HYDROGEN
Cu	Copper
Hg	Mercury
Ag	Silver
Pt	Platinum
Au	Gold

* The first part of the list is easily memorized by referring to the synthetic name of the "Russian chemist," P. C. S. Mazintl.

3. From Solutions of Alkalies. Zinc, aluminum, or silicon will act with a solution of lye (NaOH) or caustic potash (KOH) to liberate hydrogen vigorously.

The action may be represented thus:

$$2Al + 2KOH + 2H_2O \rightarrow \underset{\text{potassium aluminate}}{2KAlO_2} + 3H_2\uparrow$$

Pure Hydrogen. When hydrogen is prepared by the reaction of an acid and iron or zinc, the gas has a disagreeable odor due to impurities in the commercial metal. Most of the impurities may be removed by passing the impure gas through solutions that absorb and react with the impurities but do not affect the hydrogen. Moisture is removed by passing the gas through a tube that contains a drying agent. We then have pure, dry hydrogen, which has no odor or taste.

Apparatus for obtaining pure and dry hydrogen by such a method is shown in the figure. (See Fig. 5-10.) The solution of sodium hydroxide (NaOH) removes any acid impurities, and the potassium permanganate solution ($KMnO_4$) oxidizes others. The drying agent, commercial Drierite (anhydrous $CaSO_4$) or calcium chloride ($CaCl_2$) in small lumps, removes any moisture.

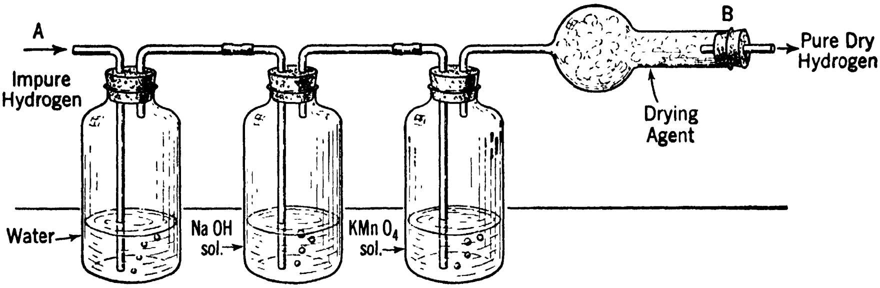


FIG. 5-10.—When pure hydrogen is required, the gas may be passed through a purifying train such as the one above.

QUESTIONS

1. By whom and when was hydrogen discovered?

2. What does the name *hydrogen* mean? Who gave this name to the gas?

3. If a bottle of hydrogen is broken on a mountaintop, which way will the hydrogen tend to move?

4. Point out the danger in bringing a lighted match near a storage battery that is being charged.

5. Name the gases formed in the decomposition of water by electrolysis.

6. Complete the word equations for the action of the following active metals on water (*do not write in this book*):

Potassium + water →
Lithium + water →

7. What experimental evidence have we for arranging the elements potassium, calcium, and sodium in this order?

8. In World War I hydrogen for balloons was prepared by the action of a hot solution of sodium hydroxide on ferro-silicon, acting according to the equation

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2\uparrow$$

Copy the equation, and under each formula write the name of the substance. From what original substances might the hydrogen come?

9. (*a*) When zinc is placed in hydrochloric acid, what is the source of the hydrogen evolved? (*b*) After the zinc has disappeared and the resulting solution evaporated to dryness, a white solid remains. Name this compound.

10. Complete the word equations for the actions of zinc, magnesium, and aluminum, each, on hydrochloric acid, sulfuric acid, and phosphoric acid, respectively.

MORE CHALLENGING QUESTIONS

11. Name the products formed when metallic calcium acts on each of the following acids: hydrochloric, nitric, sulfuric, phosphoric.

12. In each case below tell whether or not a chemical action of replacement takes place. Name the products in case there is a chemical reaction.

(*a*) Zinc + magnesium chloride solution
Zinc + silver nitrate solution
Zinc + zinc sulfate solution
(*b*) Copper plus each of the same three solutions

13. Tell several possible ways in which a hydrogen-air mixture around the gas cells of a dirigible might become ignited.

14. A pupil prepared hydrogen in the laboratory and then smelled the gas. The unpleasant odor seemed to disagree with the description given in the book, that "hydrogen has no odor." Account for the disagreement.

15. Prepare pieces of different metals, each having approximately the same amount of surface. Place each in a test tube, and add equal portions of hydrochloric acid. By noting the differences in the rate of reaction, arrange the metals in order of their chemical activity. Look up more information about metals; can you explain any seeming disagreement with the replacement series given in this chapter?

Physical Properties of Hydrogen. Hydrogen is a gas at room temperature. It can be changed to a liquid, but only with great difficulty. The gas is colorless and without odor or taste. We can collect the gas by displacing water from a container because hydrogen dissolves in water even less than does oxygen. One liter of hydrogen at standard conditions weighs approximately 0.09 g. It is the lightest gas known, a fact that can be demonstrated

1. By pouring hydrogen gas from one bottle to another *upward.* (See Fig. 5-11.)

2. By catching some hydrogen in an inverted beaker that has been balanced on a scale. (See Fig. 5-12.) The pan holding the beaker will rise after hydrogen has been caught in it.

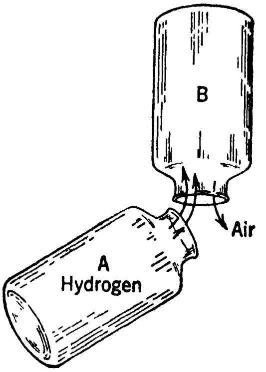


FIG. 5-11.—Hydrogen gas pours up.

3. By filling soap bubbles (use Drene or Dreft solution and two generators connected to a Y tube) with hydrogen. The bubbles rise readily and explode when brushed with a lighted taper.

4. By filling a toy paper or rubber balloon with hydrogen from a cylinder. Either will rise and carry a small load.

Hydrogen is the readiest of all gases to diffuse, that is, to pass through small openings.

If a porous clay jar is covered with a glass bell jar full of hydrogen, so much more hydrogen will pass into the clay jar than air will pass out that the pressure rises inside the jar. This pressure may be used to squirt water. (See Fig. 5-13.)

Chemical Actions of Hydrogen. The most marked chemical action of hydrogen is its ability to burn in air, a fact we have already noted. When it does so, water is the only product. When this experiment, illustrated by Fig. 5-15, is performed, the hydrogen is dried in order to prove that the moisture that collects has not been carried over from the generator to the beaker that acts as a condenser.

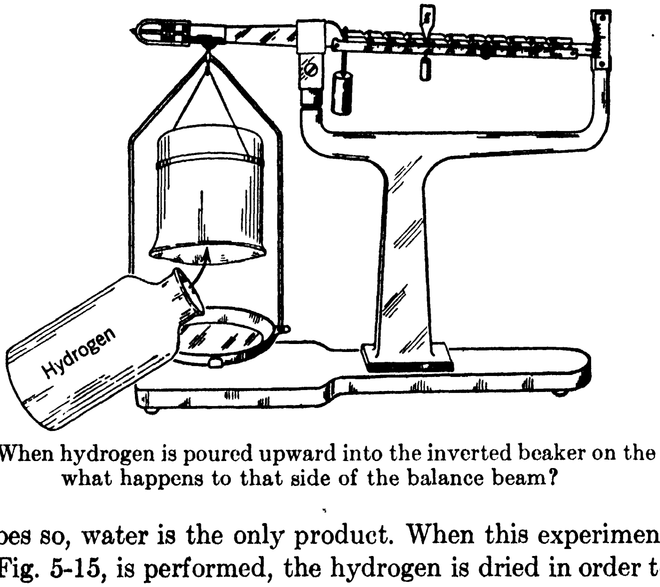


FIG. 5-12.—When hydrogen is poured upward into the inverted beaker on the balance, what happens to that side of the balance beam?

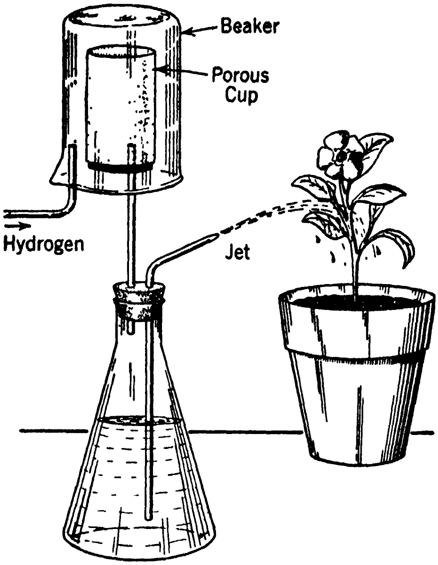


FIG. 5-13.—This shows how to water flowers the hard way. Diffusion rates vary inversely as the square roots of the densities. Hydrogen (density 1) diffuses four times as fast as oxygen (density 16).

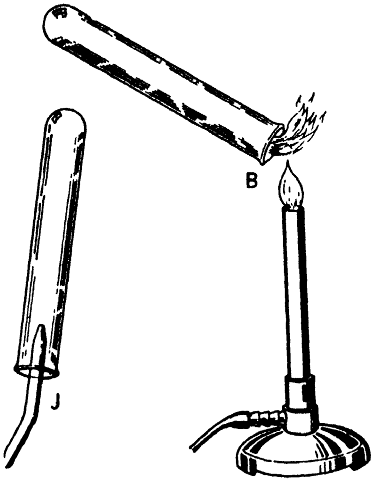


FIG. 5-14.—Here is an experiment to try: light a jet of flammable gas *J* by first catching a test tube full, carrying it to lighted burner *B*, and then returning it lighted to *J*.

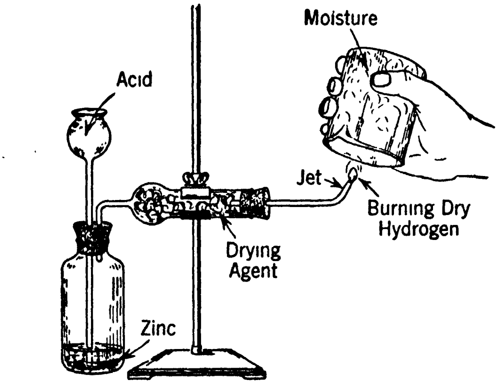


FIG. 5-15.—When this apparatus is used, we know conclusively that the water formed must be a product of the burning at the jet.

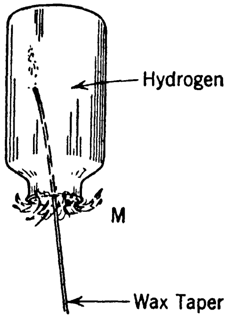


FIG. 5-16.—A lighted wax taper inserted into an inverted bottle of hydrogen ignites the gas at the mouth *M* where it meets the air. The gas burns at the mouth of the bottle and melts the wax. The taper goes out in the hydrogen but reignites on being withdrawn slowly.

In the above experiment hydrogen burns quietly in air. (See Fig. 5-16 for another illustration of the same point.) But when a bottle of mixed hydrogen and air is ignited, it explodes. This has been known to cause serious accidents to beginners in chemistry. A safe rule to follow is to keep hydrogen generators away from flames and to take them apart as soon as the necessary amount of gas has been delivered. If a test tube full of the gas burns quietly, air is not present.

A stout bottle is filled two-thirds with hydrogen and one-third with oxygen. It is then wrapped with a cloth and held at arm's length. A lighted taper applied to the mouth of the bottle containing this mixture produces a report like a pistol shot. The slight amount of steam formed with all this noise is unnoticeable.

Hydrogen will also burn in chlorine and in an atmosphere of sulfur vapor. As we recall, when hydrogen combines with oxygen, ordinary burning takes place. The combining of hydrogen with chlorine or with sulfur is a similar chemical action accompanied by the evolution of light and heat. These three burnings may be represented thus:

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$H_2 + Cl_2 \rightarrow 2HCl$$
$$H_2 + S \rightarrow H_2S$$

The second marked chemical action of hydrogen is its ability to remove oxygen from oxides; this action is said to be a replacement (see page 89).

For example, some black copper oxide is heated in a tube and dry hydrogen passed over it. (See Fig. 5-17.) Moisture collects on the cool part of the walls of the tube, and the copper oxide becomes copper. Hydrogen replaces the copper, forming the oxide of hydrogen, namely, water.

$$CuO + H_2 \rightarrow H_2O + Cu$$

Under some conditions this sort of chemical change may be made to take place with oxides of metals more active than hydrogen. An example has been given in the case of iron oxide and hydrogen forming iron and steam (see page 87).

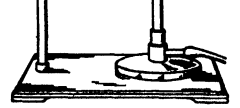


Fig. 5-17.—Hydrogen changes black copper oxide to pink copper. The copper oxide is reduced and the hydrogen oxidized.

In this action we may say that the hydrogen is a ***reducing agent,*** for it has liberated a metal from its compound. The copper oxide was reduced to copper, the product of ***reduction.*** At the same time the hydrogen was ***oxidized*** to water, the product of ***oxidation.*** The copper oxide served as the ***oxidizing agent.***

The third chemical characteristic of hydrogen is its ability to attach itself to other elements or compounds. We have already seen how hydrogen can join with oxygen, chlorine, or sulfur.

Under proper conditions

1. hydrogen adds to nitrogen to form ammonia;
2. hydrogen adds to active metals to form hydrides;
3. hydrogen adds to vegetable oils to form semi-solid fats, which are called vegetable shortenings and are sold at grocery stores;
4. hydrogen adds to coal to form synthetic petroleum;
5. hydrogen adds to petroleum, or certain oils from it, extending the supply of gasoline and improving the product.

Uses of Hydrogen. The colored toy balloons at the circus or fair were probably filled with hydrogen, especially if they floated away when not held tightly. Military observation and barrage balloons are filled with this gas, as are the weather-observation balloons. Hydrogen has proved to be too hazardous for filling dirigibles except for military necessity.

Hydrogen is very useful as a fuel gas, for it burns with an almost colorless blue flame and gives a high heat. As we have previously stated, it is found in several fuel-gas mixtures, especially water gas and coal gas. Hydrogen alone is used as a fuel in torches, the oxyhydrogen torch that is used in constructing X-ray tubes, for example. The hottest of all torches is the atomic hydrogen torch, in which a stream of hydrogen passes over an electric arc. Immediately thereafter the hydrogen burns, liberating the heat taken from the energy of the electric arc as well as the heat of burning. This makes an intensely hot spot (4000 to 5000°C), hot enough to melt quartz (SiO_2, 1710°C) or tungsten (W, 3370°C) or to boil iron (Fe, 3000°C).

In addition to being very hot, the atomic hydrogen flame is a reducing flame. Metallic oxides react with hydrogen and form the metal. A metal-to-metal bond with no oxide film between makes a strong and satisfactory welding job.

Large amounts of hydrogen are used to make ammonia, to "harden" fish and vegetable oils, and especially for the hydrogenation of petroleum.

Kinetic Molecular Theory. In order to explain the rush of air when one moves through it rapidly, the fact that hydrogen passes through porous porcelain easily, and the fact that hydrogen can be heated by an electric arc, producing extreme heat immediately thereafter, let us extend the suggestion that all gases are composed of unit particles called molecules. This useful explanation is called the ***kinetic molecular theory.*** It consists of the following points:

1. Gases are made up of tiny particles called molecules. The molecules are extremely small, and in a given sample of gas the millions of molecules are relatively far apart. A liter of oxygen at standard conditions contains 3 $\times$ 10^{22} (3 followed by 22 zeros) molecules, but the actual space that these molecules occupy is only a small fraction (about one-thousandth) of the liter volume the gas occupies.

2. The molecules of each substance are alike but are different from those of other substances. The molecule is the smallest particle of a compound that can exist. The molecules of carbon dioxide are different in composition from those of water or oxygen, but the molecules of carbon dioxide are essentially all like each other. If the molecule is broken up, the compound no longer exists as such but new substances are formed from it.

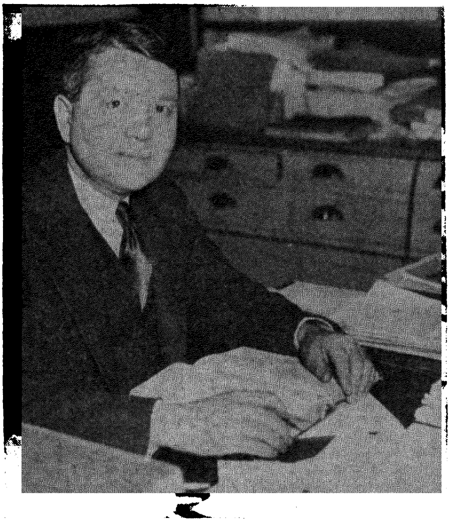
3. Molecules of a gas are always in motion. They move with extreme rapidity in straight lines until they collide with neighbors or with the walls of the container. After the collisions each molecule moves off in a different direction. We can imagine them to be something like balls moving rapidly and incessantly on a billiard table. The number of collisions occurring each second in a liter of gas at standard conditions is astonishingly large. The collisions are perfectly elastic, and no loss of energy occurs. The pressure exerted by a gas on the walls of the container is due to the ceaseless bombardment by the molecules. Another way to enable us to visualize the motion of molecules is to imagine a swarm of insane insects in a jar, darting about in all directions, each having untiring energy to keep it in perpetual motion.

Diffusion of perfume in the air of a room occurs because of the motion of the molecules. The particles bounce off each other and off the molecules in the air and gradually get farther away from the source of the odor. Soon the odor is noticeable everywhere in the room.

4. Changing the temperature of a gas changes the rate of motion of its particles. If the temperature of a gas sample is lowered, the velocity of its molecules becomes less; the molecules have less kinetic, or motion, energy. If the temperature of a gas sample is raised, the velocity of its molecules rises and they collide with each other more often and with greater force. The molecules thus have a greater amount of kinetic energy.

The four properties of molecules listed above are not facts; they are assumptions used to explain the properties of gases. If they explain well the facts that we know about gases, then they are good assumptions and we may believe them to be true, as we do in this case. If they did not explain the behavior of gases, we should reject them. If later we should find facts about gases that are not explained by the kinetic molecular theory, we should have to change the assumptions. This has actually been necessary in the case of the second assumption, that the molecules of a given gas are exactly alike. We know now that some molecules of hydrogen are twice as heavy as others. The new discovery does not make us distrust the kinetic molecular theory, but it does make it necessary for us to modify it slightly. A theory is not a ***fact*** or a ***law;*** it is an explanation of facts and laws.

Hydrogen Molecules. Several facts about hydrogen molecules are peculiar to the element. First, hydrogen molecules are the smallest molecules known and the lightest. Hence at a certain temperature, 20°C for example, they are moving faster than the molecules of any other gas at this same temperature. Further, they always come in packages of two: When they pass through an electric arc in the atomic hydrogen torch, each hydrogen molecule takes in energy and becomes for an instant two separate particles called ***atoms.*** When the atoms form molecules again, heat is liberated.



Keystone View

FIG. 5-18.—Dr. Harold Urey, while at Columbia University, was a Nobel Prize winner and a codiscoverer of heavy hydrogen.

Hydrogen diffuses more readily than any other gas. It passes through porous porcelain or through a sheet of metallic palladium at 500°C as easily as water passes through a filter paper; no other gas will do this so readily. Also, hydrogen is absorbed by platinum very readily; platinum and palladium catalyze many chemical actions of hydrogen.

Finally, there are abnormal hydrogen molecules called ***deuterium.*** These have twice the weight of ordinary hydrogen molecules, but the same size. They correspond somewhat to a double-yolked egg, and they are just about as rare. Hydrogen made up of such molecules is called ***heavy hydrogen.*** Its chemical conduct is just the same as that of normal hydrogen. When it burns, it forms heavy water. An explanation of these abnormal hydrogen molecules will be given later.

Heavy water apparently acts the same as any other water in plant and animal tissues. To prove this we can make a compound containing heavy hydrogen or heavy nitrogen and follow its course throughout the body. This can be done by analyzing parts of the body to see where the compound is located. This experiment is equivalent to feeding an animal tagged molecules.

SUMMARY

Hydrogen was discovered by Henry Cavendish in 1766 and was named "water producer" by Lavoisier 17 years later. Soon afterward it was used as a lifting gas for filling balloons.

Hydrogen is very seldom found free on the earth, although free hydrogen occurs on the sun. Compounds of hydrogen are abundant in nature. Oils, fats, living tissues, water, and ammonia are among them.

Hydrogen may be prepared (1) by the decomposition of water by electrolysis; (2) by the reaction between an active metal, such as sodium, and water (in this case sodium hydroxide is another product); and (3) by the action of hot coke or hot iron on steam. The customary laboratory method of preparation consists in reacting a strong acid with a moderately active metal, such as zinc. Strong alkalies, sodium hydroxide solution for example, will act on aluminum, zinc, or silicon and release hydrogen.

Hydrogen is collected in the laboratory by displacing water from an inverted bottle. It is colorless, odorless, and tasteless, very slightly soluble in water, and the lightest known gas. Also, it diffuses, or spreads out, very rapidly, for its molecules at a given temperature are moving faster than those of any other element or compound.

Hydrogen burns quietly at a jet, forming water as the only product. When mixed with air or oxygen and ignited, it explodes violently. Its action with chlorine is similar to that with oxygen.

Hydrogen is known as a reducing (or oxygen-removing) agent. It reacts with hot metallic oxides of relatively inactive metals, replacing the metal, that is, taking the oxygen from the metal. Hydrogen also adds to active metals, nitrogen, and to certain vegetable oils under proper conditions, a reaction of direct combination. Many shortenings sold at grocery stores today are made by adding hydrogen to vegetable oils, a process called hydrogenation. Hydrogen is also used as a lifting gas in balloons and as a fuel.

The kinetic molecular theory includes the following points: (1) All gases are composed of a multitude of particles called molecules. (2) All molecules of the same gas are alike and different from those of another gas. (3) Molecules are continually moving rapidly in straight lines and colliding. (4) Increased temperature increases the rate of molecular motion.

In hydrogen molecules the atoms are paired, that is, the molecule is thought to be composed of two atoms. A few hydrogen molecules are extra heavy because they contain a variety of hydrogen atoms called deuterium that is heavier than ordinary hydrogen atoms.

The replacement (or electromotive) series is a list of the metals and hydrogen in order of chemical activity. Any element in the list will replace those below it from solutions of their compounds. In general, the greater the spacing in the table, the more vigorous the reaction.

QUESTIONS

16. List five physical properties of hydrogen.

17. Under pressure at red heat, hydrogen passes readily through steel. (*a*) Name the phenomenon. (*b*) What conclusion may be drawn about the size of hydrogen molecules?

18. With what gas does hydrogen combine when it burns in air? Name the product. Why is this product not visible when a jet of hydrogen burns?

19. Why is hydrogen dried in the experiment in which hydrogen burns in air? (See Fig. 5-15.)

20. Describe a safe way to light a jet of hydrogen.

21. List three important chemical properties of hydrogen.

22. Give an example to illustrate each of the three important chemical properties of hydrogen.

23. What products are formed when heated hydrogen is passed over silver oxide?

24. In the chemical action of hydrogen on hot copper oxide name (*a*) the reducing agent, (*b*) the oxidizing agent, (*c*) the product of reduction, (*d*) the product of oxidation, (*e*) the substance oxidized, and (*f*) the substance reduced.

25. Examine a can or jar of vegetable shortening at home or in a store, and report what the label tells about its method of manufacture.

MORE CHALLENGING QUESTIONS

26. In which of the following cases does chemical action take place more readily?

(*a*) Mercury oxide + hydrogen →
(*b*) Magnesium oxide + hydrogen →

27. In the action of steam on iron oxide, answer the items given in question 24. Does this action seem to agree with the replacement series?

28. A solution of hydrochloric acid contains 30 per cent hydrogen chloride (HCl). Hydrogen chloride is 2.8 per cent hydrogen. What weight of hydrogen can be evolved from $\begin{cases}100\\145\end{cases}$ grams of the hydrochloric acid?[1]

---

[1] The instructor may wish to assign one of these figures to one group of pupils, the other figure to another group.

29. What is the weight of $\left\{\begin{matrix}200\\350\end{matrix}\right.$ liters of hydrogen at standard conditions?

30. What volume in liters is occupied by $\left\{\begin{matrix}90\\270\end{matrix}\right.$ grams of hydrogen at standard conditions?

31. Why is hydrogen sometimes used in balloons for sounding the "ceiling" over airports?

32. When hydrogen is used as a fuel in a torch, what change does it make in metallic oxides?

33. How can we show experimentally that city fuel gas contains hydrogen (or compounds of hydrogen)?

34. Suggest a reason for representing hydrogen by the formula H_2, not H, in chemical writing.

35. Tell how to keep hydrogen in a bottle with the least loss of gas.

36. What two conclusions can be drawn from the experiment of putting a lighted taper *into* an inverted bottle of hydrogen? (See Fig. 5-16.)

37. Write a paragraph on hydrogenation of oils, using and underlining the following terms: cottonseed oil, hydrogen, vegetable shortening, lard, substitute, price.

UNIT ONE . . . . CHAPTER VI

WATER

A dry well means trouble, but even more serious is the loss of water to a whole community. Crops wilt, livestock suffers, and people go without a necessity for life and its comforts. The parched soil, lacking a binder, is blown by the wind into dust storms. Living in such a place becomes troublesome if not impossible. Then is felt the force of the ancient metaphor, "A dry and thirsty land, where no water is." (Psalm 63.)

With plenty of water comfortable living is possible. For not only does water supply life's needs, but it also furnishes sport and recreation for thousands.

An ordinary glass of water is in many respects most amazing. It contains millions upon millions of separate particles of water, called molecules, milling about in it. Some are leaving the surface and others returning, a few million per second each way. Living creatures are present too, some large enough to be seen readily under a microscope, others so small that we have difficulty in seeing them even with the aid of the best microscope under the most favorable conditions. Some of these living plants and animals may be harmful if we drink water that contains them. Usually, however, if the body is in good health, they are not.

We have just begun to list the contents of this "museum." Dissolved in the water are several gases, oxygen chiefly, but also carbon dioxide, nitrogen, and frequently smaller amounts of other gases. Dissolved solids also make up a long list. Small traces of many chemical compounds are found in a glass of drinking water. Even some of the drinking glass itself is dissolved by the water—not much, to be sure, but some. Finally there are many small particles floating on or suspended in the water. Often a number of small, dustlike particles can be seen when a glass of apparently clear water is held up to the light. Nevertheless, in spite of its many shortcomings from the standard of absolute purity, we must

---

New Terms

deliquescent
suspended
filtration
distillation

chlorination
volumetric
gravimetric

hydroxide
water of crystallization
anhydrous
efflorescent

have water to drink. Without it we perish. One of the duties of chemists in public-health service is to see to it that the drinking water is sufficiently pure.

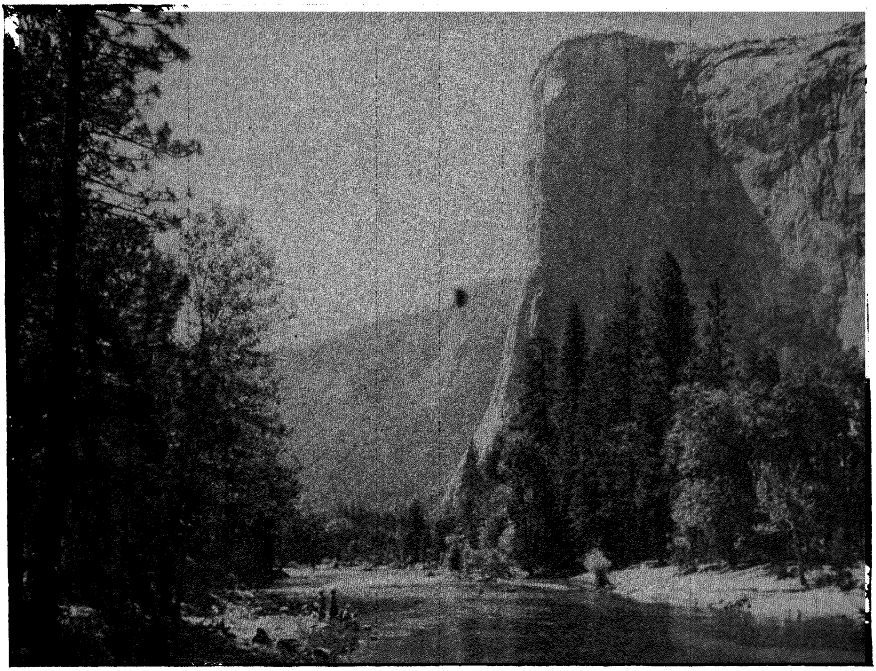
Properties of Water. Among all chemical substances, water is unique. It is the outstanding solvent, dissolving more types of substance than any other liquid, although some are dissolved only slightly. Water exists in three states on the earth, and it can be readily changed from one state to another by altering the temperature. The ordinary boiling point of water is 100°C, and the freezing point is 0°C. For a rise of temperature of 1°C, a gram of liquid water must absorb one calorie (cal) of heat energy. This amount of energy is larger than the amount required to raise the temperature 1°C for an equal weight of ***any other substance.*** This is one reason why water is an excellent liquid to use in the cooling systems of motors.

Importance of Water to Life. All living things require much water. Jellyfish and tomatoes are almost all water. About 9 per cent of the weight of the known outer portion of the earth is water. A pessimist describes the human body as "twelve pounds of ashes and eight buckete of water." Because water is present in all forms of life and because water requires a large heat change to raise or lower its temperature, living things warm up or cool off more slowly than if any other liquid were present in their bodies.

Food is of no use to the body unless it can be dissolved in water during the process of digestion. We eliminate those portions of the food that cannot be dissolved and absorbed through the walls of the digestive system. Water is the principal fluid in the blood by which food is carried to our tissues and waste matter removed. We excrete about 3 kilograms (kg) of water a day in the urine, lose other large amounts through the pores of our skin by evaporation, and still other large amounts in our breath.

The manner in which water freezes is most considerate to fish and to people who enjoy skating. We all recognize that a pond freezes from the top downward. Ice, therefore, must be a little less dense than the water on which it is floating. This property of having its solid less dense than its liquid is characteristic of only a few substances. As water cools, it contracts, which is the way most other liquids behave—mercury in a thermometer, for example. This contraction of water, however, comes to a halt at 4°C, and from that temperature downward to 0°C water expands as it cools. Water has its greatest density at 4°C; at that temperature the water is most closely compacted. One milliliter (ml) (almost a cubic centimeter) of water at 4°C weighs exactly 1 g, but at 0°C it weighs a little less; that is, 0.999841 g. One milliliter of ice at 0°C weighs 0.916 g.

Water at 4°C is left under the ice at the bottom of a pond; frozen milk rises out of milk bottles because water expands upon freezing; and vessels or pipes holding water often break when the water in them freezes. All are results of the abnormal way in which water behaves when it freezes. Water freezing and expanding in cracks of rocks causes small bits to break off. This, combined with the well-known scouring effect of water on rocks, is important in forming soil.



Courtesy of National Park Service, Photo by Ralph Anderson

FIG. 6-1.—The Merced River flows past stately El Capitan (7,564 ft elevation) in Yosemite National Park, California. From the raw materials represented in this picture—air, water, minerals, plants—chemists build "better things for better living."

Sometimes ice freezes from the bottom up. For example, in extremely cold weather running streams do not allow the water to form ice crystals on the surface. In such cases a mush of ice crystals may form throughout the water where it slows up, the crystals pack, and an ice dam results. The makers of artificial ice take advantage of this knowledge and keep water that is being frozen in motion by bubbling air through it. Then the ice forms from the outside of the cans toward the center, and in clear crystals. The central V-shaped piece of snow ice that we notice in a large cake of artificial ice was frozen without stirring.

When pure, water appears faintly blue. Large amounts of water seem to be colored blue or green as we may notice in a swimming pool, lake, river, or ocean.

Since water is essential to life, astronomers think that life is more likely to exist on those planets where there is evidence of the presence of water than on those where no evidence of water is seen. The conditions appear to be most favorable upon the earth.

QUESTIONS

1. The human body is approximately 66 per cent water. What is the weight of water in your own body?

2. How many calories are needed to change $\begin{cases}50\\75\end{cases}$ grams of water 2°C?

3. Rabbits seldom drink water. From what source do these animals obtain their water?

4. What changes in volume take place when the temperature of water rises from 0°C to 100°C?

5. What changes in density take place when water cools from 100 to 0°C? From 20 to −20°C?

6. What is the weight in grams of 50 milliliters of water? Of 5000 liters?

7. What damage may be caused by freezing the water in an automobile cooling system?

8. Many roads in temperate climates "heave" in the springtime. Suggest a cause of this trouble.

9. Describe the freezing of a pond, giving definite temperatures.

10. One liter of ice (0°C) melts. What weight in kilograms of water forms? What volume in milliliters does this water occupy at 4°C?

Why Does Salt Get Lumpy on Moist Days? On a foggy, humid day everything is covered with a thin layer of water. The salt in a salt shaker accumulates so much moisture that the crystals will not shake out easily. Chemists find that bottles containing certain compounds used in the laboratory must be kept well closed or the compounds will absorb so much moisture from the air that they become a sirupy solution of the substance. Calcium chloride is an example of these ***deliquescent***

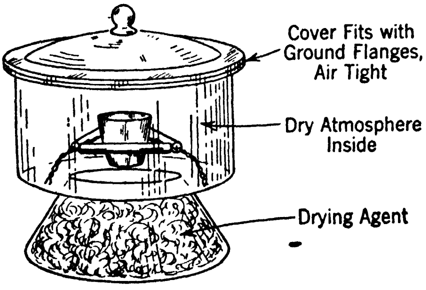


FIG. 6-2.—A region of perfectly dry air is maintained within a desiccator.

(becoming fluid) substances. Calcium chloride is often one of the impurities in common salt (sodium chloride) that makes it clog in muggy weather. Because of its water-accumulating nature, calcium chloride is sometimes used to keep dust down on tennis courts or gravel roads. Some types of hard candy are deliquescent, also.

Impurities in Water. As soon as water starts to fall as rain, it begins to accumulate impurities. First, gases dissolve in the rain. Then, as soon as the rain touches the earth, it becomes more impure by dissolving solids. The amount of solid dissolved increases until the water finally reaches the sea. The dissolved compounds in sea water do not settle out. It is thus evident that the sea is becoming saltier.

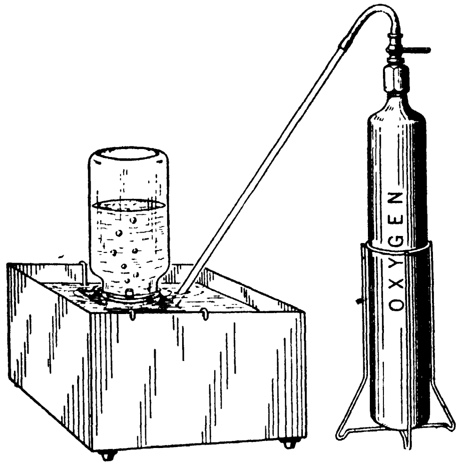


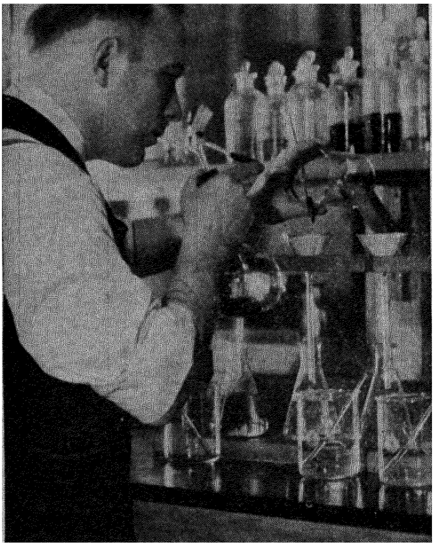
FIG. 6-3.—What properties of water determine its selection as the collection medium for gases, such as oxygen and hydrogen?

Dissolved materials in water are not to be confused with ***suspended matter,*** which consists of solids mixed in a liquid but not dissolved. Muddy water contains many solid particles suspended in it. The color of the clay suspended in a river may tint the water brown, gray, or yellow.

Chemists usually consider bacteria as a separate class of suspended materials in water. Dissolved substances are rarely harmful; on the contrary, they are often beneficial to health. Bacteria are also generally harmless, but occasionally they are dangerous. Typhoid fever and dysentery bacteria are among the harmful types that are carried in water.

"Is this sample of water good to drink?" is a question many people want to have answered, for chemists are often asked it. To answer this question completely involves a long and expensive process, requiring much equipment, experience, and skill. A satisfactory test of drinking water is to find out whether or not harmful bacteria are present. The finding of *Bacillus coli* from the intestines is sufficient to condemn water. Also, if common salt is found in water, sewage is suspected, but not proved, because, although a little is found in drinking water, salt in larger amounts is always present in sewage. In case of doubt it is always best to boil the water before using it.

How to Purify Water. Just as window screens keep out flies and mosquitoes but allow tiny gnats to go through the meshes, so a piece of uncoated paper, like newspaper, or a layer of sand offers free passage for water but acts as a strainer, so that particles suspended in the water are removed. This process of separating a suspended solid from a liquid by straining out the suspended particles is called ***filtration.*** Filtration is a process much used, both in the laboratory and in industry. Filtering through paper is common in the laboratory, but commercial filters may use sand or cloth. Filtering does not remove suspended particles that are small enough to pass through the pores of the filtering material. It is therefore not certain to remove all bacteria from water unless the filter is exceedingly fine.



Courtesy of The Travelers Insurance Company

FIG. 6-4.—The process of filtering is a common laboratory operation. Here the chemist is directing a fine stream of distilled water from the wash bottle into the beaker so the contents will all drain into the filter paper in the funnel.

Filtering may be more effective in removing bacteria if it is done through some jellylike substance, such as that formed by adding alum to water, to which the bacteria tend to stick. One city reduced the death rate from typhoid fever from 114 to 25 per 100,000 population by merely filtering its drinking water. The experience of Columbus, Ohio, and that of many other places shows that typhoid fever can be controlled and may some day be wiped out. In fact, all cases of typhoid fever are due to carelessness or neglect.

Complete purification of water removes both suspended and dissolved impurities. The process of removing the dissolved matter, although expensive to carry out on a large scale, is simple in principle. Water is boiled to form steam. The steam is then condensed back to water by cooling it below the boiling point. The process of changing a liquid to a gas and condensing the gas to a liquid again is called ***distillation.*** In general, if the impurities have boiling points above the boiling point of water, they will remain behind in the vessel in which the water was boiled. In order to carry out the process of distillation, an important process for other liquids as well as water, one uses a boiler and a condenser. The boiler changes the liquid to a vapor; the condenser changes the vapor back to a liquid. As much heat is carried away by the cooling water in the condenser as is supplied by the flame to the liquid in the boiler. (See Fig. 6-5.) If, in distilling water, some steam is first allowed to escape from the end of condenser tube, the dissolved gases are eliminated and nearly chemically pure water results. The product of the distillation of water is called ***distilled water.*** Distilled water is used in storage batteries, in making solutions in laboratories, and for other purposes.

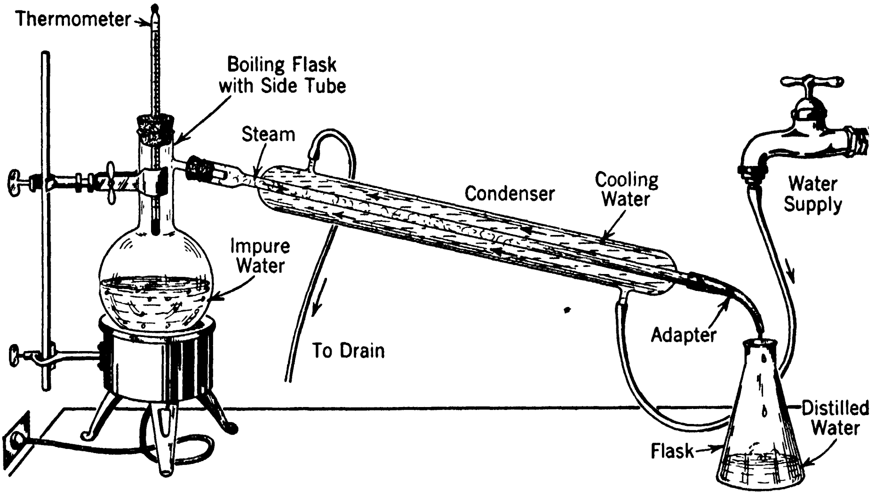


Fig. 6-5.—A simple method of purifying water is boiling it and then condensing the steam. Liebig's apparatus is a device for carrying on both processes continuously.

The Ancient Mariner, who had "Water, water, everywhere, Nor any drop to drink," made his readers suffer unnecessarily because of his lack of resourcefulness. A slight knowledge of chemistry would ruin this part of the poem completely. Any practical mariner could make steam by boiling sea water in a teakettle obtained in the galley. The steam will condense on a sloping board held above the kettle into many a "drop to drink."

To kill bacteria in water, many methods are used. Boiling water kills most germs. This method of purifying water is used by many Chinese who live on boats. Thousands of families discharge all their wastes into the stream and yet drink the water, after it is boiled.

The element oxygen attacks bacteria and kills them. The element chlorine is also used for the same purpose. The amount of chlorine used in purifying water for drinking [0.7 gallons (gal) of chlorine per million gallons of water] is sufficient to kill most of the bacteria, but not to harm the users of the water. Experience has shown that ***chlorination*** of water is safe and economical and a reliable way to make water fit to drink. Often ammonia is used with chlorine. Swimming pools, which are contaminated by constant use, must obviously be chlorinated more highly than reservoir water. In times of flood when river water may unexpectedly "back up" into city water mains the amount of chlorine used is increased to ensure safe drinking water.

Photo by Joe Koller

FIG. 6-6.—Sugar beets are shown here growing under irrigation. This is the Belle Fourche Project in South Dakota.

Through many experiments the preparation and properties of the element chlorine have been worked out. Its effects on other elements, on bacteria, and on the human body are all recorded in scientific writings. This knowledge may be used to save human lives, as it is when chlorine is used to purify drinking water; or the knowledge may be abused, as it was when chlorine was used as a poison gas in World War I to destroy human beings. This contrast forms a good example of one of the limitations of science, for the scientific investigator is content to find knowledge and thus far cannot control its use.

City Water Supplies. Fortunate indeed is that city which has available an adequate supply of pure, soft, clear, uncolored drinking water with no taste or odor. Some cities are located without much regard to available sources of water supply, so that water must be brought to them in pipes over hundreds of miles at enormous expense. Los Angeles, California, for example, brings water from the mountains 223 miles away.

A city that needs an unusually large water supply buys a suitable stream that can be dammed up. A watershed is cleared, a dam built, and a lake created. By doing this, in some cases a large community may benefit to the disadvantage of smaller ones. Boston draws some of its water from streams that are located near the center of the commonwealth of Massachusetts. The neighboring state of Connecticut felt aggrieved because it was deprived of this water, which normally flowed southward through the Connecticut River Valley. A lawsuit between the states was brought in the United States Supreme Court. The right of Boston to direct the water eastward was maintained.

QUESTIONS

11. Define *deliquescence*.

12. What causes salt to cake in a salt shaker in damp weather? Suggest a practical way of preventing this inconvenience.

13. Free-running salt is often sold in cardboard cartons. What substance is added to the salt? HINT: See the carton.

14. (*a*) List the harmful impurities in natural water. (*b*) List the harmless ones.

15. Distinguish between pure water for drinking (potable water) and chemically pure water.

16. Thousands of families live on boats in the Yangtze River in China. All their waste is discharged into the water. The same water is used for drinking. What home purification method is used to make the water fit for drinking?

17. Tell how the process of filtering is used in jelly-making.

18. African explorers are sometimes forced to use ill-smelling water, green with assorted vegetation. What method is used to purify such water?

19. What methods are economical to use for purifying water on a large scale? What methods may an army adopt?

20. Distinguish: water, ice, steam, water vapor, fog.

Hard and Soft Water. Water that does not contain a great amount of dissolved mineral matter (elements or compounds of inorganic substances) is called soft water. Those who use soft water do not know what a convenience it is until they are confronted with hard water. Hard water contains dissolved compounds of the elements calcium and magnesium. These compounds react with soap to form a curdy solid to such an extent that washing with hard water becomes a test of patience. This curdy material deposits in cloth, making streaks.

Much trouble results from using hard water in boilers because a scale forms on the inside. This scale, which forms from hard water when it is heated, is a hard, crusty layer, often mixed with rust.

In order to make hard water suitable for most uses, it must be ***softened.*** The process of softening will be explained later. Sea water is very hard water and except with special suds-making substances is not at all satisfactory for washing clothes. Hard water is discussed in more detail later.

Producing Water from the Elements. We have already pointed out (page 83) that water is a stable compound and that it can be decomposed into its elements when an electric current is passed through it.

$$\underset{\text{Water}}{2H_2O} \rightarrow \underset{\substack{\text{hydrogen} \\ \text{(2 parts by volume)}}}{2H_2\uparrow} + \underset{\substack{\text{oxygen} \\ \text{(1 part by volume)}}}{O_2\uparrow}$$

A remarkable 2-to-1 volume relationship exists between the hydrogen and oxygen gas volumes, respectively. The questions naturally arise, "Can this be reversed? Do hydrogen and oxygen combine in any special amount?"

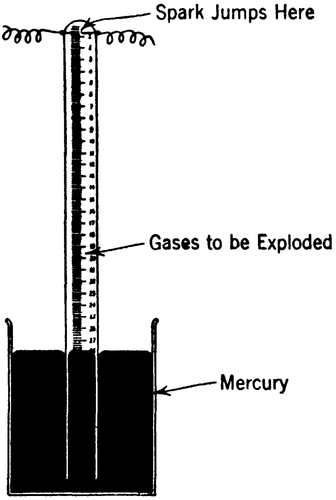


FIG. 6-7.—The eudiometer is a stout-walled glass tube within which chemists carry on small gas explosions.

To answer these questions let us use a long glass tube that has measuring marks on the side (see Fig. 6-7) and two wires sealed in through the glass almost touching inside at the closed end. We then fill the tube with mercury and invert it in a dish of mercury. For a start, let us select by chance equal amounts of the gases, say, 10 ml of pure hydrogen and 10 ml of pure oxygen (20 ml of mixed gas), and introduce them into the tube; we now connect the two wires to an electric sparking machine and make a spark jump across between the wires through the mixed gases inside the tube. The hydrogen burns rapidly—indeed, a mild explosion takes place. The mercury absorbs the shock of the explosion to some extent but immediately rises inside the tube. Measuring shows that 5 ml of gas is left, and also a small volume of liquid water is seen floating on the mercury. The gas may be hydrogen, oxygen, a mixture of both, or perhaps some new substance. A glowing splinter inserted into the gas burns brightly, showing that the gas is oxygen.

10 ml hydrogen + 10 ml oxygen → liquid water and leaves 5 ml oxygen

Now we repeat the experiment, leaving out the extra 5 ml of oxygen that was found to be unused; thus 10 ml of hydrogen and 5 ml of oxygen are put into the tube.

After sparking, we see this time that mercury fills the tube except for the small volume of liquid water formed. No gas remains.

$$\text{10 ml hydrogen} + \text{5 ml oxygen} \xrightarrow[\text{(tube cold)}]{} \text{liquid water (and no gas)}^{1}$$

For a third experiment the entire apparatus is enclosed in a jacket heated with vapor of some liquid so that the temperature at which all the measurements are made is over 100°C. The previous experiment is repeated: 10 ml of hydrogen and 5 ml of oxygen are put into the tube, and a spark is sent across the gap between the wires. This time after the explosion the volume of gas has shrunk two-thirds, 10 ml of gas remaining. What can this gas be? If tested, we find that it does not burn, nor does it cause a spark on the end of a splinter to burst into flame. When the gas is cooled, it changes to a liquid that freezes at 0°C and boils at 100°C at 760 mm pressure. This is proof positive that the liquid is water and, therefore, that the gas is steam.

The experiment can be summarized as

$$\text{10 ml hydrogen} + \text{5 ml oxygen} \xrightarrow[\text{(tube heated)}]{} \text{10 ml water vapor}$$

or, in general, since the amounts of gas in the first place were selected by chance,

$$\text{2 volumes hydrogen} + \text{1 volume oxygen} \xrightarrow[\text{(tube heated)}]{} \text{2 volumes water vapor}$$

This experiment shows the formation of water (steam) from the gases hydrogen and oxygen and the measurement of the volume of the gases formed in the experiment. Sometimes it is called the ***volumetric*** (measured by volume) ***synthesis*** (putting together) of water.

What Is the Percentage of Hydrogen and Oxygen in Water? W. A. Noyes (1857–1942), an American experimenter, repeating more accurately the method of Jöns Jakob Berzelius (1779–1848) of Sweden and of Jean Baptiste André Dumas (1800–1884) of France many years before, passed carefully purified hydrogen over a weighed amount of pure copper oxide in a heated tube (1). (See

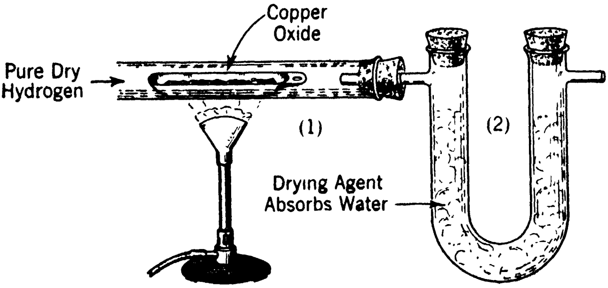


FIG. 6-8.—This apparatus is used to determine the approximate composition of water by weight.

---

[1] This experiment is not practical for demonstration in most elementary laboratories.

Fig. 6-8.) The chemical change that took place is expressed

$$\begin{array}{ccccccc} H_2 & + & CuO & \rightarrow & Cu & + & H_2O \\ \text{Hydrogen} & + & \text{copper oxide} & \rightarrow & \text{copper} & + & \text{water} \end{array}$$

The copper oxide gave up its oxygen to the hydrogen to form water. The water was collected in another tube (2) attached to the first and containing a weighed amount of a substance, such as calcium chloride, that would absorb water. In this reaction, the tube (1) containing copper oxide lost weight because it lost oxygen, while the absorption tube (2) containing calcium chloride gained weight because it gained water. By using the measurements of weight changes, the percentage of oxygen in water could be found by the following:

$$\frac{\text{Loss of weight in tube (1)}}{\text{Gain in weight of tube (2)}}\ \frac{(O)}{(H_2O)} \times 100 = \quad \%\ \text{oxygen in water. } \mathit{Ans.}$$

The answer is 88.81 per cent. The percentage of hydrogen is found by subtracting 88.81 from 100, the result being 11.19 per cent. This experiment is sometimes called the ***gravimetric*** (measured by weight) ***synthesis*** of water.

The Chemical Nature of Water. Water enters into many chemical changes, although it is a stable substance. So important are chemical changes in water solution as a medium that we shall consider them later. All growth of plants and animals takes place in cells a large part of which is water. Sometimes water is one of the substances in a chemical change; more often it is the medium in which the change takes place.

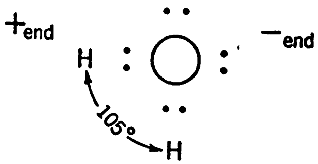


FIG. 6-9.—The water molecule is composed of two sorts of atoms.

Many substances that act chemically on water can be considered in two groups: (1) elements; (2) oxides.

1. We have seen from experiments that water, the formula for which is H_2O, has two parts of hydrogen. Active metals take the place of one part and leave the other part in a new compound, called a ***hydroxide,*** which is made of the metal, hydrogen, and oxygen. For example,

$$\begin{array}{ccccccc} 2K & + & 2HOH & \rightarrow & H_2 & + & 2KOH \\ \text{Potassium} & + & \text{water} & \rightarrow & \text{hydrogen} & + & \text{potassium hydroxide} \end{array}$$

$$\begin{array}{ccccccc} 2Na & + & 2HOH & \rightarrow & H_2 & + & 2NaOH \\ \text{Sodium} & + & \text{water} & \rightarrow & \text{hydrogen} & + & \text{sodium hydroxide} \end{array}$$

$$\begin{array}{ccccccc} Ca & + & 2HOH & \rightarrow & H_2 & + & Ca(OH)_2 \\ \text{Calcium} & + & \text{water} & \rightarrow & \text{hydrogen} & + & \text{calcium hydroxide} \end{array}$$

Other less active elements act on water when they are strongly heated, driving out the hydrogen and forming an oxide of the element. Another way to consider this reaction is that the element has substituted itself for the hydrogen of water. The exchange is similar to the ballroom custom according to which a young gentleman leaves the "stag line" and "cuts in" on a couple dancing on the floor. In this comparison the part of the young lady is played by oxygen.

$Zn + H_2O \rightarrow H_2 + ZnO$
Zinc + steam (hydrogen oxide) → hydrogen + zinc oxide

$C + H_2O \rightarrow H_2 + CO$
Carbon + steam (hydrogen oxide) → hydrogen + carbon monoxide

$3Fe + 4H_2O \rightarrow 4H_2 + Fe_3O_4$
Iron + steam (hydrogen oxide) → hydrogen + iron oxide

2. Some oxides of nonmetals unite with water. The chemical change is one of simple addition, one product being formed.

$CO_2 + H_2O \rightarrow H_2CO_3$
Carbon dioxide + water → hydrogen carbonate (carbonic acid)

$SO_2 + H_2O \rightarrow H_2SO_3$
Sulfur dioxide + water → hydrogen sulfite (sulfurous acid)

$SO_3 + H_2O \rightarrow H_2SO_4$
Sulfur trioxide + water → hydrogen sulfate (sulfuric acid)

$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$
Phosphorus pentoxide + water → hydrogen phosphate (phosphoric acid)

Oxides of a few metals combine with water to form hydroxides. The most important one is

$CaO + H_2O \rightarrow Ca(OH)_2$
Calcium oxide + water → calcium hydroxide

Water in Crystals. Most solids found in nature and those made in the laboratory are crystalline. When heated, a great many crystalline solids crumble to a powder, lose weight, and sometimes change their color. Investigation shows that in such cases when the crystal is heated water is lost. Such a substance is gypsum, sometimes represented by $CaSO_4 \cdot 2H_2O$ (the dot is read "combined with"). Great masses of solid rock are made of gypsum; an examination of its formula shows that with each particle of gypsum two particles of water are associated. When this substance is heated, water is lost and plaster of Paris is formed. As anyone knows who has ever broken a bone and worn a cast, plaster of Paris takes this water back to form a mass of hard crystals. It "sets" to a rigid mass and is used to support the bone structure while it heals. Washing soda crystals (sodium carbonate), alum crystals (potassium aluminum sulfate), and blue vitriol crystals (copper sulfate) are all examples of crystalline solids that contain water. When they form from solution, they take some ***water of crystallization*** with them. Such substances are called ***hydrates.*** All hydrates have water chemically held in the crystal. Common salt and sugar are crystals that have no combined water with them and are therefore not hydrates.

Some hydrates lose their water of crystallization without being heated, merely on being exposed to air. Washing soda ($Na_2CO_3 \cdot 10H_2O$) turns to a dry powder and becomes Na_2CO_3, ***anhydrous*** (without water) powder, when it is exposed to the air.

$$\underset{\text{Washing soda}}{Na_2CO_3 \cdot 10H_2O} \rightarrow \underset{\text{soda ash}}{Na_2CO_3} + \underset{\text{water}}{10H_2O}$$

A package of washing soda loses weight while it stands on a grocer's shelf unless it is packed in a carton from which moisture cannot escape. Crystals of this sort are said to be ***efflorescent*** (flowering out or blooming) because the powder formed on the surface of the crystal resembles the blooming of a flower.

Courtesy of E. I. du Pont de Nemours & Company

FIG. 6-10.—One chemical change makes way for others. The pictures show a drainage ditch being blasted and the ditch after the blast.

SUMMARY

Water is important as a solvent for plant and animal food, as the chief constituent of living tissues, as a temperature regulator for life processes, as a catalyst in chemical actions, and as the solvent in which many chemical actions take place quickly.

Water most closely approaches the "universal solvent." It boils at 100°C at 760 mm pressure (standard) and freezes at 0°C. One calorie is required to change the temperature of a gram of water 1°C. Its approximate density is 1 g per ml, and its maximum density occurs at 4°C.

Some substances, calcium chloride for example, have the property of absorbing water from the air and dissolving in it. Such substances are called deliquescent.

Dissolved impurities in water include gases and mineral compounds called salts, of which common salt is one. Suspended impurities are abundant in muddy water. Harmful bacteria may be present. Some suspended matter may be invisible, but the larger particles are readily removed by the process of filtration.

Methods of purifying water include

1. Filtration, a process of straining water through cloth, paper, sand, or soil
2. Distillation, which consists in boiling and condensing the vapors
3. Boiling, which removes dissolved gases and kills most of the bacteria
4. Mixing with air (aeration), to kill bacteria and to oxidize organic matter
5. Chemical treatment with chlorine, often plus ammonia, to kill germs

Hard water is difficult to use for laundry purposes and for making steam in boilers. It contains dissolved inorganic compounds that act on soap and also produce a scale deposit in boilers. Soft water has relatively little dissolved mineral salts and is better than hard water for almost all purposes.

Water is relatively stable, being difficult to decompose. Essentially, water is decomposed by passing an electric current through dilute sulfuric acid solution. The process is called electrolysis of water, and the products are two volumes of hydrogen and one volume of oxygen.

Water is synthesized and the results determined by weight in the experiment of passing dry hydrogen over heated copper oxide. The results show 88.81 per cent oxygen and 11.19 per cent hydrogen. Water is synthesized by exploding measured volumes of hydrogen and oxygen in a strong glass tube. The results by volume show that two volumes of hydrogen join one volume of oxygen to form two volumes of steam, all gases being measured at the same temperature and pressure.

Chemical actions of water include

(1) Water + active metal → metallic hydroxide + hydrogen
(2) Water + moderately active metal → metallic oxide + hydrogen
(3) Water + nonmetal oxide → acid
(4) Water + metallic oxide → metallic hydroxide
(5) Water is a catalyst in many chemical actions

Certain crystals include definite (molecular) amounts of solvent chemically combined when they form. They are called hydrates. For example, washing soda has the formula $Na_2CO_3 \cdot 10H_2O$. Some hydrates lose water when exposed to air, thus becoming anhydrous, leaving a dry powder. Washing soda loses water when exposed to air.

QUESTIONS

21. Distinguish hard water from soft water.

22. State two disadvantages of hard water.

23. What is the meaning of the term *unstable?*

24. In the decomposition of water,

(*a*) Energy in what form is used?

(*b*) What substance is added to improve the electrical conductivity of the water?

(*c*) What gaseous products are formed?

(*d*) Compare the volumes of the products.

25. When $\left\{\begin{matrix}50\\40\end{matrix}\right.$ liters of hydrogen is made by electrolysis of water, what volume of oxygen is formed at the same time?

26. What volume of hydrogen is formed at the same time when $\left\{\begin{matrix}124\\38\end{matrix}\right.$ milliliters of oxygen are collected from the electrolysis of water?

27. When a mixture of $\left\{\begin{matrix}50\\40\end{matrix}\right.$ milliliters of hydrogen and $\left\{\begin{matrix}25\\20\end{matrix}\right.$ ml of oxygen is exploded in a hot tube, what volume in milliliters of steam is formed?

28. When $\left\{\begin{matrix}27\\17\end{matrix}\right.$ milliliters of oxygen is used, how much hydrogen can be burned and how much steam is formed?

NOTE: Assume all temperatures and pressures at which volumes of gases are measured remain the same in each question.

MORE CHALLENGING QUESTIONS

29. When $\left\{\begin{matrix}150\\235\end{matrix}\right.$ liters of hydrogen forms from the electrolysis of water, what volume of oxygen can be recovered at the same time if 4 per cent dissolves in the water?

30. When $\left\{\begin{matrix}50\\70\end{matrix}\right.$ milliliters of hydrogen and $\left\{\begin{matrix}40\\45\end{matrix}\right.$ milliliters of oxygen are mixed in a tube, warmed above 100°C, and exploded, what gases remain, and what is the volume in milliliters of each?

31. When $\left\{\begin{matrix}40\\35\end{matrix}\right.$ milliliters of hydrogen and $\left\{\begin{matrix}50\\40\end{matrix}\right.$ milliliters of oxygen are mixed and exploded as in question 30, what volume of gases remain?

32. In a pupil's experiment for synthesizing water the copper oxide tube weighed $\left\{\begin{matrix}45.2\\87.3\end{matrix}\right.$ grams before and $\left\{\begin{matrix}44.5\\86.6\end{matrix}\right.$ grams after the experiment. The drying tube weighed $\left\{\begin{matrix}38.7\\75.6\end{matrix}\right.$ grams before and $\left\{\begin{matrix}39.5\\76.4\end{matrix}\right.$ grams after. From these figures find the percentage of oxygen in water.

33. What weight of oxygen is present in a ton of water? Oxygen helps fires burn. In view of these two facts account for the seeming contradictory use of water as a fire extinguisher.

34. How can shipwrecked sailors get drinking water from fish?

35. Why do not engineers design an automobile that utilizes the burning of hydrogen and oxygen for automotive power? Could the decomposition of water by electrolysis be carried out in such an automobile from the energy produced by the combustion?

UNIT ONE - - - - - - - - - - - - - - CHAPTER VII

THE NATURE OF GASES, LIQUIDS, SOLIDS

Galileo Galilei (1564–1642) of Italy will always be remembered as a man who did not rely on the teachings of Aristotle but who sought truth while carrying out his experiments with objects falling from the leaning tower of Pisa. Besides these famous experiments, he was the first person to weigh air.

People, to be sure, had always recognized the tremendous force of the wind and feared it. Then, too, other "airs" were known. At various spots on the earth evil-smelling or poisonous gases made their presence known; birds were killed by flying into such regions. It became recognized, therefore, that all gases, or "airs," are not the same.

Scientific experiments take nothing for granted; and the fact that a gas is invisible neither proves that it does not exist nor that it is the same substance as air. Today many different gases are known, many of which are of great service to mankind. Natural gas is piped to houses and factories in many cities. Trucks use tanks of compressed gas for fuel. "Laughing gas" puts patients to sleep for minor operations. Fumigating gas destroys vermin. Gases are used extensively for refrigeration.

In order to distinguish one kind of gas from another, we describe each by answering the questions, "What is its composition? What is its name? How much does a liter weigh at a given temperature and pressure?"

Automobile tires lose air easily on a hot day; the air expands when warm, forcing its way through the somewhat porous wall. If the wall is weak, a "blowout" may occur. A milk bottle is washed in warm soapsuds and placed mouth downward to drain. If a soap film forms across the mouth of the bottle, which way will the film move as the bottle cools? Upward, of course, for the air in the bottle contracts when it becomes

---

New Terms

Kelvin, or absolute, degrees
attractive force
cohesion
condensation
evaporation
vapor pressure
boiling point
melting point
crystal

cooler. Most of us have noticed that gases expand when heated and contract when cooled. Gases likewise contract when put under increased pressure and expand again when the pressure is reduced.

Blueprint of a Gas. Let us consider a cubic foot of air. Let us assume that the volume of this gas is measured when the barometric pressure is 760 mm of mercury and the temperature is 0°C, or 273°K (Kelvin degrees, sometimes called ***absolute*** degrees). These conditions are called ***standard conditions,*** often referred to as STP. Now let the pressure on the air be doubled, namely, increased to 1520 mm, the temperature remaining constant. The volume of the air now measures only $\frac{1}{2}$ cu ft. When the pressure is doubled, the volume of the gas becomes one-half if the temperature is constant. Experiments of this sort are summed up in Boyle's law: ***The volume of a definite amount of dry gas is inversely proportional to the pressure on it, provided that the temperature is not changed.*** (See Fig. 7-1.)

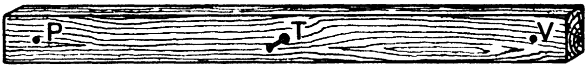


Fig. 7-1.—A mechanical model of this type may be used to illustrate the mathematical principle of Boyle's law.

If the $\frac{1}{2}$ cu ft of air is now warmed to 273°C, or 546°K, with the pressure remaining unchanged, its Kelvin temperature is doubled and its volume again becomes 1 cu ft. That is, at constant pressure, doubling the temperature (in Kelvin degrees) of a sample of a gas doubles the volume the gas occupies. Experiments of this sort are summed up by Gay-Lussac's (Charles') law: ***The volume of a definite amount of dry gas is directly proportional to its Kelvin temperature, provided that the pressure is not changed.***[1]

The next step in the scientific method is to develop a theory about the nature of gases. Items to be taken into account in building this theory, or mind picture, include the fact that

1. Boyle's and Gay-Lussac's (Charles') laws hold true for all elements, mixtures, and compounds alike, provided only that they are in the gaseous state. Some similarity of all gases is suggested.
2. The fragrance of perfume penetrates a space that already contains air. The fact that empty spaces exist in gases is evident from this observation. One gas may spread into the space already occupied by another, an action called diffusion. Gases tend to fill the entire container in which they are placed.

---

[1] The application of Boyle's and Gay-Lussac's (Charles') laws is given in the Appendix.

3. If no leaks interfere and the temperature is kept constant, the pressure of a gas is maintained eternally. Once an automobile tire is blown up, it will stay that way, keeping the air at the original pressure, provided that there is no loss of air from chemical action with the rubber or from leaks. Actually, for reasons suggested here, automobile tires "go down," and more air must be supplied if the same pressure is to be maintained.

4. A rubber toy balloon whose walls are uniformly thick will tend to form a sphere when blown up because the gas inside exerts equal pressure in all directions. The behavior is the same with hydrogen, illuminating gas, carbon dioxide, or any other gas.

These properties of gases are explained in the molecular theory of gases, often called the kinetic (motion) molecular theory. The different statements in the theory are assumptions used to explain the observed behavior.

The student will recall

1. Gases are made up of tiny particles called molecules. A liter of oxygen gas at STP, for example, is made up of an enormous number of these molecules.

2. Molecules of oxygen are alike on the average, as are molecules of any given kind of gas; different kinds of molecules of gases are, however, unlike. For example, carbon dioxide molecules are different from oxygen molecules.

3. Molecules of a gas are always moving rapidly in a straight line for a short distance. Then they hit something, bounce off, and move in another direction with the same speed.

4. Changing the temperature of a gas changes the rate of motion of its molecules. If a gas is cooled, the motion of the molecules becomes slower. If a gas is heated, the molecules set about their haphazard, tireless colliding at an increased rate.

Effect of Temperature Change. If a certain amount of oxygen is heated to twice its present temperature on the Kelvin (absolute temperature) scale (see page 118), say from 300 to 600°K, the energy of molecular motion is doubled. Each molecule on the average has twice the motion energy it had previously and hits the walls more often and harder. Consequently, 1 cu ft of oxygen tends to occupy 2 cu ft, or just twice the original volume, if the pressure is to remain the same. Each molecule doubles its energy, quadruples its speed. ($K.E. = \frac{1}{2}mv^2$.) If the gas is held within a container so that it cannot expand and the temperature is doubled, then the pressure will also be doubled. This means that the molecules will hit the wall of the vessel that holds the gas with twice the former energy, tending to push the wall back with greater total force.

Effect of Pressure Change. If a gas is compressed, its particles are moved closer together. With a larger crowd in a given space, the pressure is increased since the number of collisions with the walls will be increased. This explains Boyle's law, according to which the pressure of a gas increases as the volume becomes less. (See Fig. 7-2.)

Molecular Motion Explained. A cool gas has slow-moving molecules, and the same gas when warm has faster moving molecules. The temperature of a gas is a measure of the energy due to the motion of its molecules. Absolute zero, 0°K, which is 273° below 0°C, is the condition that would be reached if molecular motion stopped.

When a tennis ball is dropped on a hard floor, it bounces several times; but gradually the energy of the fall is reduced, owing to friction, and it finally comes to rest. Molecules, however, lose none of their energy in friction; for friction produces heat, and heat is molecular motion. No loss of motion energy takes place, as no change in temperature is observed. The collisions of gas molecules with each other, and with the walls of the container, if at the same temperature as the gas, are perfectly frictionless.

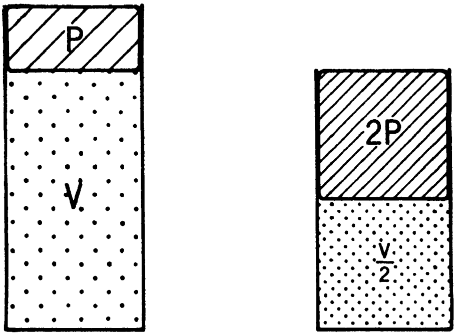


FIG. 7-2.—When the pressure of a gas is increased, the distance between the molecules becomes less.

If the motion of gas molecules is haphazard and the number of particles greater than the upper stretches of our imagination, then we can understand the reason why gases exert their pressure equally in all directions. It is important to realize that the size of the individual gas molecule is small compared with the distance between any two molecules and that the velocity of these tiny projectiles at room temperature is about 1 mile per sec.

Using the Gas Theory. The theory that gases are made up of molecules is so well established that no one doubts its truth. As our knowledge becomes more complete, a few details may be altered, but the picture as a whole is essentially correct.

This theory will be useful in explaining changes of state of matter. As an illustration, we want to see how it is possible to change a substance from the gaseous into the liquid state. Molecules are present in liquids, but they are closer together than they are in gases. In order to change a gas into a liquid, the problem is one of making the molecules come closer together. Frequently all that we need to do to accomplish this change is to increase the pressure and to remove the heat produced. Usually, however, we lower the temperature (remove heat) and keep the pressure at atmospheric. By applying sufficiently high pressure and by sufficiently lowering the temperature, all known gases have been changed to liquids, and even to solids. Helium, the most difficult gas to change to a liquid, has now been liquefied in several laboratories.

An illustration of the fact that the molecules are farther apart in a gas than in liquids is that 1 ml of water becomes about 1700 ml of steam, even though both are at the same pressure, 760 mm, and temperature, 100°C.

QUESTIONS

1. What two conditions of a gas are called *standard conditions?*

2. State Boyle's law. (This question means to give the sentence or statement that is the law.)

3. Name the two most important conditions that affect the volume occupied by a given weight of gas.

4. What is the effect on the volume of 1 liter of gas at 300°K when the temperature becomes $\left\{\begin{matrix}150 \\ 75\end{matrix}\right.$°K with no pressure change?

5. The pungent odor from an open bottle of household ammonia can soon be smelled anywhere in a room. Explain.

6. State Gay-Lussac's (Charles') law.

7. Explain the ball-like shape of soap bubbles.

8. Summarize the four main points of the kinetic molecular theory.

9. When a confined gas has its pressure doubled and its temperature as measured on the Kelvin scale halved, what changes take place in the condition of the molecules? What is the observed change in the volume of the gas?

10. What happens to the volume of 1 cubic foot of oxygen when its temperature on the Kelvin scale is doubled and at the same time its pressure is halved?

MORE CHALLENGING QUESTIONS

11. When a gas is compressed to one-fourth its original volume and the temperature is restored to the starting temperature, what change, if any, takes place in.

(*a*) The size of the molecules?
(*b*) The average distance between any two molecules?
(*c*) The average velocity of the molecules?
(*d*) The pressure the gas exerts?

12. Prove that at a given temperature the velocity of hydrogen molecules (mass = 2) must be four times that of oxygen molecules (mass = 32). Kinetic energy is proportional to mv^2.

13. What two conditions must be altered to change a gas to a liquid?

14. What force holds together (*a*) glue and wood, (*b*) glue and glue, (*c*) chewing gum and hair, (*d*) two flat steel gauge blocks?

15. Some desert cactus plants are shaped like a ball. What advantage is this shape to the plant in its struggle for existence in a hot, dry climate?

16. Concentrated sulfuric acid usually runs down the outside of the bottle when it is poured. Explain this observation in terms of cohesion and adhesion.

17. A stirring rod is sometimes used to transfer liquids from one vessel to another. (See Fig. 2-9.) Try the experiment, or one like it, and explain the result.

Observe Dropping Water. As we have said, a liquid differs from a gas chiefly because the molecules, in general, are closer together in a liquid than in a gas.[1] When molecules are close together, the ***attractive force*** between them becomes apparent, a force that can be illustrated by observing a drop of water fall from a water faucet. We notice that the water takes a shape resembling a sphere. This is because the molecules of water are pulling each other together, causing the water to take the form that has the least surface for a given volume, a sphere. Mercury droplets show this effect even more strikingly than water droplets. The forces holding the molecules together in the case of a liquid are not enough to keep it from flowing. In the case of a solid, the molecules are held together even more firmly, and a more or less rigid structure results.

An oil film on water shows this ***cohesion*** of oil molecules for one another, because the film spreads out until it sometimes becomes only one molecule thick. Afterward it ceases to spread because of the cohesive force among the oil molecules. Again, at a pressure of 100 times atmospheric, the contraction of carbon dioxide due to cohesive forces alone can be shown to be over 4.5 times the contraction due to pressure increase.

How Gases, Liquids, and Solids Compare. A gas has no definite shape. It fills whatever container holds it, the molecules being distributed evenly in the space allowed. A liquid is also shapeless but differs

[1] Substances that are gases at room temperature are called by the name ***gas***. The term ***vapor*** is sometimes applied to the gas from substances that are normally liquid or solid at room temperature.

from a gas in that it has a surface; this means that it has a definite volume. A liquid takes the shape of the container; its surface remains at right angles to the force acting upon the liquid. A drinking glass full of water has an upper surface parallel to the floor of the room, at right angles to the downward force of the earth's pull that acts on the water. A solid has surfaces and shapes of its own.

A gas can be compressed readily; but the effect of pressure in decreasing the volume of a liquid is slight. A gas expands when heated, but, as a rule, a heated liquid changes in size much less than a gas, and a solid still less. A liquid tends to evaporate (become a vapor or a gas) at its free surface. Some solids evaporate, but much more slowly than liquids. Moth crystals (naphthalene or paradichloro-benzene), camphor, and Dry Ice all evaporate. Even snow evaporates, but at an exceedingly slow rate.

Condensation. Steam readily changes back to water. The changing of any gas to a liquid is called ***condensation.*** This is a physical change, and it is the opposite of evaporation. When a gas or vapor is cooled sufficiently, the gas becomes liquid. The molecules move less rapidly when the gas is cooled. The attractive force, or their cohesion for one another, becomes relatively strong enough for them to form a liquid.

On the other hand, increasing the pressure on carbon dioxide causes it to become liquid, and it is marketed in this form in steel tanks. Ammonia, sulfur dioxide, water vapor, and many other gases liquefy when their pressure is increased. The heat generated during the process of liquefaction by increasing the pressure is considerable. It is removed by some cooling device.

Molecular Motion. Consider a closed room the size of a small gymnasium. If people are packed in tightly, the capacity is about 500. Motion is possible, but extremely limited. The people "mill about" but do not progress far from their starting places. If the people are to move, as in dancing, the hall will hold only 100. The same area will hold 10 basketball players, leisurely "warming up." All may be in motion at the same rate, but the distance through which any one person travels is limited by the nearness of his neighbor. Such is a partial picture of a solid, liquid, and gas of a given substance, all at the same temperature. The molecules are all moving with the same speed, on the average, although some molecules, because of a fortunate combination of collisions, will be moving faster than their neighbors. Others will be moving somewhat more slowly. The distance a molecule can move is determined by the free space about it. The molecules of a liquid (or a solid) are in motion just as they are in a gas, but the distance they go before colliding is more limited in a liquid, and still more limited in a solid, because the molecules are closer together.

Our comparison would be better if people could move naturally in every direction like birds, for molecules do not stay on one level. Thus molecules of water vapor, ice, and liquid water all at 0°C have the same average velocity.

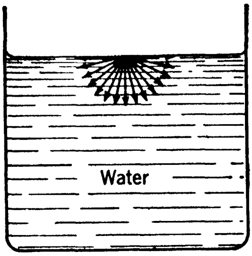
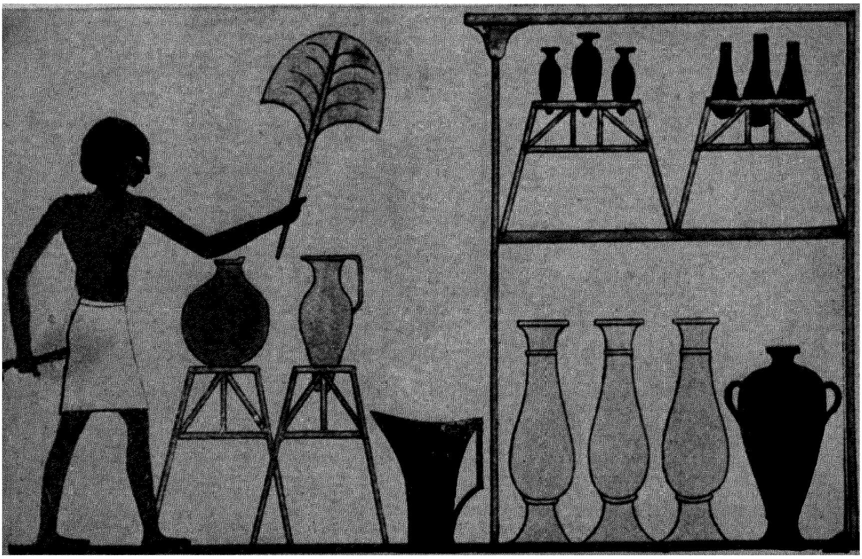


FIG. 7-3.—The surface layer of a liquid has no upward cohesive force acting on it, a unique situation since all other molecules in the liquid are covered.

Evaporation. The layer of molecules on the surface of a liquid is different from the molecules elsewhere in the liquid. Inside the liquid all the molecules are subjected to the attractive force of their neighbors, which is equal in all directions; but on the surface there is no cohesive force acting on the molecules from above. A film is formed on the surface of water because this outer layer of molecules has only downward cohesive forces acting on it. (See Fig. 7-3.) Water insects skate about the surface of a pond on this film; this layer of surface molecules is even strong enough to keep a razor blade from sinking.

Not only are there no cohesive forces pulling the molecules in the surface film upward, but also there are no collisions from molecules of the liquid from above. Occasionally some of the especially energetic molecules of the liquid are moving fast enough to "take off" from the



Courtesy of General Ceramics Company

FIG. 7-4.—An Egyptian is here evaporating the moisture from the surface of a porous earthenware jug filled with water. By this means he will be able to serve a cool drink.

surface of the liquid into the space above. For this reason we always find some of the molecules of the liquid above its surface.

We may ask, "How can the molecules of the liquid escape into the space above if that space is already filled with air?" The answer is that any space which contains air is far from "filled." Plenty of room is left between the molecules in the air for the molecules that come from the liquid. Thus the space above a liquid contains air molecules and molecules of the vapor of the liquid.

This tendency of molecules at the surface of a liquid to escape or to form vapor, called ***evaporation,*** increases when the temperature of the liquid is raised. Warm water evaporates more quickly than cold water. This is because the molecules of the liquid are moving faster when the liquid is heated, and thus more molecules have sufficient energy to leave the liquid. Fanning a liquid or causing a draft of air to blow over it will also hasten the rate of evaporation. (See Fig. 7-4.) Let us see why this is true.

Cooling by Evaporation. As we have discovered, above the surface of every liquid are molecules from the liquid. These are constantly moving about so that they collide with one another. Some of them hit the liquid again, and then they are close enough to the molecules of the liquid to allow the force of cohesion to act. They join the liquid again and hence condense. (See Fig. 7-5.) If, instead, a draft of air takes these vapor molecules away, they cannot reach the liquid to become part of it again. The liquid cools because the molecules, moving away from the surface, take excess energy along with them. A windy day favors the drying of clothes, and damp clothes are cooler than dry clothes hanging on the same line.

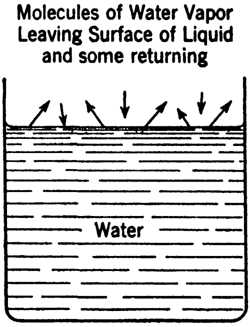


FIG. 7-5.—The molecules constantly "take off" and return to the surface of a liquid during evaporation.

Vapor Pressure. A balance of molecular action, or equilibrium, as it is often called, can be illustrated by considering the surface of gasoline in a partly filled closed tank. The air in the space above the gasoline is saturated with gasoline vapor. The gasoline vapor is continually forming liquid gasoline again and just as rapidly evaporating. (See Fig. 7-6.)

It is interesting to consider what happens in general when evaporation of a liquid goes on in an enclosed space at a constant temperature. The molecules from the liquid hop out and mix with the vapor in the space above. The air molecules are relatively few and act as spectators for this procession of acrobatic molecules from the liquid. Some of these molecules rejoin the liquid, while others continue to escape from it. The rate of return grows as the vapor molecules increase in number. The temperature of the liquid layer becomes the same as that of the vapor, and the rate of molecules leaving and returning becomes the same. The two actions are equal in rate, but exactly opposite in their effect.

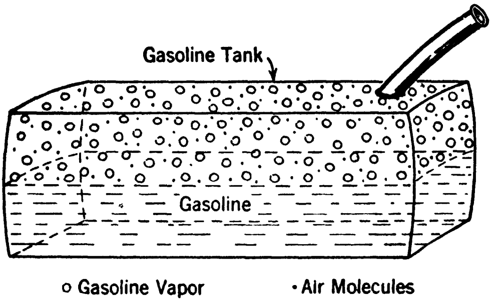


FIG. 7-6.—An equilibrium between the rate of "take-off" of molecules and their return is set up within a closed tank partially filled with liquid.

The vapor molecules of a liquid exert a constant pressure under the conditions just described because the number of vapor molecules is fixed. This pressure of the vapor is called the vapor pressure. ***Vapor pressure*** is defined as the pressure at any temperature of the vapor molecules in equilibrium with the liquid. It increases as the temperature is raised.

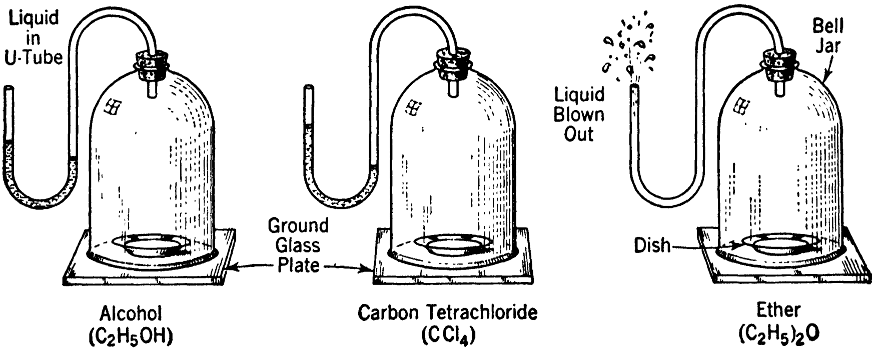


FIG. 7-7.—The extent to which liquid in the U-tube is pushed down from its closed end is a measure of the vapor pressure of the volatile liquid enclosed by the bell jar.

Boiling. Let us observe an open flask of water as it is heated to the boiling point. We notice first the escape of bubbles of air that were dissolved in the water. At the surface, a mist forms that is often considered steam but is actually comprised of little droplets of water condensing from the evaporated liquid. Next, little bubbles of water vapor form on the bottom of the vessel, rise part way up the liquid, but collapse and condense again before they reach the surface. Finally, these bubbles of vapor do rise out of the liquid, growing larger as they rise nearer the surface of the liquid, where the (hydrostatic) pressure on them is less. These bubbles contain water vapor at sufficient pressure to prevent collapse. Since the vapor is now at the boiling temperature of water, it is called steam. We say that the liquid is boiling and that a temperature has been reached called the ***boiling point.*** More heat applied makes the evaporation faster, but the temperature does not rise because more heat merely increases the rate of evaporation. At the boiling point the average velocity of the molecules of the liquid and of the vapor is the same. In fact, the molecules of liquid, solid, and gas of the same substance are moving at the same average velocity if they are at the same temperature, no matter what the temperature may be.

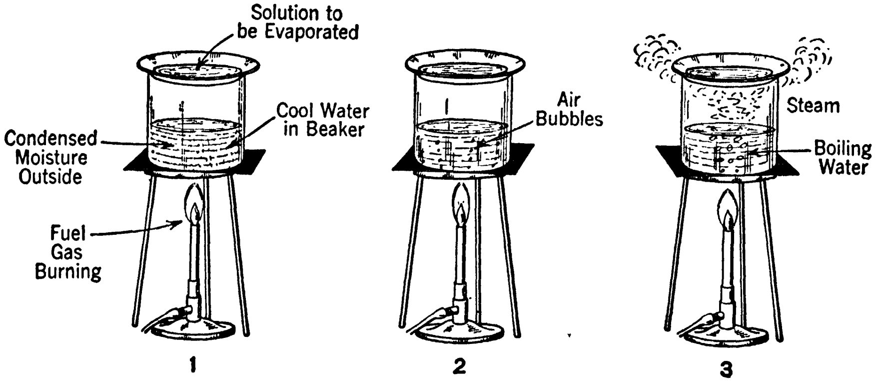


FIG. 7-8.—1. Moisture condenses on the cool outside walls of the beaker. The moisture is a product of burning the hydrogen in the fuel gas. 2. The moisture on the outside walls evaporates as the temperature rises. Small bubbles of air that were dissolved in the water appear around the sides of the beaker. 3. Bubbles of steam form within the water during the boiling. The steam heats the underside of the evaporating dish and condenses, warming the dish and hastening evaporation of the liquid within it.

Obviously, the boiling point is not a definite temperature but depends upon the pressure on the surface of the liquid. That is, the vapor in the bubbles must have enough pressure to prevent their collapse. If the liquid with which a chemist is working happens to be one that is chemically decomposed at a temperature below its normal boiling point under atmospheric pressure, it may nevertheless be boiled by reducing the pressure at its surface. Vitamin A can be distilled and purified, and orange juice can be concentrated in this way. Boiling-point temperatures are usually stated at standard pressure, 760 mm.

The boiling point may be defined as the temperature at which the vapor pressure becomes equal to the pressure at the surface of the liquid.

A demonstration to show that the boiling point may be changed is worth following.

A strong, round-bottomed flask is selected, filled partly with water, and heated until the contents boil vigorously. (See Fig. 7-9.) A thermometer inserted reads about 100°C. The space above the boiling water in the flask contains steam but no air. The flask is closed tightly with a rubber stopper through which a thermometer has been inserted. The flask is then removed from the heat, inverted, and placed under running cold water. The steam in the flask changes to liquid water, occupying about $\frac{1}{1700}$ of its former volume. The pressure on the water in the flask becomes less than it was previously. Vigorous boiling takes place inside the flask. In fact, finally the flask of boiling water can be comfortably held in the bare hands. The thermometer now shows a temperature very much lower than 100°C.

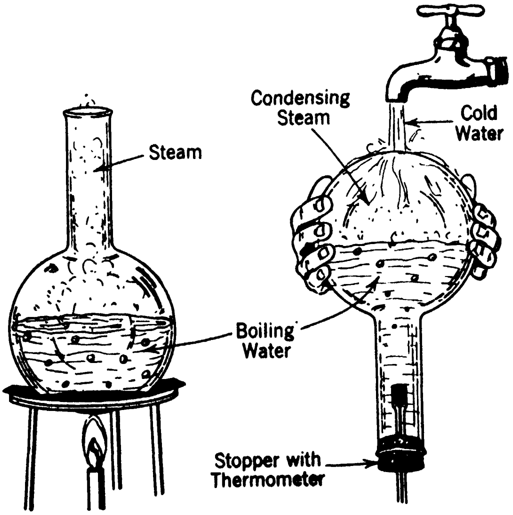


FIG. 7-9.—This experiment must be seen to be appreciated. Vigorously boiling (but lukewarm) water in a flask can actually be carried in the bare hands. That is, boiling depends upon pressure as much as upon temperature.

Energy Changes. If a person holds his hand in a stream of air escaping from a tire, he finds that the expanding air is cool (I).

Every time a person washes his hands and face, the slight cooling of the skin as it dries is noticeable. The same effect of cooling by evaporation is noted when gasoline, ether, or dry-cleaning fluid gets on the hands and evaporates. An alcohol rub is useful in cooling the surface of the body because the alcohol evaporates (II).

The opposite effect is evident when we pump up a tire, using a hand pump of the plunger type. Of course motor-driven pumps show the same effect to a greater degree. Both get warm (III).

In order to explain these three effects, let us consider that one of us is holding a tennis ball in his hands. The ball is pulled toward the earth. The two objects (the earth and the ball) have a force of gravity acting between them. If the ball is allowed to drop to the earth, the rate of motion becomes faster and faster. On the rebound, as the ball moves away from the earth, the rate of motion becomes slower. From this illustration we get the idea that as two bodies that have a mutual attraction move toward each other their speed increases, potential energy is changed to motion, or kinetic, energy; and as the objects separate their speed is retarded, kinetic energy is stored as position, or potential, energy.

Compressing a gas means reducing the space between the molecules. The molecules move toward each other; the molecules attract each other also. As molecules approach, their speed increases owing to forces of attraction. Hence the average motion energy has become greater, and the gases are raised to a higher temperature (III).

Following the same reasoning for evaporation (II) or an expanding gas (I), in each case the molecules move apart, against forces of attraction. A slowing up of their rate of motion is caused, and the temperature is thus lowered.

Practical Applications. Steam heating and mechanical refrigeration both use these simple principles, that evaporation causes cooling and condensation causes heating. In steam heating the water takes energy from the chemical change of oxidation going on in the fire under the boiler. Evaporating the water requires energy to drive the molecules apart. The steam formed travels to radiators, where it strikes a large surface of cooler metal. The steam now condenses to water. The molecules come closer together. Heat is evolved.

Steam burns are especially painful, for in addition to the high temperature of the steam the extra heat from its condensation is liberated on the unfortunate victim.

Measurement of Heat Energy. Heat intensity is measured by a thermometer. The thermometer tells the temperature at the position where it is located, but it does not tell how much material is heated to that temperature. In order to measure the amount of heat, the amount of material must be included with that of the temperature. The convenient standard amount of material for heat measurements in the laboratory is 1 g of water. ***When the temperature of* 1 *g of water is changed* 1°C, 1 *cal of heat is required.*** The Calorie used for measuring the energy value of foods is 1000 times larger, and is the large or kilocalorie. To heat 1 g of water 10°C requires 10 cal; to heat 10 g of water 1°C requires 10 cal; to heat 10 g of water 10°C requires 100 cal.

The calorie is the unit used to express the energy change accompanying a change of state of a substance, to measure the heat of combustion of fuels, and to measure the heat absorbed or liberated in chemical actions generally.

Amount of Heat in Change of State. When ice melts, it remains at the temperature called the ***melting point*** (0°C) until it has all melted. Adding more heat will hasten the melting but will not raise the temperature until all the ice has melted. The molecules of ice at 0°C and of water at 0°C move with the same average velocity, since they are at the same temperature. After all the ice has melted, the water will rise in temperature as the molecules move more rapidly, absorbing 1 cal per g per deg in so doing, until it reaches its boiling point, 100°C (standard pressure is assumed). Now the water boils. As we have previously stated, adding more heat now will hasten the boiling but will not raise the temperature while any water is left. Molecules in the liquid and vapor are now moving with the same average velocity. Steam can be separately heated to any higher temperature desired, or superheated. Molecules of superheated steam are moving at a much higher velocity than those in ordinary steam at 100°C.

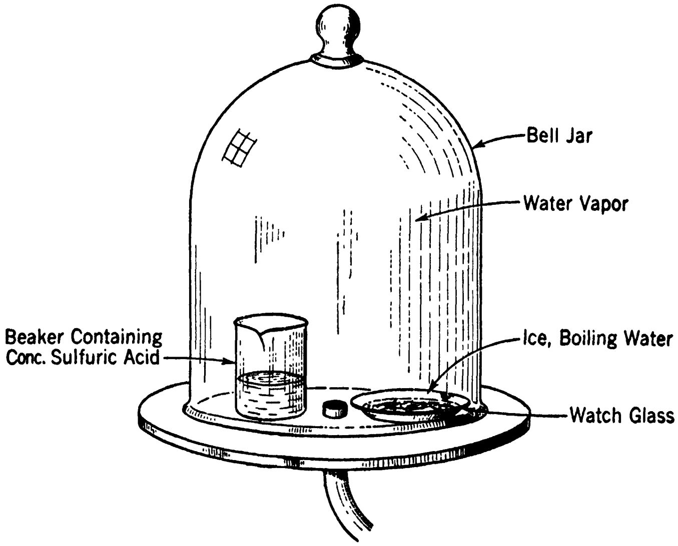
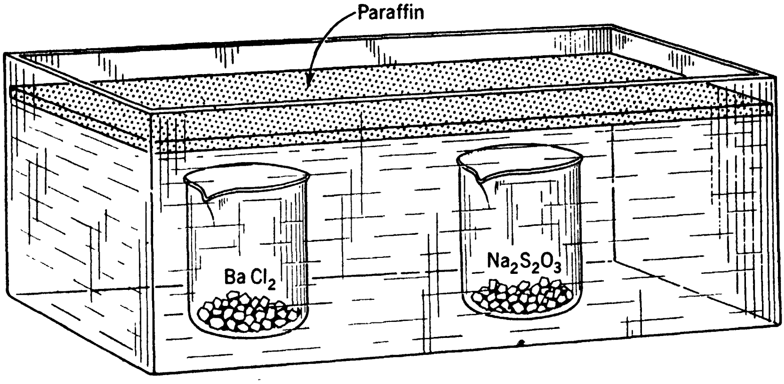


FIG. 7-10.—Under reduced pressure it is possible to have ice, liquid water, and water vapor all in equilibrium at the same temperature. This diagram illustrates the so-called "triple point."

In terms of molecules, those of the solid ice become freer to move about when ice is changed into liquid water (although slightly closer together). Heat is required to overcome the cohesion that the molecules have for one another in the solid and to give them the greater liberty of motion that they have in a liquid. After this change, the molecules in the liquid condition move faster and faster as the temperature is raised. When finally the boiling point is reached, enough heat energy is absorbed to free each molecule from the forces of attraction of its neighbors.

The amount of heat energy required for these changes, in terms of 1 g of water, gives some measure of the force of cohesion that is overcome by the water molecules. To change 1 g of ice to 1 g of water without changing the temperature, both ice and water staying at 0°C, 80 cal is necessary. ***The amount of heat required to change* 1 *g of a solid to* 1 *g of liquid without raising the temperature is called the heat of fusion.*** In the case of water the heat of fusion is 80 cal.



Courtesy of Journal of Chemical Education

FIG. 7-11.—An interesting way to grow crystals. Saturated solutions of barium chloride and sodium thiosulfate in beakers are covered carefully with distilled water and the whole covered. Large crystals of barium thiosulfate form slowly. Other pairs of solutions that can be used are lead nitrate and potassium iodide, silver nitrate and sodium nitrite.

Still with respect to 1 g of water, the amount of heat needed to raise its temperature from 0 to 100°C is 100 cal. The temperature now stays at 100°C, while 540 cal of heat, a relatively large quantity, is absorbed. This shows the great amount of energy that is needed to free the molecules from the cohesive forces that they have for each other in liquid water. ***The number of calories needed to change* 1 *g of a liquid to* 1 *gram of a gas of the same substance at the same temperature is called the heat of vaporization.*** The heat of vaporization of water is 540 cal.

Solids. We are now ready to consider the most familiar form of matter—solids. Strange as it seems, only recently has much been learned about the structure of solids. Rocks of a peculiar coloring or formation have always attracted people. One of the rocks that people often pick up because of its attractive appearance is quartz. Some quartz has six-sided and pointed crystals, often clear, but sometimes tinted in delicate colors, purple as in amethyst, for example. Quartz is an oxide, silicon dioxide

(SiO_2). At this point we are not so much interested in its chemical nature as in its form. Quartz and other ***solids that have regular form, flat surfaces, and edges are called crystalline.*** Salt and sugar are common examples of crystalline solids. Large crystals are frequently found in nature. But most rocks consist of small crystals, matted together. Solid metals are crystalline, usually masses of tiny crystals. Since we consider even very minute solid particles as crystalline, every true solid is crystalline.

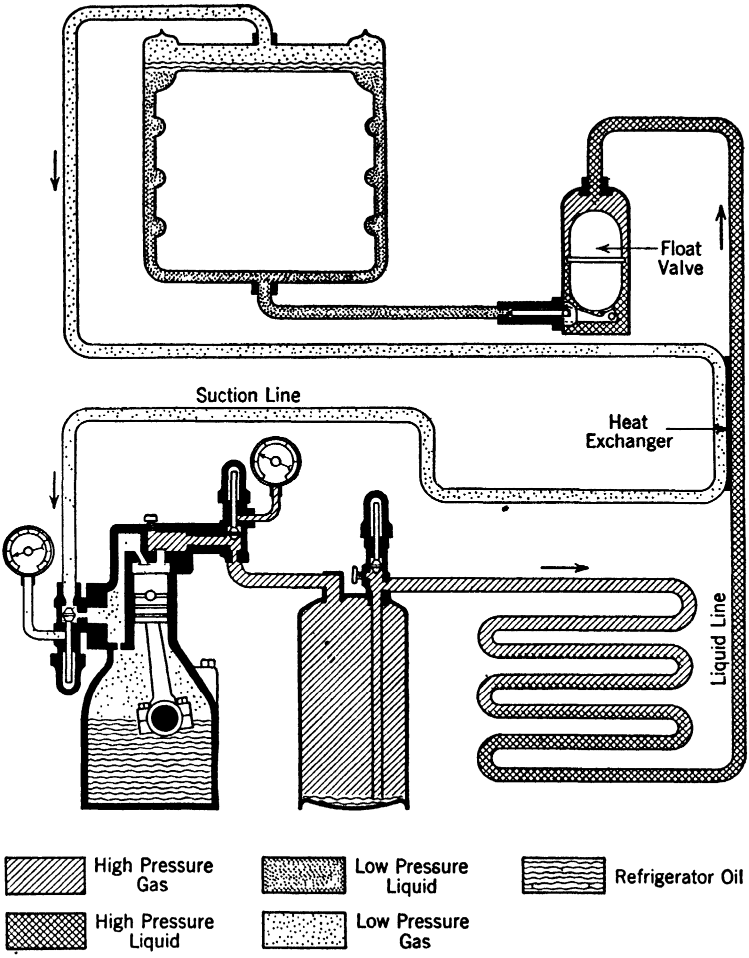
Materials evidently not crystalline are called amorphous (without shape). Glue, glass, and flesh are examples of amorphous materials. The dividing line between amorphous materials and crystalline substances is not sharp; the classification is a general one, but quite useful.

Crystalline substances have a definite melting point and, like ice, remain at that temperature until all the solid has melted. Amorphous substances gradually become softer with no change of state and hence have no definite melting point. As the temperature is raised, they finally flow so readily that anyone would recognize them as liquid.

The fact that crystals of a given substance are perfectly regular is interesting. Any given substance always forms the same kind of crystals under like conditions. There must be something quite regular about the way in which the molecules or other building stones are arranged in these crystals. X-ray examination of crystals shows this to be the case.

Refrigeration. When ice is used for cooling, its success as a cooling agent is due chiefly to its melting. In melting 1 g of ice to 1 g of water, both at 0°C, 80 cal of heat is absorbed. This heat is absorbed from whatever is near the ice. If the ice is in a refrigerator, then the heat is taken from the contents of the refrigerator. The change of state from solid to liquid is the active process in producing cooling, for the molecules take in heat to overcome the cohesive forces in a cake of crystalline ice. Unless ice is melting in a refrigerator, there can be but limited cooling effect.

Household refrigeration of the mechanical type may be of the sort which for its success depends upon another change of state, that from liquid to gas. In many mechanical refrigerators electricity supplies energy, which runs a motor, which in turn drives a pump. This pump compresses a vapor. For small models the vapor is often sulfur dioxide (SO_2) or one of several other vapors that easily change into a liquid, such as Freon (CF_2Cl_2). For larger installations, as for a cold storage warehouse, ammonia (NH_3) is most commonly used, although carbon dioxide (CO_2) may be used on ships. The compressed vapor from the pump is sent to a coil (a long pipe wound in a spiral so that there is much pipe in a small space), where it is cooled, for during compression the vapor becomes heated. The cooling may be brought about by forcing air or water across the pipe or by simply allowing air to go over it naturally, since the warmer air near the coil will rise. All this goes on outside the refrigerator. The cooling changes the compressed vapor to a liquid, which runs through a tube into the "unit" inside the refrigerator. The liquid passes an expansion valve, which is equivalent to letting it enter a larger pipe.



Courtesy of Temperature Research Foundation of Kelvinator Corporation

FIG. 7-12.—The heart of a household refrigerator is a pump run by an electric motor. The pump compresses a gas that becomes a liquid when it is cooled in air. The liquid evaporates within the "unit," producing the desired cooling within the box.

Here the liquid rapidly evaporates, forming the vapor again. Heat energy is absorbed in this process of evaporation. The entire system is closed so that the gas does not escape but is taken back to the pump, compressed again, cooled, condensed, and then allowed to evaporate for another cycle. (See Fig. 7-12.) The cooling process is not continuous but is controlled by a thermoregulator (temperature regulator) so that it goes into action only when the temperature inside the refrigerator rises to a certain point. On modern refrigerators this temperature can be adjusted by the temperature-control knob.

SUMMARY

The volume that a given amount of gas occupies is influenced by the conditions of temperature and pressure on it. The effect of pressure alone is described by Boyle's law: The volume of a given quantity of gas is inversely proportional to the pressure, provided that the temperature is unchanged. The effect of temperature alone is described by Gay-Lussac's (Charles') law: The volume of a given quantity of gas is directly proportional to the Kelvin or absolute temperature, provided that the pressure is unchanged. Kelvin, or absolute, temperature is based on the centigrade scale. Absolute zero is −273°C, and 0°C is 273°K. (C + 273 = K.)

Evidence for the correctness of the kinetic molecular theory includes

1. Boyle's and Gay-Lussac's (Charles') laws apply to all gases (within limits).
2. The phenonemon of diffusion, or continual spreading of a gas by its own motion.
3. The pressure exerted by a gas is continual.
4. A gas exerts its pressure equally in all directions.

The kinetic molecular theory is reaffirmed and used to explain many phenomena.

There is a relatively large space between molecules in the gaseous condition. The force of attraction between like molecules is called cohesion; the force of attraction between unlike molecules is called adhesion. When molecules move apart, energy must be supplied. When molecules come closer together, energy is liberated.

When a gas changes to a liquid, the process is called condensation. The opposite process of changing a liquid to a gas is called evaporation. The process of evaporation may be hastened by heating, lowering the pressure above the evaporating liquid, stirring the liquid, and increasing the circulation of air over the liquid. The process of evaporation in the open produces cooling. When the rates of escape and return of molecules at the surface of a liquid in a closed vessel are the same, the liquid and vapor layers are in equilibrium. We may measure the vapor pressure of a liquid; and it rises with the temperature. Boiling takes place at such a temperature that the vapor pressure is equal to the pressure of the atmosphere above the liquid. Then evaporation can take place at any point in a liquid. The boiling temperature is usually given at standard pressure (760 mm of mercury), but boiling points may be changed by altering the pressure.

The unit of heat quantity is the calorie, the amount of heat needed to change the temperature of 1 g of water 1°C. To change 1 g of ice at 0°C to water at 0°C requires 80 cal, and to change 1 g of water at 100°C to steam at 100°C requires 540 cal. The fact that energy changes accompany changes of state has many practical applications, as in refrigeration and in steam heating.

Solids may be classed as amorphous or crystalline. Amorphous solids like glue have no definite shape, but crystalline solids like common salt have smooth flat surfaces, sharp edges, and definite angles between surfaces.

TEMPERATURE SCALES

Kelvin or absolute	Centigrade	Fahrenheit
373°	100°	212°
Boiling point of water		
273°	0°	32°
Freezing point of water		
0°	−273°	−459.4°
Absolute zero		

Helpful conversion formulas
$\frac{C}{F - 32} = \frac{5}{9}$ $K = C + 273$

QUESTIONS

18. A glass of water held at arm's length can be whirled over one's head and back to the original position. If this is done rapidly and skillfully, no water spills. Explain.

19. List four factors that change the rate of evaporation. How should each be altered to hasten evaporation?

20. Portions of a gasoline-engine carburetor may become so cold when the engine is running that ice may form. How is this effect explained?

21. What is the vapor pressure of water at its boiling point under standard pressure?

22. Pipes made of plastic material can stretch considerably without breaking. Suggest conditions under which plastic plumbing could be used advantageously.

23. (*a*) In temperature measurement, distinguish between a degree and a calorie. (*b*) What is specific heat?

24. How many calories are needed to heat $\left\{\begin{matrix}20\\10\end{matrix}\right.$ grams of water from $\left\{\begin{matrix}30\\40\end{matrix}\right.$ to $\left\{\begin{matrix}40\\65\end{matrix}\right.$°C?

25. How many calories are needed to melt $\left\{\begin{matrix}1\\8\end{matrix}\right.$ gram(s) of ice and to raise the temperature of the resulting ice water to $\left\{\begin{matrix}20\\30\end{matrix}\right.$°C?

26. How many calories are needed to change $\left\{\begin{matrix}1\\7\end{matrix}\right.$ gram of water at $\left\{\begin{matrix}20\\30\end{matrix}\right.$°C to 100°C and to boil away the resulting hot water?

27. Water on a stove in an open pan is boiling gently. The heat is now suddenly increased. What is the effect on (*a*) the temperature of the water and (*b*) the rate of boiling?

28. Certain home-heating systems include a boiler that boils water under reduced pressure. What is the effect of such an arrangement on the boiling point of water?

29. Define and give an example of crystallization.

30. How many prominent axes has a snow crystal?

31. Describe the changes that a raindrop undergoes on its way back to rejoin a cloud.

32. Trace the course of a refrigerant in a mechanical refrigerator.

MORE CHALLENGING QUESTIONS

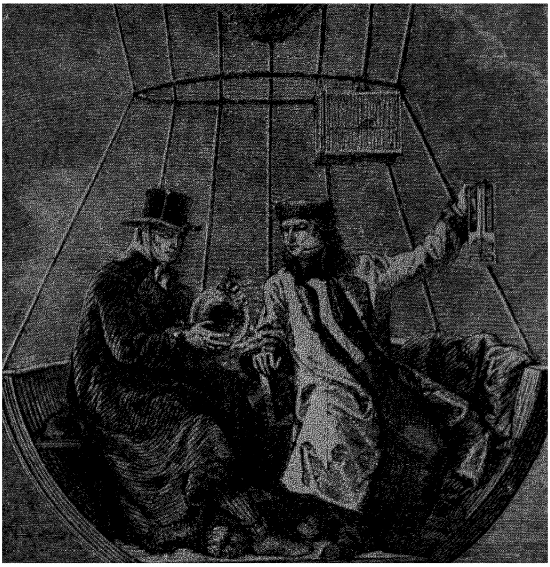
33. How many calories are needed to change $\left\{\begin{matrix}20\\33\end{matrix}\right.$ grams of ice at 0°C to steam at 100°C?

34. Do locomotives use steam at a temperature of 100°C?

35. Can a person cool a kitchen on a hot day by opening the door of a mechanical refrigerator in the kitchen?

36. List the properties of an ideal refrigerant.

UNIT TWO



Gay-Lussac and Biot made a balloon ascension for scientific observations in 1804.

CHEMISTRY'S BUSINESS OFFICE

A CERTAIN pupil, who had become intensely interested in the subject of chemistry during his high-school years, reached college with even more intense curiosity about this branch of science. There he consulted the dean in regard to planning his courses so that he might prepare wisely for the chemical profession. "It is advisable to be able to read either French or German," said the dean.

The freshman was surprised; but later when he learned from a senior that many reports of chemical work have never been translated from the language in which they were written, the reason became clearer. "My chemistry professor," said the senior, "is now studying Russian in order that he may find out the information discovered in that country about his pet research field."

"Are the symbols and equations different in other languages?" asked the freshman.

"No. They are substantially the same in every language, even in Chinese books on chemistry," was the comforting reply.

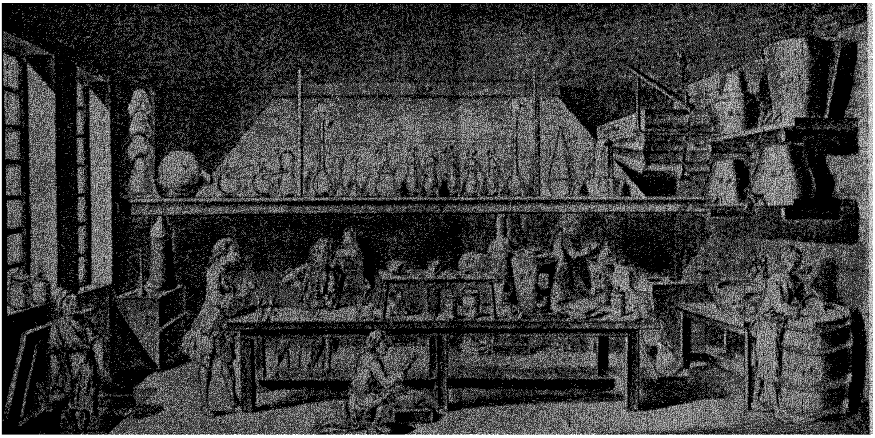
A group of chemistry pupils was once being guided through an industrial plant. The chemist who was conducting the party stopped near a gasmaking machine and explained the process by which it worked. "In the generator of the water-gas machine, we heat coke by burning it in a forced draft of air. Then the air is shut off and steam forced through the deep bed of hot coke. A chemical reaction takes place, as your instructor has probably shown you, as follows:

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

In this process heat energy is absorbed, and the coke is thus cooled."

In these two instances we see that symbols play an important role in chemistry study and industrial processes. While all chemists do not have the same mother tongue, it is an enormous advantage that all use the same scientific language, the same symbols and formulas, and understand all common abbreviations.

This sketch shows chemistry's business office in action in Paris in 1760. Some of the work consisted of the preparation of medicines. Can you notice any similarity between these apparatus and those common today?



Courtesy of General Ceramics Company

UNIT TWO ------------- CHAPTER VIII

THE INVENTORY—ATOMS AND MOLECULES

Once again it is profitable to go behind the scenes. In our previous trip to the backstage of chemistry we found out something about molecules. These little particles are useful in explaining many things. Perhaps asking a few more questions about molecules will lead somewhere. Are they the smallest particles? How do molecules of elements and compounds differ?

Avogadro's Reasoning. In the early nineteenth century Amadeo Avogadro (1776–1856), who did not claim to be a chemist and who is little known for his laboratory investigations, hit upon a simple idea that has greatly aided the progress of science. In 1811, while England and the youthful United States were warming up for their second war, this professor of physics at the University of Turin, Italy, wrote an article. In it he claimed that ***equal volumes of all gases have the same number of molecules,*** if the gases are measured under the same conditions of temperature and pressure. This holds true whether the gas is a mixture, an element, or a compound. One liter of air, oxygen, or carbon dioxide each contains the same number of molecules. Avogadro did not state what the number was; nor is the number important for our present purpose.

In arriving at his conclusions the imagination of Avogadro had been fired by some facts that were found to be true about all gases. Robert Boyle, over 100 years before, had shown that the volume of any given amount of gas changes inversely with the pressure at constant temperature (Boyle's law). Charles' law (1787) that the volume of a given amount of gas at constant pressure changes directly with the ***absolute*** temperature also applied to all gases was given exact expression in 1802 by Gay-Lussac (1778–1850), a French investigator.

A few years before Avogadro reached his conclusions, Gay-Lussac had carried out extensive experiments with gases. In this work he studied

---

New Terms

atom
molecular weight
liter
atomic weight
density

the chemical reaction between the gases hydrogen and oxygen, measuring the volumes used. He was impressed by the simplicity of his results, namely, that 2 liters of hydrogen combines with 1 liter of oxygen. Studying the combining volumes of other gases he found that the volumes which combined completely were all whole-number volumes. For example 1 liter of chlorine joins with 1 liter of hydrogen exactly to form 2 liters of hydrogen chloride. Also, 1 liter of nitrogen joins with 3 liters of hydrogen to form 2 liters of ammonia. In general, he concluded that ***gases take part in a chemical change in simple volume ratios,*** $1/2$, $1/3$, and the like. The statement in boldface italics is called ***Gay-Lussac's law of combining volumes.***

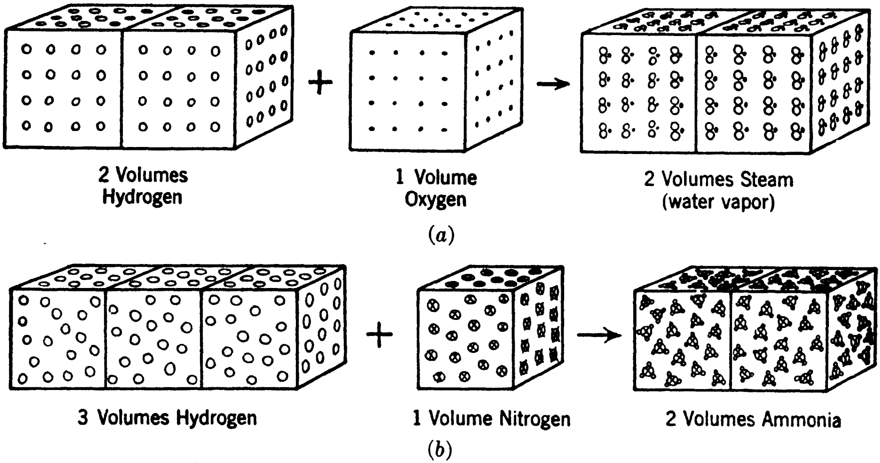


FIG. 8-1.—In (*a*) and (*b*) the molecules are represented as circles. The diagrams suggest the actual volumes of gases that combine in a chemical change. Gay-Lussac's law points out that these volumes are small whole numbers.

Avogadro was greatly impressed by Gay-Lussac's law. He reasoned in terms of molecules that, in the union of hydrogen and oxygen, two molecules of hydrogen joined with one molecule of oxygen to form two molecules of steam (see Fig. 8-1*a*), while, in the union of hydrogen and nitrogen, one molecule of nitrogen joined with three molecules of hydrogen to form two molecules of ammonia. (See Fig. 8-1*b*.) He concluded that the reason why two molecules of hydrogen and one molecule of oxygen did not form three molecules of steam and one molecule of nitrogen and three molecules of hydrogen did not form four molecules of ammonia was because the steam molecule and the ammonia molecule were made up of ***parts.*** The number of parts (atoms) present in the molecules of steam and of ammonia was not the same as in the molecules of the elements that formed the compounds.

Let us translate the excellent reasoning of Avogadro into terms of a chemical change. From the laboratory we find that

2 volumes of hydrogen + 1 volume of oxygen → 2 volumes of steam

The one volume (any definite number of liters, milliliters, cubic feet, or other volume measure) of oxygen contains a certain number of molecules. The two volumes of hydrogen or of steam contain just twice that number of molecules.

Molecules of Compounds. Compounds are made up of two or more elements joined together in definite proportion by weight. Some compounds can be decomposed easily into their elements; water, for example, can be decomposed into parts. Probably these parts are smaller than the molecules. What are they called? The name ***atoms*** (not divisible) has been given to them. For our explanation, let us carry our thought back to England just a few years before the time of Avogadro's work at Turin.

The Atomic Theory. When he was not too busy making notes about the weather in his collection of notebooks, John Dalton (1766–1844), an English schoolteacher, relaxed and thought. His mind was of the sort that generalizes, sees fundamental ideas clearly in spite of many confusing situations. His thoughts were often about the structure of matter, a subject that had been considered from the earliest times. The result was Dalton's atomic theory.

In this theory ***an atom is defined as the smallest particle of an element that can exist in a molecule.*** It is the smallest particle of an element that has all the chemical properties of larger amounts of that element. Since 92 natural elements are now known, 92 sorts of natural atoms must exist—1 for each kind of element. An atom is a fundamental building stone of matter. All molecules are made of 1 or more atoms.

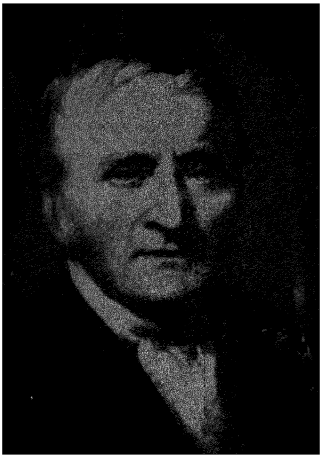


FIG. 8-2.—"While at Kendal employed his leisure in studying Latin, Greek, French, and the Mathematics with Natural Philosophy, removed thence to Manchester in 1793, as Tutor in Mathematics and Natural Philosophy in the New College, was six years in that engagement, and afterwards was employed as private and sometimes public Instructor in various branches of Mathematics, Natural Philosophy and Chemistry chiefly in Manchester, but occasionally by invitation in other places, namely London, Edinburgh, Glasgow, Birmingham, & Leeds." So writes John Dalton of his career.

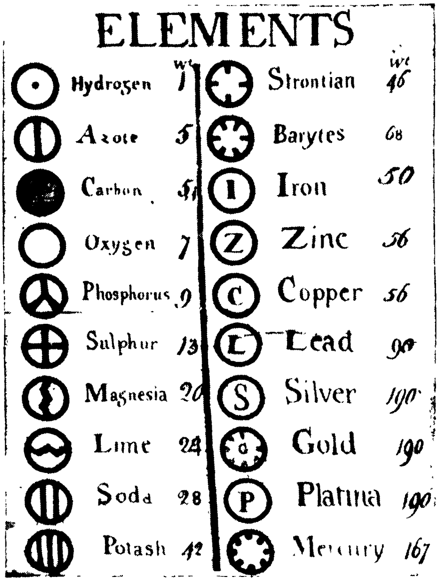
Each sort of atom is different from every other sort of atom in weight and properties. All atoms of the same element are alike in weight and properties.[1] When elements combine, atoms of the elements are combin-

---

[1] Subject to later developments.

ing. When compounds are decomposed, new molecules are formed in which the original atoms are rearranged. The entire world is built up of atoms, so small that they are invisible to us. (See Fig. 8-3.)

These, Dalton's ideas, were accepted slowly by the people of his day. The atomic theory has won its place in science because it is successful in explaining facts as we know them. We may wonder at believing that which cannot be definitely proved by direct evidence or that which cannot be seen. We can, however, see effects caused by a single particle of atomic size in the Wilson cloud chamber. The theory is accepted today to the extent that one dictionary defines chemistry as a science that considers matter to be composed of atoms.



Courtesy of Fisher Scientific Company

FIG. 8-3.—This lecture diagram was used by John Dalton to illustrate his famous atomic theory in 1803. It is a reproduction from the original chart by the Science Museum, London.

Applications of the Atomic Theory. The test of a theory is its value in explaining the situations to which it refers. The atomic theory enables us to explain the law of constant composition. The composition of nitric oxide is always 46.67 per cent nitrogen and 53.33 per cent oxygen, no more and no less. This is one illustration of the law of constant composition. A certain number of nitrogen atoms (one) combined with a certain number of oxygen atoms (one) is a molecule of nitric oxide. Since the weight of each element in the compound does not change, the percentage of each in the molecule is constant..

A second application of the atomic theory is its explanation of the ***law of multiple proportions.***[1] In numerous cases two or more compounds are made of the same two elements. Both water and hydrogen peroxide are made of hydrogen and oxygen. There are two oxides of carbon, namely, carbon monoxide and carbon dioxide. Many compounds of hydrogen and carbon exist, among them ethane, ethylene, and acetylene. Laboratory experiments give the following figures (columns *A* and *B* in the table below) for the composition of these compounds:

Compounds	Percentages		Parts by weight	
	A	*B*	*C*	*D*
Case I:	Oxygen	Hydrogen	Oxygen	Hydrogen
Water	88.81	11.19	7.94	1
Hydrogen peroxide	94.07	5.93	15.86	1
Case II:	Oxygen	Carbon	Oxygen	Carbon
Carbon monoxide	57.14	42.86	1.33	1
Carbon dioxide	72.73	27.27	2.67	1
Case III:	Hydrogen	Carbon	Hydrogen	Carbon
Ethane	20.00	80.00	0.25	1
Ethylene	14.29	85.71	0.17	1
Acetylene	7.69	92.31	0.08	1

The figures in column *C* are obtained by dividing the percentages in column *A* by those in column *B*. The two sets of columns of figures (percentages and parts by weight) are therefore equivalent. Column *D* is 1 in each case, since it represents the element in column *B* expressed as one part by weight. When the hydrogen is expressed as one part by weight in case I, then the parts of oxygen are 7.94 and 15.86, a ratio of 7.94/15.86, or practically $\frac{1}{2}$. In case III, three compounds are considered, each composed of hydrogen and carbon. The carbon is represented as one part by weight; the hydrogen has the ***ratio*** 0.25/0.17/0.08, or approximately 3/2/1. In each example one element has been represented as one part by weight. Also, the weights of the other elements can be represented by a small fraction made up of whole numbers. This is found to be true every time two or more compounds composed of the same elements are studied. These facts can be summarized as follows: ***If two or more compounds are made of the same two elements and the weight of one of the elements be***

---

[1] The law of multiple proportions may be omitted in a general study of chemistry.

represented by one part, then the weightS of the second element are related as a simple fraction. This statement is called the ***law of multiple proportions.***

The explanation of the law just stated is based on the existence of atoms. The one part by weight represents one or more atoms (often one) of a certain element in each of two compounds. Both these compounds also contain another element in common. The numbers of atoms of the other element are related as 1 to 2, 2 to 3, or a like group of small numbers.

In case I both water and hydrogen peroxide have two atoms of hydrogen in each molecule (one part by weight); and both have the element oxygen in common. There is one atom of oxygen in a molecule of water, and two oxygen atoms in a molecule of hydrogen peroxide (per means "extra"). The weights of the oxygen in these two compounds are related in the ratio of $\frac{1}{2}$, a simple fraction.

In case II both oxides of carbon have one atom of carbon, one part. The one oxygen atom in carbon monoxide and the two oxygen atoms in carbon dioxide have a ratio of $\frac{1}{2}$, a fraction of small whole numbers. This fact is shown by the ratio of the weights of oxygen, 1.33/2.67, which reduces to approximately $\frac{1}{2}$.

The law of multiple proportions was first stated by John Dalton. It was undoubtedly very influential in establishing in his mind the truth of the atomic nature of matter.

Atoms and Molecules. To summarize, the smallest part of a compound is a molecule. The molecule of a compound is made up of atoms of two or more different sorts; the molecule of an element is made of one, two, or more atoms, all of the same sort. Thus elements differ from compounds in that the atoms present in the molecule of an element are all of the same kind, while those in the compound molecule are of two or more different kinds.

If the element is normally a gas, like oxygen, or can be changed into a gas readily, we can find out how many atoms are present in its molecule. For example, let us seek an answer to the question, "How many atoms are present in a molecule of oxygen?"

Chemical Geometry. Whatever our feelings about the subject of geometry, we all admire the method it uses in establishing truths. Once demonstrated, the conclusions of geometry cannot be denied. Let us use the method of geometry, to show that the molecule of oxygen has two atoms.

Proposition: The oxygen molecule has two atoms.
Given: Avogadro's law; laboratory equipment.
To prove: The molecule of oxygen has two atoms.

Statements	Reasons
(1) 2 volumes hydrogen + 1 volume oxygen → 2 volumes steam (water)	(1) Laboratory measurement
(2) Let 1 volume of gas hold 1000 molecules	(2) NOTE: Any number may be assumed
(3) 2000 molecules hydrogen + 1000 molecules oxygen → 2000 molecules steam	(3) Avogadro's law
(4) Each molecule of steam (water) contains at least 1 atom of oxygen	(4) Water can be decomposed into elements in the laboratory. The least amount of an element is 1 atom
(5) 2000 molecules of water contains 2000 atoms of oxygen	(5) From statements (3) and (4)
(6) 1000 molecules of oxygen have accounted for 2000 atoms of oxygen	(6) Statements (3) and (5)
(7) Therefore 1 molecule of oxygen has 2 atoms	(7) Dividing by 1000 (or whatever number was assumed)

More strictly, the conclusion of this proposition is as follows: One molecule of oxygen has ***at least*** two atoms. However, since we have no evidence that more than two atoms are present in a molecule of ordinary oxygen, the "at least" may be omitted. By using a similar method, we can prove that the molecules of chlorine, hydrogen, and nitrogen also contain two atoms.

Not all elements have two atoms per molecule when in the gaseous state. For example, phosphorus vapor has four, arsenic vapor four, and sulfur vapor eight. The inert gases of the air have only one atom per molecule.

Weight of an Atom. By very careful calculations, it is possible to obtain the actual gram weight of one atom of oxygen. This weight is exceedingly small, 0.000,000,000,000,000,000,000,026,39 g. It can be seen that so small a weight has no practical meaning; in fact, no balances in the laboratory can weigh one atom. An ounce or a gram weight from a set of weights is so large compared with the weight of an atom that the comparison is like telling the weight of a grain of sand in terms of the weight of the earth.

This perplexing situation was solved by selecting an atom of the element oxygen as a standard of weight. Experience has shown it wise to assign it the weight 16. This is because the lightest substance, hydrogen, would then have a relative weight of at least 1. Oxygen was originally selected as a standard because it is able to combine with so many other elements. Since two atoms are present in a molecule of oxygen, the weight that represents the oxygen molecule is 32. The weights of the other atom are represented in terms of the oxygen atom. Sulfur has atomic weight 32; this means that the sulfur atom is twice as heavy as the oxygen atom. Copper with atomic weight 64 (approximately) is four times as heavy as oxygen, atom for atom. The atom of carbon to which is assigned the weight 12 compares in weight with the oxygen atom as 12 to 16, or $\frac{3}{4}$.

We must be sure to realize that the relative weights do not tell how much atoms actually weigh. However, careful laboratory experiments were performed in finding the relative atomic weights. Moreover, the work is revised when necessary by an international committee of distinguished scientists.

International Atomic-weight Table. At the end of this book is a list of all known elements and their atomic weights. This table summarizes the work of chemists in many countries; it is a clearing-house for scientific information of this nature. The table is used by chemists and students of chemistry in every country. The information is the best available on the relative atomic weights of the known elements. It may, of course, be slightly in error in some details; thus we may expect small revisions as our knowledge becomes more complete and our methods of performing accurate experiments become better. Yet in this table as it now stands chemical accuracy has risen to a great height. It is a common meeting ground for chemists all over the world.

History of Atomic-weight Determination. Dalton's atomic theory had been presented in 1808, closely followed by Avogadro's law in 1811. These ideas were not fully accepted at once; in fact, the first real appreciation of Avogadro's work came as late as 1860 from his pupil, Stanislao Cannizzaro (1826–1910), a brilliant Italian professor of chemistry. The actual laboratory work needed to translate these theories into use was carried out by Berzelius. He is known as the "organizer of science," for he purified and analyzed over 2000 compounds and determined the atomic weights of over 50 elements. It will encourage many readers of this book to learn that this distinguished chemist did not have a happy time in his school days. He was graduated with a diploma which stated that his work "justified only doubtful hopes." He almost "flunked" his regular course in chemistry, but after his school days he worked along chemical lines with steady persistence. The facts presented in his article, "An Attempt to Determine the Definite and Simple Proportions in Which the Constituents of the Inorganic World Are Combined with Each Other," are famous for their accuracy. His results are remarkable when we consider that at this time the science of chemistry was no more than a husky youngster cutting its first teeth. This work of Berzelius gives proof of his skill and thoroughness.

Elements	Atomic weights	
	Berzelius (1826)	International Table (1945)
Nitrogen	14.05	14.008
Sulfur	32.18	32.06
Chlorine	35.41	35.457
Potassium	39.19	39.096
Silver	108.12	107.880
Lead	207.12	207.21

The challenge to obtain more accurate atomic weights was accepted by a Belgian, Jean Servais Stas (1813–1891), who showed remarkable genius for the task, "making his weighings on balances of hitherto unequaled precision, and exercising extraordinary care in his manipulations."

The mantle more recently descended on the shoulders of Theodore William Richards (1868–1928), of Harvard University. (See page 3.) He found the atomic weights of no less than 22 elements. For his researches in this field he was awarded many honors, among them the Nobel Prize in chemistry in 1914.

Modern physics has developed new methods, including use of the mass spectrograph, for finding atomic weights. These methods have been used with fine results by Dr. F. W. Aston, Dr. K. T. Bainbridge, and others—present-day successors to the heritage of Berzelius.

Laboratory Facts. The atomic weight of an element may be found by using a combination of facts and theories already considered. For example, let us learn how to determine the atomic weight of carbon. We select several compounds that contain the element carbon and in the laboratory find the percentage of carbon in each one. Several such compounds with their percentage of carbon have been listed in the table on page 143. Carbon dioxide, containing 27.27 per cent carbon, is found to weigh 1.98 g per liter. Carbon monoxide, containing 42.86 per cent carbon, is found to have a density of 1.26 g per liter. Oxygen gas weighs 1.43 g per liter.

Finding Molecular Weights. According to Avogadro's law, a liter of any of these three gases contains the same number of molecules (under the same conditions of temperature and pressure). Their densities and also the weights of the molecules compare (oxygen to carbon dioxide to carbon monoxide) as the figures 1.43 to 1.98 to 1.26. The standard molecular weight is that of oxygen, with the figure 32 selected to represent it. To find the molecular weight of carbon dioxide a simple ratio is used.

$$\frac{\text{Oxygen}}{\text{Carbon dioxide}} = \overset{\text{densities}}{\frac{1.43}{1.98}} = \overset{\text{molecular weights}}{\frac{32}{x}}$$

$$\text{Molecular weight carbon dioxide} = \frac{1.98 \times 32}{1.43}, \text{ or } 44$$

In the case of carbon monoxide,

$$\frac{\text{Oxygen}}{\text{Carbon monoxide}} = \frac{1.43}{1.26} = \frac{32}{x}$$

$$\text{Molecular weight of carbon monoxide} = \frac{1.26 \times 32}{1.43}, \text{ or } 28$$

Since 27.27 per cent of carbon dioxide is carbon, then

$$0.2727 \times 44,$$

or 12 parts by weight of carbon dioxide's 44 is due to carbon.

Also, 42.86 per cent of carbon monoxide is carbon. Therefore,

$$0.4286 \times 28,$$

or 12 parts by weight of carbon monoxide's 28 is due to carbon.

The smallest part of the molecular weight due to an element in any of its compounds is selected as the atomic weight of that element. In all compounds of carbon, at least 12 parts by weight are due to carbon. No less a number has been found. Twelve is therefore accepted as the atomic weight of carbon.

22.4 Liters at STP. Let us find out what volume of oxygen gas will be needed to obtain a quantity that will represent its molecular weight in grams, or 32 g. One liter of oxygen weighs about 1.43 g. The volume that is needed to make up 32 g, 1.43 g for each liter, will be found by dividing 32 by 1.43. The answer is 22.4 liters.

Nitrogen has a molecular weight of 28. One liter of the gas weighs 1.25 g. $28/1.25 = 22.4$ liters, the volume that is required to include a molecular weight in grams of nitrogen.

Methane gas, a compound, has a molecular weight of 16. Its density is 0.72 g per liter. $16/0.72 \risingdotseq 22.2$ liters, approximately 22.4 liters.

In a similar manner, other gases give the same approximate answer; that is, ***22.4 liters at standard conditions of any gas is the volume that holds the molecular weight in grams.*** In general,

$$\frac{\text{Molecular weight (g)}}{\text{Density (g/liter)}} = 22.4 \text{ (liters)}$$

If we clear fractions by "cross-multiplying," this expression becomes

$$\boxed{\text{Molecular weight} = 22.4 \times \text{density}}$$

Here is a simple way to find the molecular weight of a gas: Weigh a given volume (find the density), and then calculate the weight of 22.4 liters. The molecular weight of any gas is the number that represents the weight in grams of 22.4 liters of the gas. We have emphasized the fact that atomic weights are relative weights; this is also true of molecular weights; no unit, such as a gram, is expressed or meant.

Another Method of Finding Atomic Weights. The atomic weight of nitrogen might be found this way. A liter weighs 1.25 g; 22.4 liters weighs (22.4 × 1.25) 28.0 g. We have shown that each molecule of nitrogen, like the molecule of oxygen, has two atoms. If the molecular weight is 28, then the atomic weight (weight representing one atom) is $^{28}\!/_{2} = 14$. The formula of nitrogen, thus, is N_2.

SUGGESTION: In considering the new ideas of atoms, their relationship to the molecule, and their atomic weights, we should not assume that we have completed our discussion. If the molecule is represented as a bunch of grapes, then the atom will be represented as a single grape, for that is the smallest unit that is like another. Each single grape is a complex structure in itself, having skin, pulp, and seeds. We may think of the atom in this way, a fundamental unit, but one that can be investigated in more detail later.

SUMMARY

Statement of Avogadro's principle. Equal volumes of gases at the same temperature and pressure have the same number of molecules; that is, the number of molecules is proportional to the volume of a gas.

Avogadro's principle was based on the following laws about gases: Boyle's law, Charles's law, Gay-Lussac's law of combining volumes. The statement of the law of combining volumes is as follows: ***the volumes of gases used or produced in a chemical change have the ratio of small whole numbers.***

Dalton's Atomic Theory.

1. Matter is composed of atoms. Each atom is the smallest part of a molecule, and every molecule contains one or more atoms.
2. All atoms of the same element are alike in weight and properties.
3. Atoms of one element differ from atoms of another element.
4. Compounds are formed by the combination of atoms.

The atomic theory explains (1) the law of definite composition (each compound has a definite composition by weight) and (2) the law of multiple proportions (if two or more compounds are made of the same two elements and the weights of one of the elements are represented by one part, then the weights of the second element are related as a simple fraction).

Certain conclusions follow if Avogadro's principle is true. Among them are the following:

(1) Molecules of hydrogen, oxygen, nitrogen, and chlorine have two atoms. Hence we represent them as H_2, O_2, N_2, and Cl_2, respectively.

(2) Molecular weights may be determined by comparing densities of gases. For this work the oxygen molecule at 32 is standard.

(3) The gram-molecular weight of any gas at standard conditions occupies 22.4 liters. The expression

$$\frac{\text{Molecular weight (g)}}{\text{Density (g/liter)}} = 22.4 \text{ (liters)}$$

summarizes this statement.

Atomic weights were determined by chemical methods by Berzelius, Stas, Richards, and many others. More recent determinations by physical methods have been carried out by Aston and others.

The smallest part of a molecular weight of a compound due to a single element is its atomic weight. The standard of atomic weights is the oxygen atom taken as 16. Ninety-two different natural elements are known.

QUESTIONS

NOTE: Assume all gases measured at standard conditions of temperature and pressure.

1. State Avogadro's principle.

2. How does the number of molecules in $\left\{\begin{matrix}5\\7\end{matrix}\right.$ liters of oxygen at standard conditions compare with the number of molecules in $\left\{\begin{matrix}2\\3\end{matrix}\right.$ liters of nitrogen?

3. When $\left\{\begin{matrix}50\\75\end{matrix}\right.$ liters of hydrogen burns, how many liters of oxygen are used? What is the ratio between the volume of hydrogen and the volume of oxygen?

4. Name and state the law illustrated in question 3.

5. How many cubic feet of hydrogen will combine with $\left\{\begin{matrix}15\\24\end{matrix}\right.$ cubic feet of nitrogen? What volume of ammonia is formed? Assume complete reaction.

6. When hydrogen chloride is formed, what volume ratio exists between its elements?

7. Distinguish a molecule of an element from a molecule of a compound.

8. Define *atom.*

9. What is the original (Greek) meaning of the word *atom?*

10. Name two theories that are firmly established, and name one that has been rejected.

11. What is the percentage composition of water by weight?

12. State the law illustrated in the answer to question 11.

13. Sulfur dioxide is 50 per cent sulfur and 50 per cent oxygen. Sulfur trioxide is 40 per cent sulfur and 60 per cent oxygen. Show that this is a case of multiple proportions.

14. Show that the three compounds in the following group illustrate the law of multiple proportions:

	Percentage nitrogen	Percentage oxygen
Nitrous oxide	63.6	36.4
Nitric oxide	46.7	53.3
Nitrogen dioxide	30.5	69.5

15. State the law of multiple proportions.

16. Using the synthesis of hydrogen chloride from its elements, prove that
a. The hydrogen molecule has two atoms.
b. The chlorine molecule has two atoms.

17. Using the synthesis of ammonia from its elements, prove that the nitrogen molecule has two atoms.

18. The atomic weight of magnesium is 24. How does the weight of a magnesium atom compare with the weight of (*a*) an oxygen atom; (*b*) an oxygen molecule?

19. What was the percentage of error in Berzelius's determination of the atomic weight of sulfur?

20. Sulfur dioxide has a molecular weight of 64 and a density of 2.93 grams per liter. What volume does a gram-molecular weight of this gas occupy at standard conditions?

21. Acetylene (C_2H_2) has a molecular weight of 26 and a density of 1.17 grams per liter. What volume does a gram-molecular weight of this gas occupy at standard conditions?

22. Find the density in grams per liter of a gas that has a molecular weight of (*a*) 17; (*b*) 2; (*c*) 44; (*d*) 160.

23. What are the molecular weights of gases having the following densities in grams per liter: (*a*) 1.43; (*b*) 1.98; (*c*) 0.178; (*d*) 5.45?

MORE CHALLENGING QUESTIONS

24. Two oxides of lead have percentages of oxygen of 7.18 and 13.4, respectively. Show that these two oxides illustrate the law of multiple proportions.

25. Complete this table (*do not write in this book*):

Molecular weight, g	Density, g/liter	Molecular volume, liters
2	0.09	?
28	?	22.4
?	3.2	22.4
58	?	22.4

UNIT TWO . . . . CHAPTER IX

SHORTHAND AND TRANSCRIPTION —WRITING AND NAMING FORMULAS

In the writings of the alchemists many mysterious signs and figures were used. The records of these "fire philosophers" were designed to confuse outsiders and to keep secret whatever discoveries had been made. In those days few people could read or write. For this reason the inn, cobbler's shop, or tavern would be known by a symbol, such as a white horse, rather than a printed sign. Some of the symbols used by the alchemists were so common that even today we are able to decipher them and thus understand the meaning of parts of their writings. For example, the symbols for the metals became associated with the heavenly bodies: ☽ (luna, the moon) was the symbol for silver; ☉ (sol, the sun), was the symbol for gold; ♀ (Venus), copper; ♂ (Mars), iron; ♃ (Jupiter), tin; ♄ (Saturn), lead; and ☿ (Mercury), quicksilver. These signs can be found in some almanacs of the present day.

While the alchemists used symbols to keep their discoveries secret, modern chemists use symbols to understand one another. Another important reason for the use of symbols in chemistry is that time is saved. If we were required to write down information in which the word oxygen occurred often, we should soon begin to write O, an abbreviation, to represent the word. But chemical symbols are more than abbreviations. One of their great advantages lies in the fact that they express so much in so small a space.

Many false starts were made in selecting chemical symbols. John Dalton made little pictures to represent the atoms about which he built his theory. A circle with a cross in it stood for sulfur; a large black dot stood for carbon; and, equally sensibly, a large O stood for oxygen. (See Fig. 9-1.) Lavoisier used symbols that resembled those of the alchemists. The modern symbols were introduced by the great organizer, Berzelius.

New Terms

symbol
formula
radical
combining number
percentage composition

Chemical Symbols of Today. In the modern system of representing elements the first letter of the name of the element is used as its symbol.

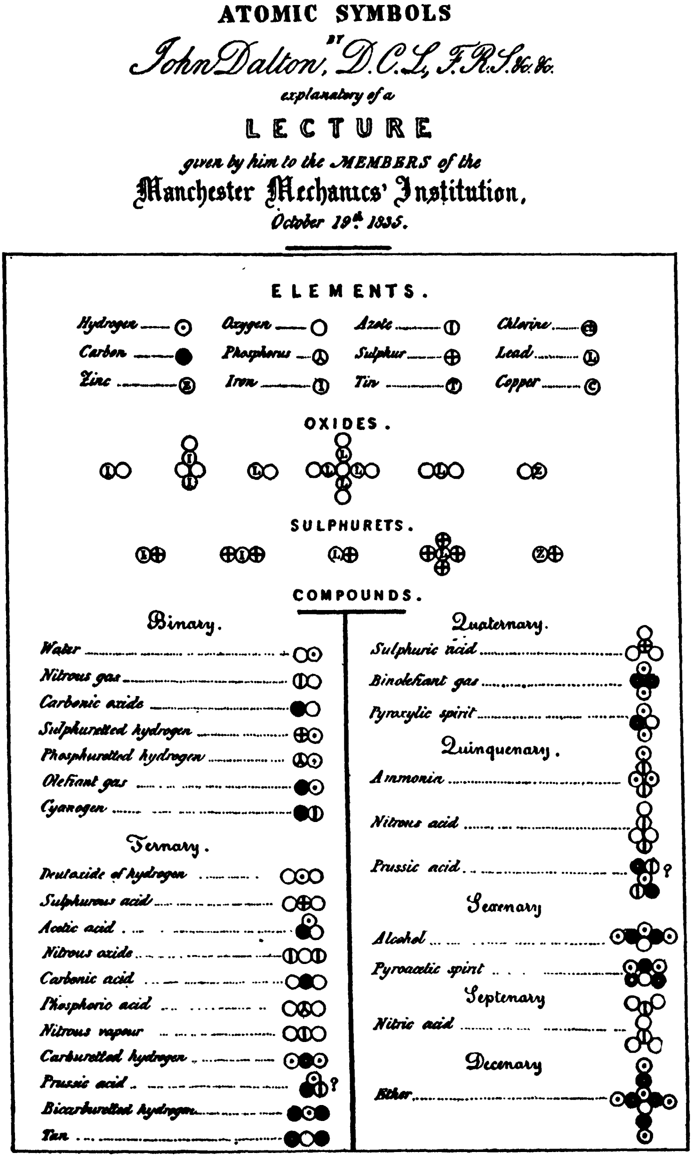


FIG. 9-1.—John Dalton's atomic symbols and his representation of certain compounds.

O is the symbol for oxygen, H for hydrogen, and N for nitrogen. Where the names of two or more elements begin with the same first letter, two letters are used for all but one: C is the symbol for carbon; Ca, that for calcium;

Cd, that for cadmium; Cr, that for chromium. Notice that the first letter only is capitalized.

It should be remembered that English is not the only language which has contributed names for elements. It is not surprising to find that Na is the symbol for sodium (Latin *natrium*) and K for potassium (*kalium*). Some elements were known in ancient times, and these have symbols from the names by which they were known in ancient Rome. The symbol Fe for iron is from the Latin *ferrum*. The symbol Cu for copper comes from *cuprum*, and Pb for lead comes from *plumbum*.

The list of elements and their symbols included at the end of the book need not be memorized. It is convenient, however, to know a few of the most important symbols.

The Full Meaning of a Symbol. Symbols are abbreviations for elements, but the entire meaning of a symbol includes (1) one atom of that element and (2) one atomic weight of the element expressed in grams. The symbol O stands for one atom of oxygen and 16 g of oxygen (a gram-atomic weight). Zn means, not only one atom of zinc, but 65 g of zinc.

Chemical Formulas. A symbol represents an atom; a formula stands for a molecule. If a molecule has only one atom, the symbol and the formula are the same. In most cases, however, this is not so. Molecules that contain two atoms of the same element have a small 2 written below the line, following the symbol for the element. The formula O_2 means one molecule of oxygen, two atoms in the molecule. In like manner another number of the same atoms may be written. The formula O_3 represents one molecule of ozone, a variety of oxygen, and shows that the molecule contains three atoms of oxygen.

Formulas for compounds contain the symbols for the several different elements joined chemically in the compound. The symbols are written side by side.

Where more than one atom of an element is contained in the compound, a subscript number is placed following the symbol to designate the number of atoms of that element in the compound. As everyone knows, H_2O is a formula for water. The entire meaning of H_2O, as everyone may not know, is (1) one molecule of water; (2) two atoms of hydrogen and one atom of oxygen; (3) two gram-atomic weights of hydrogen ($2 \times 1 = 2$) and one gram-atomic weight of oxygen (16); (4) $2 + 16 = 18$ grams of water. This last figure, 18, the sum of the weights of all the atoms in the molecule, is called the gram-molecular weight, or the gram-formula weight.

Sometimes parentheses are used in formulas. The number outside the parentheses is a multiplier and indicates the number of times that all atoms in the parentheses are to be taken. $(C_2H_5)_2O$ represents one molecule of ether. The ***molecular weight*** of this formula can be figured as out follows:

Carbon	$2 \times 2 =$	4 atoms	$4 \times 12 =$	48 parts by weight
Hydrogen	$2 \times 5 =$	10 atoms	$10 \times 1 =$	10 parts by weight
Oxygen	$1 \times 1 =$	1 atom	$1 \times 16 =$	16 parts by weight
			One molecule of ether $=$	74 parts by weight

The gram-molecular weight of ether is 74 g.

If in a formula a symbol has no subscript number, the number 1 is understood. The formula HCl for hydrogen chloride tells that one atom of each element is present in the molecule. Also, 1 is understood before the entire formula, meaning one molecule of the substance. If we wish to represent some other number of molecules, that number appears before the formula. Three molecules of hydrogen chloride are represented by 3HCl. If we write $5NH_3$, we mean five molecules of ammonia containing a total of five atoms of nitrogen and 15 atoms of hydrogen.

Formulas do not tell how a compound is made. The formula for table sugar is $C_{12}H_{22}O_{11}$. This does not mean that 12 atomic weights of carbon ***mixed*** with 22 atomic weights of hydrogen and 11 of oxygen together with the necessary energy will produce sugar. In some instances the elements can be combined in this way, but in the case of sugar they cannot. In fact, there is no way of telling from the formula alone how the compound may be made. The methods of making compounds are a separate problem.

Chemical formulas for compounds and elements differ from recipes. We can find in the proper books the recipes, commonly called the "formulas," for iron rust remover, photographic developing solution, and other useful mixtures. These, of course, are not formulas in the sense in which the word is used in chemistry texts. In both senses, formulas tell "what's in it and how much."

Developing a Formula. Like candidates being initiated into the mysteries of a secret order, we have received instruction in the meaning of our symbols and signs. We are now to learn how the correct formulas came into existence, formulas that are not several meaningless letters and figures put together. These chemical formulas represent the composition of substances as created by nature (or synthetically), and they are true to nature to the letter. To find a formula we turn to the place where nature answers our questions, the laboratory.

From laboratory experiments we can find the percentage composition of compounds. For example, ordinary water contains 11.19 per cent of hydrogen and 88.81 per cent of oxygen. From these facts finding the formula of water would be an easy matter if hydrogen and oxygen atoms were of equal weight. Then about one part of hydrogen would go with eight parts of oxygen, and we should write H_1O_8. But, if we think back to our discussion of weights of atoms, we shall recall that the atomic weights of the two elements are different. An oxygen atom is sixteen times heavier than a hydrogen atom. If we divide the numbers of atoms in H_1O_8 by their respective atomic weights, we get $H_{1/1}O_{8/16}$ or $H_1O_{1/2}$. In order to avoid the impossible one-half atom, we multiply by 2 and write H_2O.

A good way to understand the mathematics of percentages is to consider an example from school life. Helen has the following grades for her senior work: English 80, French 60, chemistry 90, trigonometry 80, art 90. The first four are regular full-time subjects, studied once each day for a full period; art, an extra subject, is studied twice a week. Art counts as one credit, and the others count four credits each. In finding Helen's final average we multiply the grades in each subject by its number of credits, or weights, to obtain the total number of points on which to base her average.

80 × 4 = 320	17)1330(78.2	Final average of all subjects
60 × 4 = 240	119	
90 × 4 = 360	140	
80 × 4 = 320	136	
90 × 1 = 90	40	
Sum 17 = 1330	34	

In this case it would be unfair obviously to omit the grade in art, for the 90 raises her average. Likewise, it would be equally unfair to count the grade in art on the same basis with her other subjects. As we figured the average, the art grade counts one-fourth that of any other subject, just what it is worth on the basis of the credits allowed.

In chemistry we deal with elements, not subjects, with different weights, not credits. Sometimes we are given only the percentages, not the final average, and are told to figure back to the value for each element. In reversing the process we divide the percentages by the atomic weights of the respective elements, rather than multiplying as was done in finding the school average.

Below is given a table that we shall use to find the formula for water:

Elements of water	Percentage composition	Atomic weight of elements	Quotients	Ratio of quotients
Hydrogen..................	11.19	÷ 1 =	11.19	2
Oxygen....................	88.81	÷ 16 =	5.55	1

The numbers 11.19 and 5.55, if both are divided by the smaller, have the ratio of approximately 2 to 1.[1] The ***simplest formula*** for water is

---

[1] If the accurate atomic weight for hydrogen (1.008) is used, the ratio will come

therefore H_2O. Of course, H_4O_2, H_6O_3, and so forth, are equally correct from the figures given. In many compounds the simplest formula is also the correct one.

Another illustration will again show how the formula is obtained from laboratory figures. Some white crystals are found to contain 32.37 per cent of sodium, 22.58 per cent of sulfur, and 45.05 per cent of oxygen. The simplest formula is to be found.

Elements in compound	Percentage composition	Atomic weight of elements	Quotients	Simplest ratio of quotients
Na	32.37 ÷	23 =	1.41	2
S	22.58 ÷	32 =	0.705	1
O	45.05 ÷	16 =	2.81	4

From the table above the simplest formula $Na_2S_1O_4$, or, better, Na_2SO_4 is obtained.

The method of obtaining a simple formula illustrated by these examples is that of first finding in the laboratory the percentage weight due to each element, then dividing these figures by the atomic weights of the respective elements. The final answer, expressed as a simple ratio, is the relative number of atoms of the elements in the compound. If no simple ratio is evident when the quotients are divided by the smallest, divide by one-half, one-third, etc., of the smallest quotient.

How to Derive Formula Weights from Formulas. If we know the formula for a substance, it is possible to find the formula weight. Since the formula weight is the sum of the weights representing all the atoms in the compound, the process is one mainly of addition. The formula weight of salt (NaCl) is 23 + 35.5, or 58.5. For the second example let us turn back to the illustration of finding the molecular weight of ether (page 156).

Here is another illustration, one of the most complicated that we shall meet. Beef suet (hard fat) is chiefly stearin $[C_3H_5(C_{18}H_{35}O_2)_3]$. Let us find the formula weight of this substance.

The weight of the part in the parentheses is found first, then multiplied by 3 and added to the rest.

$$\begin{array}{lrcr}
\text{(C)} & 18 \times 12 = & 216 & \\
\text{(H)} & 35 \times 1 = & 35 & \\
\text{(O)} & 2 \times 16 = & \underline{32} & \\
 & & 283 \times 3 = & 849 \\
\text{(C)} & 3 \times 12 = & & 36 \\
\text{(H)} & 5 \times 1 = & & \underline{5} \\
 & & & 890 \text{ formula weight}
\end{array}$$

---

out more closely 2 to 1. In all examples the approximate figures will be given to center the attention on the idea rather than on the arithmetic.

Percentage Composition from the Formula. If we know the value of each part and the value of the whole, then we can find the relationship each part bears to the whole. This process is the familiar one of finding the percentage one quantity is of another. The percentage is equal to

$$\text{The part} \times 100 \div \text{the whole}$$

To find the ***percentage composition*** (percentage of each element in the compound) of potassium nitrate (saltpeter) (KNO_3), the formula weight is first found.

$$\begin{array}{lll} (K) & 1 \times 39 = & 39 \\ (N) & 1 \times 14 = & 14 \\ (O) & 3 \times 16 = & \underline{48} \\ & & 101 \text{ formula weight} \end{array}$$

$$\boxed{\frac{\text{Part} \times 100}{\text{Whole}} \quad \text{is the way to find the percentage.}}$$

The percentage of potassium in potassium nitrate is

$$39 \times 100 \div 101 = 38.6\ \%$$

The percentage of nitrogen in potassium nitrate is

$$14 \times 100 \div 101 = 13.9\ \%$$

The percentage of oxygen in potassium nitrate is

$$48 \times 100 \div 101 = 47.5\ \%$$

The sum of the percentages found should equal 100 per cent. This check on the arithmetic does not tell whether the formula weight is correct or not. Usually such calculations are sufficiently accurate if expressed to the nearest tenth of 1 per cent.

Sometimes we wish to calculate the percentage of a part or group in a formula. An illustration is the answer to the question, "What is the percentage of water in the gypsum ($CaSO_4 \cdot 2H_2O$)?"

$$\begin{array}{ll} \text{Formula weight} & 40 + 32 + (4 \times 16) + 2 \times (2 + 16) \\ & 40 + 32 + \quad 64 \quad + \quad 36 \quad = 172 \end{array}$$

The water is represented by 36 parts of the 172. The percentage of water in gypsum is

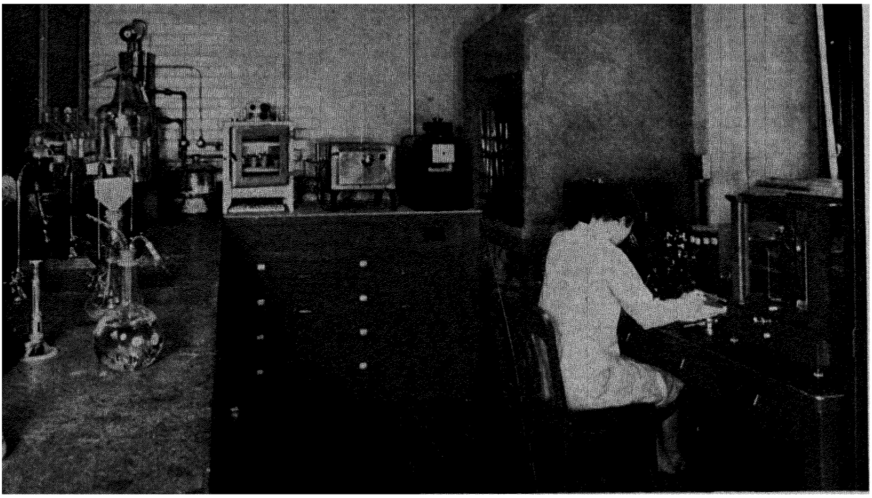
$$36 \times 100 \div 172 = 20.9\% \qquad \textit{Ans.}$$

Let us carefully note that the formula weight of the entire substance is first found, not merely the weight representing the $CaSO_4$, for this, of course, has no water in it.

Method of Finding the True Molecular Formula. The true ***molecular formula*** of a compound is not necessarily the simplest formula.

The molecular formula can be found if the molecular weight and percentage composition are both known.

The molecular weight of methyl chloride gas is found in the laboratory to be 50.5. Analysis of the compound shows 23.8 per cent of carbon, 5.9 per cent of hydrogen, and 70.3 per cent of chlorine. Find the correct formula. Of the total molecular weight, 50.5,



Courtesy of National Archives

FIG. 9-2.—The chemical laboratory of the National Archives in Washington, D.C., is concerned, among other things, with the preservation of documents. Here, as in all chemical laboratories, symbols, formulas, and equations are all a part of the day's work.

23.8 per cent is carbon, or 12 parts; *one* atomic weight (12) of C
5.9 per cent is hydrogen, or 3 parts; *three* atomic weights (1) of H
70.3 per cent is chlorine, or 35.5 parts; *one* atomic weight (35.5) of Cl

The correct molecular formula for methyl chloride is therefore, CH_3Cl.

How Is the Simplest Formula Related to the Molecular Formula? Ethylene gas has been used since 1926 as one means of changing the color of oranges and other fruits to make their appearance more attractive. Of this gas 85.7 per cent is carbon, and 14.3 per cent hydrogen. One liter of the gas weighs 1.26 g. What is the correct formula?

Elements in compound	Percentage composition		Atomic weight of elements		Quotients	Ratio
C	85.7	÷	12	=	7.1	1
H	14.3	÷	1	=	14.3	2

The simplest formula for the compound is then CH_2. If the formula is CH_2, the formula weight of the compound is 12 + 2, or 14.

The molecular weight of any gas is the weight in grams of 22.4 liters of that gas at standard conditions. One liter of ethylene weighs 1.26 g. The weight of 22.4 liters (22.4×1.26) is 28.6 g, the true molecular weight. This answer is about twice 14. This shows that the true molecular formula has twice the weight of the simplest formula and that the true formula is $2 \times CH_2$, or C_2H_4. This molecular formula is the one accepted for ethylene, and the compound has a molecular weight of 28.

In general, the way to tell whether or not the simplest formula is also the molecular formula is to compare the weight found by adding the weights of the elements in the simplest formula with the molecular weight found experimentally by measuring the density or by some other means.

When the formula weight of the simplest formula is the same as the molecular weight found experimentally, then the simplest formula is the correct molecular formula. Chemists have not always known how to find correct formulas, nor have the figures from the experiments always been accurate enough to give good results. This was particularly true in the early days of chemistry. John Dalton's notebook shows that he considered water to be composed of one atom each of hydrogen and oxygen, for he represents the formula for water as ⊙O (HO).

QUESTIONS

1. What element is represented by each of the following symbols: C, Cl, Cu, Zn, W, P, S, Na, K, A?

2. Tell the full meaning of each of these symbols: Fe, Ca, Sn, Mg, N.

3. What is the complete meaning of each of the following formulas: SO_2, CH_4, P_4S_3, N_2O, CHI_3?

4. (*a*) How many different kinds of atoms are represented in the following formulas and (*b*) what is the total number of atoms represented by each formula: HNO_3; $Ca(C_2H_3O_2)_2$; $C_{17}H_{35}COONa$; H_2O_2; $Fe_3[Fe(CN)_6]_2$?

5. What is the simplest formula of a compound that is composed of 40 per cent calcium, 12 per cent carbon, 48 per cent oxygen?

6. Chemical analysis shows that a certain compound contains 67 per cent zinc and the rest oxygen. What is the simplest formula of this oxide?

7. An oxide of carbon contains $\left\{\begin{matrix}27.3\\42.9\end{matrix}\right.$ per cent carbon. What is its simplest formula?

8. A compound is composed of 90.9 per cent carbon and 9.09 per cent hydrogen. Find its simplest formula.

9. A professor, with a twinkle in his eye, likes to tease his class with this one: "An inventor in New York claims to have discovered a green fluid that when added to water, 1 teaspoonful to a gallon, produces a motor fuel equivalent to high-test gasoline. We have analyzed the compound and find that it contains 3.6 per cent boron, 78.9 per cent uranium, 4.6 per cent nitrogen, 12.9 per cent potassium." What is the formula of this compound?

10. Find the formula weight of (*a*) pearls ($CaCO_3$); (*b*) zinc white (ZnO); (*c*) milk of magnesia ($Mg(OH)_2$); (*d*) silver tarnish (Ag_2S); (*e*) Prussian blue $\{Fe_4[Fe(CN)_6]_3\}$; (*f*) soft soap ($C_{17}H_{35}COOK$).

11. Find the percentage composition of the $\left\{\begin{matrix}\text{odd}\\ \text{even}\end{matrix}\right.$-numbered compounds in question 10.

12. Find the percentage of water in
a. Plaster of Paris [$2(CaSO_4)\cdot1(H_2O)$]
b. Blue vitriol ($CuSO_4\cdot5H_2O$)
c. Washing soda ($Na_2CO_3\cdot10H_2O$)

13. The simplest formula of a compound has a formula weight of 13. The true molecular weight is $\left\{\begin{matrix}26\\ 78\end{matrix}\right.$. How many times should the simplest formula be multiplied to give the molecular formula?

14. From experiments we find that ethyl alcohol has a molecular weight of 46. It is composed of 52.2 per cent carbon, 13.0 per cent hydrogen, and 34.8 per cent oxygen. Find its molecular formula.

15. Hydrogen peroxide consists of 5.9 per cent H and 94.1 per cent O. Its true molecular weight is 34. Find the molecular formula.

16. Hydrogen fluoride gas of a certain sort is composed of 5 per cent hydrogen and 95 per cent fluorine. Its density is 5.4 grams per liter. Find the molecular formula.

17. Cyanogen gas, 2.34 grams per liter, is composed of 46.1 per cent C and 53.9 per cent N. Find its molecular formula.

18. Chloroform (mol. wt. 119.5) consists of 10.05 per cent C, 0.83 per cent H, and 89.12 per cent Cl. Find its molecular formula.

19. What is the percentage composition of Freon (CF_2Cl_2)?

Radicals. In politics the word "radical" has a far different meaning from the sense in which the word is used in chemistry. A ***radical*** is a small group of chemical elements that keeps its identity in many reactions. A radical is a sort of synthetic element. These groups act as a whole in many chemical changes, although a radical may be altered in more drastic chemical changes. Such groups are sulfate ($-SO_4$), hydroxide, ($-OH$), ammonium (NH_4-), nitrate, ($-NO_3$), carbonate, ($-CO_3$), and many others. Each group is a part of a compound, but each acts as if it were a single element. Vinegar contains the acetate radical, $-C_2H_3O_2$. Radicals are not at all uncommon in substances.

Compared with words, radicals are like syllables such as ***-ing, pre-,*** or ***-tion,*** which alone have no meaning but often are found as part of a word. Radicals are found as parts of compounds.

Combining Number (Valence). Let us carefully examine the formulas of these compounds:

I		II	
HCl	Hydrogen chloride	$NaCl$	Sodium chloride
H_2O	Dihydrogen oxide (water)	$CaCl_2$	Calcium chloride
H_3N	Hydrogen nitride (ammonia)	$AlCl_3$	Aluminum chloride
H_4C	Hydrogen carbide (methane)	$SnCl_4$	Tin chloride

We notice that in column I all the substances are compounds of hydrogen and that the number of hydrogen atoms in each compound is different. Chlorine has the ability to hold one hydrogen atom in a compound; oxygen, two; nitrogen, three. In methane, carbon holds four hydrogen atoms. The numbers of hydrogen atoms that an element can hold in a compound is called its ***combining number*** (often called valence number). Chlorine has a combining number of 1; oxygen, of 2; and so on. What is the combining number of phosphorus if the formula for phosphine is PH_3?

In column II all the substances are compounds of chlorine. What was said about hydrogen in the preceding paragraph can be repeated about chlorine. The combining number of any element is that number of chlorine atoms which an element can hold in a compound. From column II calcium has a combining number of 2 and aluminum has a combining number of 3. What is the combining number of carbon if its chloride has the formula CCl_4?

In addition to elements, we must also consider radicals that act as if they were elements. From the formula H_2SO_4 we see that the combining number of the radical $-SO_4$ is 2, because it holds two hydrogen atoms. NH_4Cl shows that the combining number of the ammonium radical (NH_4-) is 1, for it holds one atom of chlorine in a compound. Both these radicals happen to contain the figure 4. The subscript figures in a radical do not tell the combining number. These figures show the number of atoms of the elements that they contain. In the formula H_3PO_4 the 4 tells us that four atoms of oxygen are present. The combining number of the phosphate radical is learned from the fact that the group $-PO_4$ is combined with three hydrogen atoms—a combining number of 3.

By definition, a combining number is ***the number of hydrogen or chlorine atoms that an atom of an element or a radical can hold in a compound.***

How to Write Chemical Formulas. In order to write formulas correctly we should have for a start a knowledge of a few correct formulas. If we know these well, it is a simple matter to write the formulas of other compounds. In fact, it is something of a game.

CORRECT FORMULAS

Commit this list to memory.

1. HCl	Hydrogen chloride *(hydrochloric acid)*	9. $NaCl$	Sodium chloride
2. $H\underline{NO_3}$	Hydrogen nitrate *(nitric acid)*	10. $Ag\underline{NO_3}$	Silver nitrate
3. $H\underline{ClO_3}$	Hydrogen chlorate *(chloric acid)*	11. $K\underline{ClO_3}$	Potassium chlorate
4. H_2S	Hydrogen sulfide *(hydrosulfuric acid)*	12. CuS	Copper sulfide *(cupric)*
5. $H_2\underline{CO_3}$	Hydrogen carbonate *(carbonic acid)*	13. $Ca\underline{CO_3}$	Calcium carbonate
6. $H_2\underline{SO_4}$	Hydrogen sulfate *(sulfuric acid)*	14. $Mg\underline{SO_4}$	Magnesium sulfate
7. $H_3\underline{PO_4}$	Hydrogen phosphate *(phosphoric acid)*	15. $Al\underline{PO_4}$	Aluminum phosphate
8. $H\underline{OH}$ or H_2O	Hydrogen hydroxide Hydrogen oxide *(water)*	16. $\underline{NH_4}\underline{OH}$	Ammonium hydroxide
		17. HgO	Mercury oxide *(mercuric)*

The compounds in the first column are compounds of hydrogen; thus in each compound the combining number of the part not hydrogen can easily be ascertained by inspecting the number of hydrogen atoms present. All the radicals are underlined to aid in selecting them. The combining number of the chlorate radical is 1, for it joins with one hydrogen atom in the formula $HClO_3$. SUGGESTION: Read down the list, finding the combining number of each element or radical present.

The second column contains a list of compounds that can be related to the first column by taking the hydrogen out and putting another element (or radical) in the place of the hydrogen. For example, consider HCl and $NaCl$. The sodium atom in $NaCl$ is in the place of the one hydrogen atom in HCl. Its combining number, therefore, is 1. Also, the fact that the atom of sodium is found combined with one chlorine atom shows that its combining number must be 1. Continuing this procedure, we find that the combining number of Mg is 2; of Al, 3.

For practice, find the combining number of the first part of each formula in the second column. The combining number of the second part of each formula in the second column is the same as it is in the first column.

Experience has shown that, if this list (quite short if we except those formulas which are already known) is memorized perfectly, no trouble will be encountered in writing correct formulas.

The formula for ammonium hydroxide is interesting, for this compound is composed of two radicals.

The order of writing elements of radicals in a compound is chiefly a matter of custom. Usually the metal element, hydrogen, or the radical NH_4- is placed first. A table of combining numbers of those elements or radicals which are placed first in compounds is valuable.

Combining number	1	2	3
	H Ag Na K NH_4-	Most metals	Al Sometimes Fe

A way of showing how atoms are put together in compounds is to suppose that each element has a number of links, or bonds, equal to its combining number. An element of combining number 1 has one link; of combining number 2, two; and so on. In ordinary compounds these links are always connected, never dangling or unsatisfied. The formulas of several compounds are shown pictured in this way.

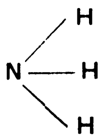
Hydrogen chloride (HCl)

$$H—Cl$$

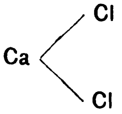
Water (H_2O)

$$H—O—H$$

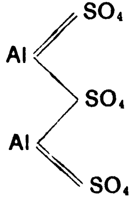
Ammonia (NH_3)



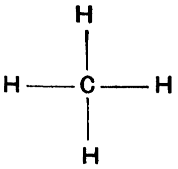
Calcium chloride ($CaCl_2$)



Aluminum sulfate [$Al_2(SO_4)_3$]



Methane (CH_4)



$$H—\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—H$$

One of the most stimulating discoveries in modern chemistry is the knowledge of the nature of the linking of the atoms in a compound. We can now explain the combining number of 2 for calcium and 1 for hydrogen. Finding the explanation of combining numbers is a real adventure into the nature of matter and its structure, a search into the very foundation stones of the universe. A later chapter will carry this hunt further.

How is the correct formula for sodium carbonate written? Sodium has a combining number of 1; the carbonate radical, of 2 [see carbonic acid (H_2CO_3) in table, page 164]. The skeleton is Na CO_3. A "one" element like sodium will have to be taken twice to furnish the two links to join to a "two" radical, carbonate. Na_2CO_3 is the right formula.

What is the formula for calcium oxide (lime)? The combining number of calcium is 2 (table, page 164), as is that of oxygen. The two imaginary links on each element will just match, and they will satisfy each other, nothing remaining. One unit of each element will give the formula CaO; Ca_2O_2 might seem to be the correct formula at first, but this is a multiple of the simplest formula, CaO, and unless experimental data give means of obtaining the true formula the simplest formula is always taken.

In order to practice writing formulas for chemical compounds, let us take a large sheet of paper, about twice the size of a page of this book, and write across the top, as follows, the symbols for elements and radicals that are written second in chemical compounds:

<table>
<tr><th></th><th>—Cl
chloride</th><th>—NO_3
nitrate</th><th>—OH
hydroxide</th><th>—S
sulfide</th><th>—O
oxide</th><th>—SO_4
sulfate</th><th>—CO_3
carbonate</th><th>—PO_4
phosphate</th></tr>
<tr><td>Ag—
Na—
K—
NH_4—
Ca—
Mg—
Cu—
Zn—
Hg—
Fe—
(combining number 3)
Al—</td><td colspan="8">Down the left-hand side let us write the symbols for those parts of compounds usually written first, as is done here on the left; then block in all the squares with a ruler, and write the formula in the proper square. For example, the upper left-hand square should contain the formula for silver chloride; the lower right-hand square that for aluminum phosphate. We should be sure to take account of the combining number of each element or radical. No harm will be done in writing a practice formula for ammonium oxide and silver hydroxide, although these two compounds are very unstable.</td></tr>
</table>

We should recall at this point that when the combining numbers are both the same, both parts having the combining number of 1, 2, or 3, no combining (subscript) numbers are necessary in the simplest formula. The number of atoms in a radical is not changed in any of these formulas, but the whole radical is taken the required number of times. Aluminum carbonate, for example, where aluminum has a combining number of 3 and the carbonate radical a combining number of 2, is written $Al_2(CO_3)_3$. In this formula we should notice that (1) the combining number of aluminum is written as the subscript of the carbonate radical and the combining number of the carbonate radical is written as the subscript of aluminum and that (2) the CO_3 radical is written unchanged.

While this practice list contains many of the formulas we shall need, a few more should be mentioned. The name alone suggests the formula in some cases. Carbon dioxide is CO_2; silicon tetrafluoride, SiF_4; phosphorus pentoxide, P_2O_5.

We have proved that the elementary gases, oxygen, nitrogen, chlorine, and hydrogen, have two atoms in each molecule. When ***alone*** and representing the gas, their formulas are written O_2, N_2, Cl_2, and H_2, respectively. In compounds, these elements may have any required subscript numbers as in NH_3 (ammonia).

Elements of More than One Combining Number. Most of the elements are fickle enough to have two or more combining numbers. In carbon monoxide (CO), carbon has the unusual combining number of 2. Usually carbon has the combining number of 4 as in carbon dioxide (CO_2). $FeCl_2$ and $FeCl_3$ are the formulas for two common chlorides of iron, ferrous chloride and ferric chloride. In the former the combining number of iron is 2; in the latter, 3. In such cases the element's lower, combining number is designated by ***-ous;*** the higher, as ***-ic.*** HgCl is mercurous chloride; $HgCl_2$, mercuric chloride. For the beginner a general rule that may be helpful is that with oxygen or its equivalent an element tends to take its higher combining number, while hydrogen or its equivalent with an element favors the formation of compounds of lower combining number. With hydrogen, sulfur forms H_2S, in which the combining number of sulfur is 2. With oxygen, SO_2 is formed, in which the combining number of sulfur is 4. With more oxygen, SO_3 (sulfur trioxide) is formed, in which sulfur has a combining number of 6.

Naming Compounds. After a stenographer has taken her dictation in shorthand, she must transcribe her shorthand symbols. In similar manner chemists write formulas of compounds in symbols but usually call each compound by name. It is convenient to group compounds for the purpose of naming them.

Hydroxides. We name the element or radical and add the word ***hydroxide.*** NaOH (lye) is sodium hydroxide; $Ca(OH)_2$ (limewater) is calcium hydroxide. What is the chemical name of milk of magnesia [$Mg(OH)_2$]? Of caustic potash (KOH)?

Acids. It is customary to represent acids by formulas that start with the element hydrogen. Two-element acids, compounds of hydrogen and one other element, are named ***hydro*** ***ic.*** In the blank space most of the name of the element other than hydrogen is written. HCl is ***hydro***chlor***ic*** acid; H_2S, ***hydro***sulfur***ic***. What is HBr?

Three-element acids—hydrogen, a second element, and oxygen—are named on the basis of the second element present, with the ending ***-ic*** for the most common one. H_2SO_4 is sulfur***ic*** acid; $HClO_3$, chlor***ic*** acid. What is H_3PO_4?

With one oxygen atom fewer, the ending is changed to ***-ous***. H_2SO_3 is sulfur***ous*** acid; $HClO_2$, chlor***ous*** acid. What is H_3PO_3?

With two fewer oxygen atoms, the prefix ***hypo-*** (under) is used with the ***-ous*** ending. H_2SO_2 is ***hypo***sulfur***ous*** acid; HClO, ***hypo***chlor***ous*** acid.

With one oxygen atom more than the common ***-ic*** acid, the prefix ***per-*** is used. $HClO_4$ is ***per***chlor***ic*** acid. HIO_4 is ***per***iod***ic*** acid; H_2SO_5, however, is peroxymono-sulfuric acid, named according to a different system.

Salts. These are crystalline compounds considered to have a metal atom or radical in the place of the hydrogen atom of the acid.

Hydro- ***-ic*** acids form ***-ide*** salts. NaCl is sodium chlor***ide;*** BaS, barium sulf***ide.*** What is KBr?

-ic acids form ***-ate*** salts. Na_2SO_4 is sodium sulf***ate;*** KNO_3, potassium nitr***ate.*** What is $Ca_3(PO_4)_2$?

-ous acids form ***-ite*** salts. Na_2SO_3 is sodium sulf***ite;*** KNO_2, potassium nitr***ite.*** What is NH_4ClO_2?

The ***hypo-*** and ***per-*** prefixes are used as in the names of the acids.

NAMING COMPOUNDS

Acid		Potassium salt		Acid		Calcium salt	
HCl	hydrochloric	KCl	-chloride	H_2S	hydrosulfuric	CaS	-sulfide
HClO	hypochlorous	KClO	-hypochlorite	H_2SO_2	hyposulfurous	$CaSO_2$	-hyposulfite
$HClO_2$	chlorous	$KClO_2$	-chlorite	H_2SO_3	sulfurous	$CaSO_3$	-sulfite
$HClO_3$	chloric	$KClO_3$	-chlorate	H_2SO_4	sulfuric	$CaSO_4$	-sulfate
$HClO_4$	perchloric	$KClO_4$	-perchlorate				

SUMMARY

The purpose of writing chemical symbols and formulas is to save time and to aid understanding. Chemical symbols represent (1) an atom of an element and (2) an atomic weight of the element.

The meaning of the formula of a compound may be illustrated as follows: H_2O means

1. One molecule of water
2. Two atoms of hydrogen and one of oxygen chemically combined

3. Two gram-atomic weights of hydrogen, plus 16 of oxygen
4. 18 g of water, the gram-molecular weight

Formulas are found from percentage composition, determined by laboratory analysis. The formula weight is the sum of the atomic weights of the elements represented by a given formula.

The true molecular formula is found from the simplest formula by comparison of molecular weights.

Radicals are groups of elements that act as a unit in many chemical reactions. An example is the sulfate radical, $-SO_4$. Each element or radical in a chemical compound has a combining number that is used to write formulas of compounds.

Hydrogen and chlorine each have a combining number of 1 and may be considered the unit for comparison of the combining numbers of other elements in simple compounds. Writing correct formulas takes into account the combining number of each element or radical. Elements that have more than one combining number usually show the lowest in combination with hydrogen and the highest in combination with oxygen. Most radicals have just one combining number.

Compounds are named as follows:

Hydroxides—name of metallic element or radical and the word hydroxide

Acids—	binary	**hydro**	**ic**
	ternary, most common	ending	**-ic**
	ternary, with one oxygen atom less than **-ic**	ending	**-ous**
Salts—	of **hydro** **ic** acids	**-ide**	
	of **-ic** acids	**-ate**	
	of **-ous** acids	**-ite**	

QUESTIONS

NOTE: *Do not write any part of these exercises in this book.*

20. (*a*) Name the following radicals: $-SO_4$; $-CO_3$; $-NO_3$; $-OH$; NH_4-; $-PO_4$; $-SO_3$; $-C_2H_3O_2$.

(*b*) What combining number does each exhibit?

21. Represent the following radicals by the use of symbols: sulfate, nitrate, carbonate, phosphate, hydroxide.

22. Write the combining number above each element or radical in the following formulas: HCl, H_2S, AsH_3, NaH, Ca_3P_2, Ag_2O, $CuCl_2$, Li_3N, $Ca(OH)_2$, KNO_3.

23. Correct the following formulas by supplying the needed subscript numbers wherever necessary: $NaCl$, NaS, CaS, $CaCl$, $AlCl$, AlS, ZnS, $MgCl$, MgN, $MgOH$.

24. Correct the following formulas by supplying parentheses where needed: $CaOH_2$; $ZnNO_{3\ 2}$; $AlOH_3$; $Al_2SO_{4\ 3}$; $Ca_3PO_{4\ 2}$.

25. Write formulas for each of the following compounds: silver chloride, sodium nitrate, potassium sulfide, copper carbonate, calcium sulfide, calcium nitrate, magnesium carbonate, magnesium chloride, silver phosphate, sodium phosphate.

26. Underline each radical: $NaOH$, $(NH_4)_2SO_4$, CuO, $Zn_3(PO_4)_2$, K_2CO_3.

27. Name the following: SiO_2, CCl_4, NO_2, SiC, Mg_3N_2.

28. Write formulas for two chlorides of iron, two chlorides of copper, two oxides of copper, two sulfates of iron, and two oxides of sulfur. Name each compound.

29. Name the following: K_2SO_4; $LiClO_3$; $NaNO_3$; $Zn_3(PO_4)_2$; $Al_2(CO_3)_3$
K_2SO_3; $LiCl$; $NaNO_2$; $Zn_3(PO_3)_2$; Al_4C_3

30. Name the following: H_2SO_4; H_2SO_3; H_2S; HCl; $HClO$; $HClO_2$; $HClO_3$; KNO_2; $CaSO_3$; $Fe(NO_3)_2$; $Fe(NO_3)_3$; $KClO_4$.

31. Write formulas for the following (use $Cu = 2$, $Sn = 4$ for combining numbers):

	A	*B*	*C*
1.	Zinc hydroxide	Copper hydroxide	Magnesium hydroxide
2.	Copper chloride	Zinc chloride	Calcium chloride
3.	Hydrosulfuric acid	Chloric acid	Carbonic acid
4.	Potassium sulfate	Potassium sulfide	Potassium nitrate
5.	Aluminum sulfide	Aluminum sulfate	Sodium carbonate
6.	Ammonium chloride	Silver chloride	Silver phosphate
7.	Silver oxide	Ammonium carbonate	Ammonium sulfate
8.	Magnesium phosphate	Calcium phosphate	Copper sulfide
9.	Calcium sulfite	Magnesium nitrate	Zinc sulfite
10.	Dihydrogen oxide	Carbon dioxide	Sulfur dioxide

	D	*E*
1.	Aluminum chloride	Zinc chlorate
2.	Magnesium chlorate	Magnesium chloride
3.	Calcium sulfate	Calcium hydroxide
4.	Ammonium hydroxide	Ammonium phosphate
5.	Sulfur trioxide	Phosphorus pentoxide
6.	Potassium carbonate	Sodium sulfite
7.	Tin chloride	Potassium sulfate
8.	Silver nitrate	Tin nitrate
9.	Aluminum oxide	Silver sulfide
10.	Sodium sulfate	Aluminum carbonate

MORE CHALLENGING QUESTIONS

32. The cyanide radical ($—CN$) has a combining number of 1. Write formulas for sodium, calcium, potassium, silver, and gold cyanides and for the acid from which these salts may be made.

33. Acetate radical ($—C_2H_3O_2$) has a combining number of 1; chromate ($—CrO_4$) of 2; oxalate ($—C_2O_4$) of 2; vanadate ($—VO_4$) of 3. Write the formula for the salts of sodium, potassium, calcium, and aluminum with the acetate, chromate, oxalate, and vanadate radicals, respectively (16 different formulas).

UNIT TWO . . . . CHAPTER X

BALANCED ACCOUNTS—EQUATIONS

Chemical formulas are helpful because they save time. They are helpful also because they aid our understanding. By their use we can visualize the changes that take place in molecules during chemical changes—the chemical changes by which our power is generated, our food grown, and our medicines made. Formulas are useful in representing the composition of compounds. Formulas may be used to represent molecules alone, but more often they are used in ***equations*** to show how compounds have changed.

Chemical and Physical Changes. It is well to review here the distinction between chemical and physical changes. Physical changes studied thus far include boiling, freezing, and evaporating as a result of changing pressure and temperature. In each of these changes no new substance forms, molecules remaining unaltered after the physical change. The chemical formula representing water, steam, and ice is the same, H_2O. Since no changes that alter the composition of the molecule occur during a ***physical change,*** the formula for the molecule in the different states is identical.

On the other hand, a ***chemical change*** involves a change in the composition of molecules. One of the simplest of chemical changes is the joining of atoms to make a compound. Zinc atoms join with sulfur atoms to form zinc sulfide, a compound. Zn represents the metal, S represents the nonmetal, sulfur; the solid formed by their union is represented by ZnS, and it is a salt. Both elements have a combining number of 2. The chemist writes $Zn + S \rightarrow ZnS$, an expression called an ***equation.***

Symbols, Formulas, Equations. In order to understand clearly the meaning of an equation as contrasted with that of a formula, let us remember that an equation shows a chemical change, while a formula represents the composition of a substance.

New Terms

equation	molecular formula	balancing an equation

H_2O is the ***molecular formula*** for water; $2H_2 + O_2 \rightarrow 2H_2O$ is the ***equation*** for the formation of water. The H_2O represents a substance; the $2H_2 + O_2 \rightarrow 2H_2O$ represents a chemical change, or reaction.

The arrow in the equation, →, is read "forms," "produces," "yields," or "gives." The substances written to the left of the arrow, joined by the + sign if more than one is present, are those that enter the change. To the right of the arrow are written the substances formed during the chemical change. These are different substances from those on the left-hand side; otherwise, no chemical change would have taken place. The substances on the right-hand side are joined by a + sign if more than one product is formed.

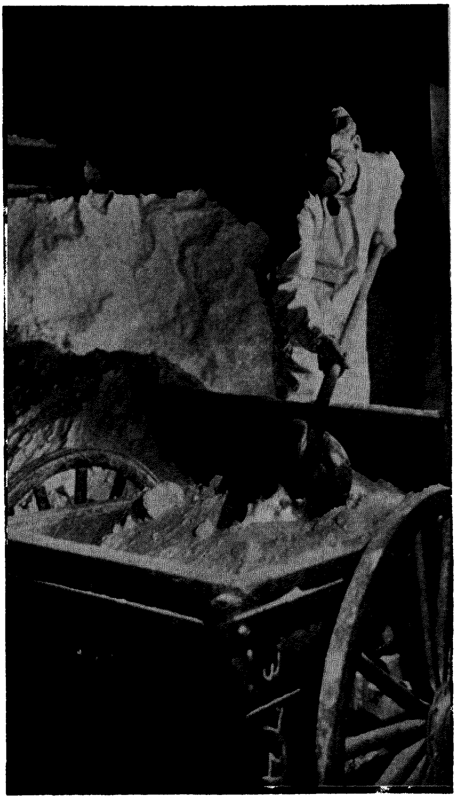
Chemists are interested in the products of a chemical change. Some of the new substances thus formed do not occur naturally. They can be obtained only as a result of the chemist's work in the laboratory. Herein lies a great measure of the charm and fascination of chemistry. We never can foresee all the possibilities of new substances formed by chemical changes.

At the start it should be emphasized that the chemical change comes first and our representation of it in writing second. Each equation represents a change that occurs in the laboratory. Our information comes from experiments. Equations may be written without laboratory experiments having preceded them, but merely to suggest the experiments that may be tried in the laboratory. Otherwise, an equation has no meaning.

We should remember that the arrow is directional. $C + O_2 \rightarrow CO_2$ tells us that an atom of carbon joins with a molecule of oxygen to form a molecule of carbon dioxide. It does ***not*** tell us that carbon dioxide breaks down into carbon and oxygen; that is, $CO_2 \rightarrow C + O_2$ is without meaning unless we know from experience that the compound is one which decomposes. Indeed, carbon dioxide is quite a stable compound, and it does not decompose directly under any ordinary conditions. The "reverse" equation just written is ***incorrect.***

Statement	Example
A symbol represents an atom of an element........	C
A formula (molecular) represents a molecule of a compound or an element..................	CO_2 or O_2
An equation represents a chemical change........	$C + O_2 \rightarrow CO_2$

Limitations of Chemical Equations. We have said that chemical equations are a useful way of representing chemical changes. Their meaning is understood by scientists of all countries, and the changes that they represent can be carried out by anyone who has the proper directions, equipment, and skill. It is obvious, however, that a chemical equation cannot represent all the facts. We often include notes with an equation to tell the details that the equation does not show. The catalyst used, if any, the temperature, and the pressure may be included in notes. We cannot tell, for example, from an equation alone whether or not the reaction occurred in the medium of water or some other liquid, or whether the substances were melted together, acted slowly, or exploded with violence. Notes are also useful in telling whether the reaction required heat to cause it take place or whether it proceeded easily and gave off heat energy.



Courtesy of Corning Glass Works

FIG. 10-1.—Weighed batches of raw materials are used in industrial processes. The sand in the cart is to be used in making glass. Notice how the worker protects himself from dust.

How to Write Equations. Equations involve formulas; therefore, in writing equations it is well to master the writing of correct formulas. An equation that contains an incorrect formula cannot represent a true chemical change.

In writing an equation a list is made of the substances (sometimes there is only one substance) that enter into the chemical change. Correct formulas for these compounds or elements are written down and connected by a + sign. The order is not important. Then an arrow is placed to the right of these formulas. After the arrow are written the formulas, connected by a + sign, of the substances (sometimes there is only one substance) formed in the chemical change. The order of writing these is also not important.

When a chemical change takes place no atom is lost or gained; the ***law of conservation of matter*** is found to apply in all cases. For this reason an equation must be balanced; that is, the same number of atoms of each element must be on both sides of the arrow. ***Balancing*** an equation is the process of counting the atoms of each element on both sides of the arrow and adjusting the number if necessary, so that the number is the same.

Balancing Equations by Inspection. In order to obtain the necessary number of atoms to balance an equation, we may take any number of molecules of any reacting substance, without limit. The formulas themselves, however, must not be altered. An illustration will make the point clear. Ammonia is heated to produce hydrogen and nitrogen; we should first write $NH_3 \rightarrow H_2 + N_2$. In writing the right-hand side of this equation we recalled (page 145) that both nitrogen and hydrogen are typical gases which have two atoms to a molecule; therefore, their correct formulas are H_2 and N_2. Also, NH_3 is the correct formula for ammonia. But, with three atoms of hydrogen in ammonia and two atoms of hydrogen gas produced, one atom of hydrogen is left over. We must have the same number of atoms on both sides of the arrow. The correct adjustment of the equation is to take two molecules of ammonia, which will give the two atoms of nitrogen needed. The number of atoms of hydrogen is thus increased at the same time from three to six, and this will call for adjustments of the hydrogen molecules, namely, to $3H_2$. The equation becomes $2NH_3 \rightarrow 3H_2 + N_2$. It would be incorrect to write NH_2 or N_2H or N_2H_2 for ammonia. This would change the formula into one that is incorrect.

A few more illustrations will be helpful in writing equations.

The decomposition of water by an electric current is represented thus:

$H_2O \rightarrow$	substance entering change
$H_2O \rightarrow H_2 + O_2$	reacting substance and products

The equation is not balanced, for one oxygen atom cannot produce two.

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

The equation is balanced and completed.

Check:

Molecular formula for water	H_2O
Molecular formulas for hydrogen and oxygen	H_2, O_2
Hydrogen atoms on left and right	4
Oxygen atoms on left and right	2

When phosphorus burns it forms an oxide, usually with a higher combining number of 5.

$P + O_2 \rightarrow P_2O_5$	reacting substances and products, all formulas correct
$2P + O_2 \rightarrow P_2O_5$	balancing phosphorus
$2P + 5O_2 \rightarrow 2P_2O_5$	balancing oxygen
$4P + 5O_2 \rightarrow 2P_2O_5$	rebalancing phosphorus

Final check:

Oxygen atoms on left and right	10
Phosphorus atoms on left and right	4

For decomposing potassium chlorate we write

$$KClO_3 \rightarrow KCl + O_2$$

and then balance the equation.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

The equation is balanced.

We do *not* write $KClO_3 \rightarrow KClO + O_2$.

for the products would be incorrectly represented.

Examples of correct equations are

$$2KClO_3 \xrightarrow[\text{MnO}_2\text{, catalyst}]{\text{heated}} 2KCl + 3O_2\uparrow$$

$$2K + 2HOH \rightarrow 2KOH + H_2\uparrow$$

$$2H_2O + 2SO_2 + O_2 \xrightarrow[\text{HNO}_3\text{, catalyst}]{} 2H_2SO_4$$

$$CaCl_2 + 2AgNO_3 \rightarrow 2AgCl\downarrow + Ca(NO_3)_2$$

SUMMARY

A symbol is a letter or group of letters standing for an atom of an element.

A formula is a group of symbols representing the composition of a compound; the simplest formula shows only the relative number of atoms, but the molecular formula also shows the true molecular weight.

An equation is a connected group of formulas representing a chemical change.

In writing equations:

1. Show substances used and substances formed, and connect by an arrow.
2. Balance by adjusting if necessary so that the same number of atoms of each element occurs on both sides of the equation.

Equations:

1. When balanced, show parts by weight of reacting substances and relative volumes of gases taking part in the reaction.

2. Do not show temperature, pressure, catalyst, energy, or any other conditions of the reaction unless especially noted.

QUESTIONS

1. Distinguish between a chemical and a physical change in terms of molecules.

2. Distinguish among a symbol, a formula, and an equation. Give an example of each.

3. What is the symbol for salt? The formula for salt? The equation for salt? (Salt is sodium chloride.)

4. What does an equation show?

5. What does an equation not show?

6. From what source do we get the original information on which to base equations?

7. Point out an error in this equation:

$$CO + O_2 \rightarrow CO_2$$

8. Why should an equation be balanced?

9. Balance the following equations:

$$\begin{aligned} Mg + O_2 &\rightarrow MgO \\ Mg + N_2 &\rightarrow Mg_3N_2 \\ Fe + H_2O &\rightarrow Fe_3O_4 + H_2 \\ Na + H_2O &\rightarrow NaOH + H_2 \\ N_2 + O_2 &\rightarrow NO \end{aligned}$$

10. When zinc is heated intensely in air, it burns, forming a white powder. (Burning in this case obviously means ordinary burning or combining with oxygen.) Write an equation to represent the burning of zinc.

11. Complete and balance the following equations, using formulas throughout (*Do not write in this book.*)

a. Potassium + oxygen →
b. Nitrogen + oxygen → nitrogen dioxide
c. Carbon + oxygen →
d. Copper + oxygen →
e. Lead + oxygen →

12. Complete and balance, using formulas:

a. Copper + chlorine →
b. Zinc + chlorine →
c. Sodium + chlorine →
d. Lead + chlorine →
e. Mercury + chlorine →

13. Complete and balance, using formulas (assume that phosphorus takes combining number $\begin{cases}3\\5\end{cases}$ in each case):

a. Phosphorus + chlorine →
b. Phosphorus + oxygen →
c. Calcium + phosphorus →
d. Phosphorus + bromine (like chlorine) →
e. Phosphorus + iodine (like bromine) →

14. Write equations to represent the following chemical changes:
a. The decomposition of water by electrolysis
b. The synthesis of water from its elements
c. The decomposition of mercuric oxide when heated
d. Mercury heated strongly in air
e. Mercury (combining number 2) rubbed with iodine
f. Decomposition of potassium chlorate when heated in the presence of manganese dioxide
g. Action of sodium on water
h. Action of zinc on hydrochloric acid
i. Action of iron on dilute sulfuric acid
j. Reduction of hot copper oxide by hydrogen

MORE CHALLENGING QUESTIONS

15. Write the equations for the reaction of metallic calcium with each of the following elements: oxygen, nitrogen, chlorine, sulfur, phosphorus.

16. Write equations for each of the following chemical changes:
a. Decomposition of hydrogen peroxide into water and oxygen
b. Decomposition of sodium chlorate when heated
c. Decomposition of potassium nitrate to form potassium nitrite and oxygen
d. Oxidation of sulfurous acid to form sulfuric acid
e. Calcium carbonate heated to form calcium oxide and carbon dioxide
f. Burning methane (CH_4) to form carbon dioxide and steam
g. Zinc and hydrochloric acid →
h. Aluminum + sulfuric acid →
i. Copper + hydrochloric acid →
j. Burning tin

REVIEW

1. Find the percentage composition of sulfur dioxide.

2. The molecular weight of a gas is 71. Find the weight of a liter. At what conditions of measurement does the answer hold true?

3. A compound analyzed in a laboratory contains 27.1 per cent sodium, 16.5 per cent nitrogen, and 56.4 per cent oxygen. Find the simplest formula of this compound.

4. A gaseous compound contains 30.4 per cent nitrogen and 69.6 per cent oxygen. One liter is estimated to weigh 4.14 grams at STP. Find the molecular formula of the gas.

5. One silicate radical, called metasilicate, has combining number of 2 and is written $-SiO_3$. Write the formulas for the metasilicates of silver, sodium, lead, copper, and aluminum.

UNIT TWO ---------------- CHAPTER XI

THE STOCKROOM—PARTICLES AND STRUCTURE OF THE ATOM

The exciting new field of the structure of the atom is a common meeting ground for both physics and chemistry. Gains in knowledge from chemical study in this field are promptly put to use by physicists. In turn the tools of the physicists—spectroscopes, fog-track chambers, Geiger counters, and cyclotrons—are used by chemists. It is amazing that enormous cyclotrons weighing many tons are being built to attack something as small as an atom. Here, indeed, is much ado about almost nothing—imagine using an instrument as large as a two-car garage to find out about something that has never been seen!

Unfortunately, the instruments used to study the atom and the training required for their use are not available for students of elementary chemistry. We must be content with a summary of the results of experiments and the ideas that the experiments suggest to skilled and highly trained workers. We can be sure, however, that these experiments are more precise by far than the taking of the census in a large city, more precise than the determination of the weight of this book.

The Electron. If we turn on an electric light, we are putting electrons to work. An invisible swarm of tiny bits of electricity rushes through the filament in the bulb and back on copper wire to the powerhouse with nearly the velocity of light—and light travels at a speed of 186,000 miles a second! Although electricity is in common use today, no one knows the complete answer to the challenging question, "What is electricity?" But the picture of an electron stream serves for most practical purposes; moreover, much is known about the behavior of electrons in motion.

The electron was discovered when electricity was passed through long glass tubes from which the air had been withdrawn. It is a simple matter

---

New Terms

electron
ion
proton
nucleus
orbit

neutron
positron
planetary electrons
isotopes

heavy hydrogen
deuterium
ionic- or electrovalence
covalence

to show that the energy passing through such a highly evacuated tube consists of a stream of ***electrically charged particles.*** We can experiment with a narrow beam of electrons if by means of a slit all but a small part of the negative end, or cathode, of the tube is shielded. When the electrons strike an object in their path they produce a greenish-purple glow. This stream can be deflected from its path by a magnet or by an electrically charged object. (See Fig. 11-1.)

Such experiments show that the electrons are charged negatively (−), a fact first announced by Sir J. J. Thomson (1856–1940) at Cambridge, England. He also announced that these electrons, separate particles, were extremely light.

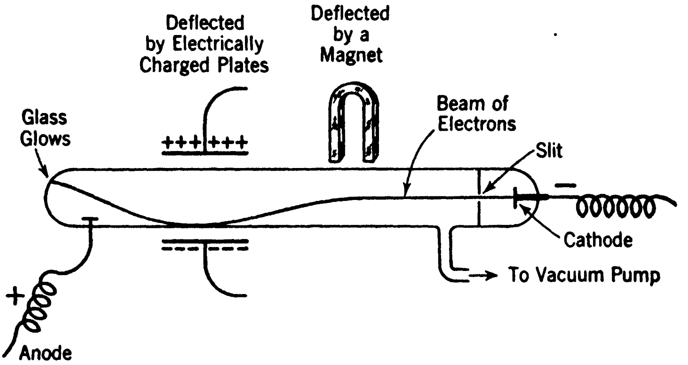


FIG. 11-1.—The deflection of cathode rays by a magnet is shown here. If the magnet were moved nearer the slot, a greater deflection of the cathode rays would be observed.

Later, the weight and the charge of the electron were found. If 1836 electrons are weighed together, their total weight equals that of one hydrogen atom. An ***electron*** (e^-) is considered to be one unit of negative electricity.

Simple Experiments with Electrons. If we wish to experiment with electrons, one of the simplest ways is to rub a closed fountain pen on woolen clothing. The pen accumulates electrons from the wool and becomes electrically charged (−), leaving the wool oppositely charged (+). Bits of paper will be attracted to the pen. In a short time this condition disappears, for the electrons readily leak off into the air. The swishing of gasoline inside an oil-tank truck causes a similar charge, which may result in a spark and an explosion. Consequently, oil-tank trucks drag a chain or use filler in the tires to conduct this charge away to the ground.

Experiments show that opposite electric charges attract each other and, conversely, that like charges repel each other. The paper that the pen attracted must have become positively charged. We explain this by saying that the electrons of the paper were repelled when the charged pen came near it, leaving the end nearer the pen positively charged. (See Fig. 11-2.)

Other experiments show that ***the amount of force between two charges is proportional to the product of the strength of the two charges and inversely proportional to the square of the distance between them*** (Coulomb's law).

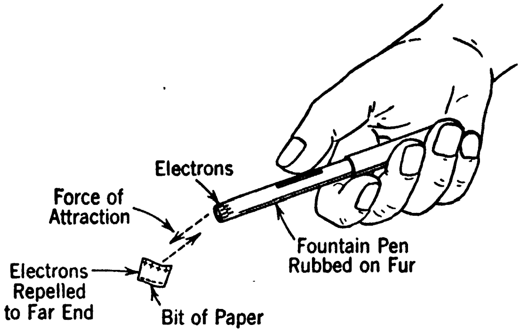


FIG. 11-2.—This convincing and simple experiment with electrons should be performed by everyone not familiar with it.

Electrical Neutrality. We have assumed one fact that does not seem contrary to experience: All matter is, as a rule, electrically neutral, that is, without electric charge. When, for example, we place a piece of copper wire across the terminals of a delicate electric meter, the needle does not move. We conclude that no electricity is flowing through the meter. Any other object held to such an electric meter shows no evidence of an electrical disturbance. This means that any object, element, or compound is composed of an equal number of negative electric units and positive electric units. Further, a positively charged object is, as a rule, one from which negatively charged electrons have been lost.

Gas Ions. Let us now go back to the experiments with glass tubes mentioned on page 180. Further investigation revealed the presence of positively charged particles in these tubes. They are called ***positive ions.*** They consist of atoms that have lost electrons.

The Hydrogen Atom and the Proton. Hydrogen is structurally the simplest element. When hydrogen is placed in the apparatus shown in Fig. 11-1 and an electric current sent through it, we interpret the experiment that each hydrogen atom is composed of one unit of negative and one of positive electricity. The positive particle is called a ***proton.*** Experimenters have shown that the positive part of an atom is located in the center, or ***nucleus,*** and that the electrons are located outside this center. The opposite signs of the electron and the proton immediately suggest an attractive force of one for the other. They would bump together if the electron were not moving. A pattern for the motion of the electron about the nucleus of an atom is seen in the rotation of the earth and the other planets about the sun; for the sun attracts all the planets, and our earth would surely fall into the sun if it did not continue to move on its orbit.

One proton as a center, with a single electron spinning about it, is our simplest picture of the hydrogen atom. The nucleus is small and dense and weighs almost as much as the neutral hydrogen atom. The electron is relatively large and light, about 1/1850 the weight of the proton. The space between the two is tremendous compared with the size of either. This is a space through which forces are exerted but is otherwise quite empty. Dr. John A. Timm writes in his *Introduction to Chemistry:*[1]

> If the hydrogen atom were magnified to such a size that the distance between its electron and its proton would be the order of the distance between New York and Philadelphia (about 90 miles), then on the same scale its electron would be as large as a 20-ft balloon revolving about the proton nucleus the size of buckshot.

The Ion. When a hydrogen atom loses its outer electron, only a proton remains. Its electrical condition becomes changed also. As an atom it is neutral electrically; for its proton had one unit of positive electricity, and the electron balanced that with its one unit of negative electricity. Without the electron, it is left positively charged, one unit. We write this in our symbol language H^+ and call it a ***hydrogen ion,*** or just a proton, p^+. Its diameter is only 1/100,000 that of a hydrogen atom. Hence it exerts a relatively large attractive force on anything that comes within range. This particle is strongly additive, joining many substances, especially water.

$$\underset{\text{Hydrogen ion}}{H^+} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{hydronium ion}}{(H_3O)^+}$$

The hydrogen atom H and the hydrogen ion H^+ present different exteriors to the world. They are quite different chemically. The ion is much smaller and carries a unit of positive electric charge.

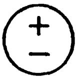


FIG. 11-3.—A neutron is an electrically neutral particle.

The Neutron. In 1932 from the same laboratory in which Sir J. J. Thomson carried out his experiments on the electron came the announcement that J. Chadwick had discovered a new particle. This newly discovered fragment of matter carried no electric charge and hence had escaped the attention of earlier experimenters. The name given to this uncharged particle is the ***neutron.*** It may be considered to be a close combination of a proton and an electron, a pair (see Fig. 11-3) or, better,

$$n^0 = p^+ + e^-$$

---

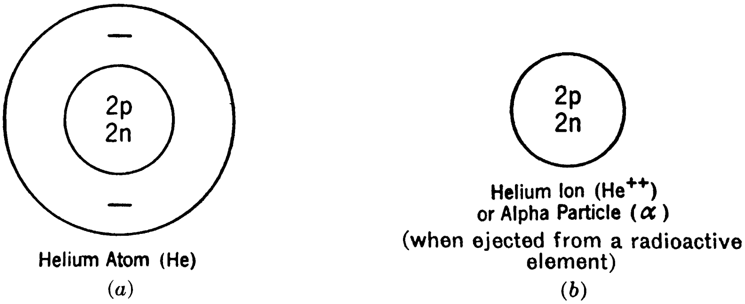
[1] McGraw-Hill Book Company, Inc.

as a unit particle in itself. It is now thought that the neutron has approximately the same weight as the hydrogen atom, but with no charge.

The Positron. Science always expects the unexpected. In recent years new developments in the field of subatomic chemistry have been rapid and numerous. One of the most startling was the discovery by C. D. Anderson at the California Institute of Technology in 1932 of a new particle that is called the ***positron.*** This newly found atom fragment, as a result of atom smashing by cosmic rays, is about the same weight as an electron, extremely light, but it carries one unit of ***positive*** electric charge. Its life is short. Later the positron was found elsewhere in entirely different experiments. Eventually we shall know its proper place in the structure of atoms. One suggestion is worth considering. There is evidence that a proton can be formed from a positron and a neutron.

$$\text{Positron } (e^+) + \text{neutron } (n^0) = \text{proton } (\text{H}^+) \text{ or } (p^+)$$

The Helium Atom. Next to the hydrogen atom in order of atomic weight comes the helium atom. Its atomic weight is 4. It has two electrons revolving about its nucleus, which has two positive charges.



Helium Atom (He)
(*a*)

Helium Ion (He^{++})
or Alpha Particle (α)
(when ejected from a radioactive element)
(*b*)

	Weight	Charge
2p =	2	2+
2n =	2	0
2e =	0	2−
Helium atom	4	0

	Weight	Charge
2p =	2	2
2n =	2	0
Helium ion	4	2

FIG. 11-4.—(*a*) The helium atom has two neutrons and two protons in the nucleus and a filled shell of two electrons; (*b*) helium ion.

The outermost electrons of an atom are called the ***planetary electrons.*** Within the nucleus of helium are two protons, which accounts for its two positive charges. This is not enough, however, for the atomic weight of helium is four times that of hydrogen. The rest of the weight must be in the nucleus, the location of the heavyweight protons. But if helium had four protons in the nucleus and two planetary electrons, we should not have an electrically neutral condition. Actually, the helium atom is electrically neutral, like other atoms. The explanation lies in the assumption that the nucleus of helium contains two protons and two neutrons; the atomic weight of 4 is the sum of the weights of these four particles, and the two positive charges are those of the two protons. The structure of helium, then, is represented by two planetary electrons revolving about a nucleus containing two protons and two neutrons. (See Fig. 11-4.)

A fast-moving helium ion (He^{++}) shot out from a radioactive element is called an ***alpha particle.***

The Nucleus. The nucleus is extremely dense. Unexpected support for the idea of extremely dense matter comes from astronomy. Many highly compact stars have been recorded. For example, the companion star of the Dog Star, Sirius, has matter that according to calculations must be much denser than any substance known upon earth; 1 cu in. weighs 40 tons. Possibly this star is a peculiar collection of nuclei of atoms, stripped of their planetary electrons.

Atomic Numbers. Our ideas of the structure of the hydrogen and the helium atoms put a new light on the meaning of atomic numbers, numbers that were assigned to atoms by H. J. Moseley (1887–1915). Hydrogen has one proton in the nucleus and one outer, or planetary, electron. Its atomic number is 1. Helium, with atomic number 2, has two protons in the nucleus.

We can say in general that the ***atomic number*** is equal to the number of positive charges on the nucleus of an atom or the number of protons in the nucleus. It is balanced in a neutral atom by an equal number of negative electrons. If we wish to find out the number of neutrons for any simple element, we subtract its atomic number from its atomic weight. Accordingly, carbon, which has an atomic weight of 12 and an atomic number of 6, must have six neutrons in its nucleus.

QUESTIONS

1. Name the fundamental electric unit. How much electric charge does it represent, and of what sort?

2. If two long ribbons of newspaper are held together at one end by one hand and the dry fingers of the other hand are drawn through their length, the papers tend to separate at the lower end. (Try it.) What happens when the fingers are brought between the diverging ribbons?

3. An inflated toy balloon is suspended by a thread. Another similar balloon is rubbed with wool and brought near the first. The two attract, touch, and then repel each other. Explain, using diagrams.

4. A fountain pen is rubbed briskly with dry fur or wool. Then it is dipped into fine cork dust. The dust forms bristling projections from which bits of the dust are ejected from time to time. Explain these observations.

5. Review the evidence for the statement that the ordinary atom is electrically neutral.

6. When a molecule of carbon dioxide (in a gas at low pressure) loses an electron(*s*), what is the remaining particle called? What sort of electric charge does it possess?

7. Make a labeled diagram to show the structure of (*a*) a hydrogen atom; (*b*) a hydrogen ion; (*c*) a helium atom; (*d*) a helium ion.

8. Make a table listing four fundamental particles of matter; the nature of their electric charge (+, −, or 0); the number of weight units in terms of the weight of a hydrogen atom.

9. Contrast an electron with a proton; an alpha particle with a helium atom.

10. Define *atomic number.*

Isotopes. Three American workers, Harold C. Urey, George M. Murphy, and Ferdinand G. Brickwidde, showed in 1931 that ordinary hydrogen contains some ***heavy hydrogen***. Today this form of the element is called ***deuterium*** and is known by the symbol D. One out of 6,400 hydrogen atoms in ordinary hydrogen is deuterium.

The atom of heavy hydrogen has one planetary electron, just like ordinary hydrogen, but its nucleus contains a neutron. That is, the deuterium nucleus contains one neutron and a single proton; hence, the weight of deuterium is twice that of ordinary hydrogen. (See Fig. 11-5.)

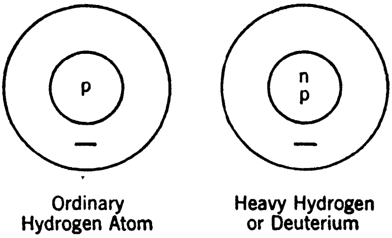
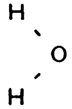
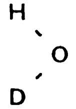


FIG. 11-5.—The nucleus of heavy hydrogen has an extra neutron. Both sorts of hydrogen present the same exterior to the world.

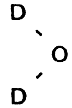
Heavy Water contains one or two atoms of deuterium in place of ordinary hydrogen. (See Fig. 11-5.) We can represent this by formulas as follows:



ordinary water (dihydrogen oxide)



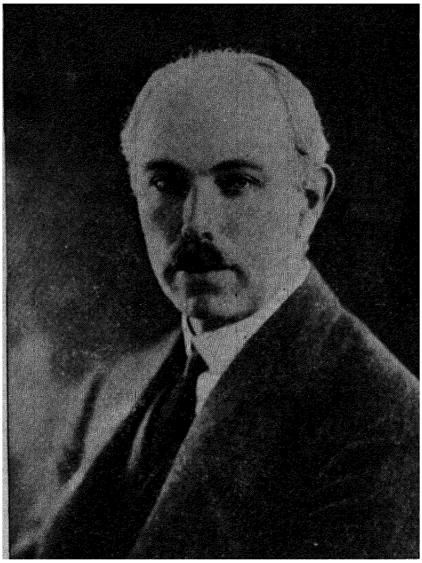
hydrogen-deuterium oxide



heavy water (dideuterium oxide)

PHYSICAL PROPERTIES OF ORDINARY AND HEAVY WATER

Property	Value for H_2O	Value for D_2O
Density at 20°C	0.9982 g/ml	1.1059 g/ml
Freezing point	0°C	3.82°C
Boiling point	100°C	101.42°C
Temperature of maximum density	3.98°C	11.6°C



Courtesy of Journal of Chemical Education

FIG. 11-6.—F. W. Aston (1877–1945), an English chemist, was famous for his work on isotopes.

Deuterium and hydrogen differ in weight, but they do not differ appreciably in their chemical actions. Such atoms of an element that have identical chemical actions but that differ in weight are called ***isotopes.*** Isotopes of the same element differ from each other in the weight of the nucleus, but they have the same number of planetary electrons.

A few common elements including some that have isotopes are shown in the table.

F. W. Aston, who did outstanding work on isotopes at the Cavendish Laboratory in England, was able to separate the isotopes of an element by an instrument called a mass spectrograph, which uses electric and magnetic fields. Almost all elements are comprised of several isotopes—uranium has 3 and tin has 11 isotopes.

Element	Symbol	Planetary electrons	Nucleus		Atomic number	Atomic weight (mass number)*	Atomic weight natural mixture
			Neutrons	Protons			
Hydrogen.....	H	1	0	1	1	1	1.008
Deuterium....	D	1	1	1	1	2	
Helium........	He	2	2	2	2	4	4
Lithium.......	^{6}Li	3	3	3	3	6	6.94
	^{7}Li	3	4	3	3	7	
Carbon.......	C	6	6	6	6	12	12
Nitrogen......	^{14}N	7	7	7	7	14	14.008
	^{15}N	7	8	7	7	15	
Oxygen.......	^{16}O	8	8	8	8	16	16.000
	^{17}O	8	9	8	8	17	
	^{18}O	8	10	8	8	18	
Chlorine......	^{35}Cl	17	18	17	17	35	35.457
	^{37}Cl	17	20	17	17	37	
	^{39}Cl	17	22	17	17	39	

* The mass number is the nearest whole number to the atomic weight. The difference is slight.

The atomic weight of chlorine, 35.457, is actually an average of the weights of its isotopes. It represents 76 per cent of chlorine with atomic weight 35, 24 per cent of isotope 37, and a trace of isotope 39. These proportions are always the same for natural samples of chlorine.

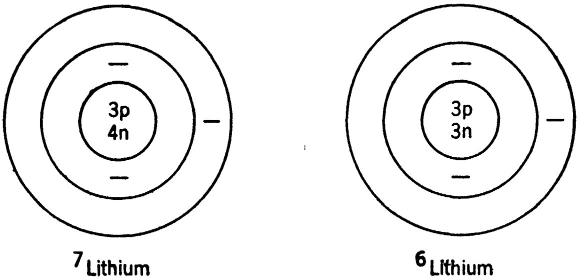


FIG. 11-7.—Two sorts of lithium atoms are possible. Both have one electron in their outermost orbits.

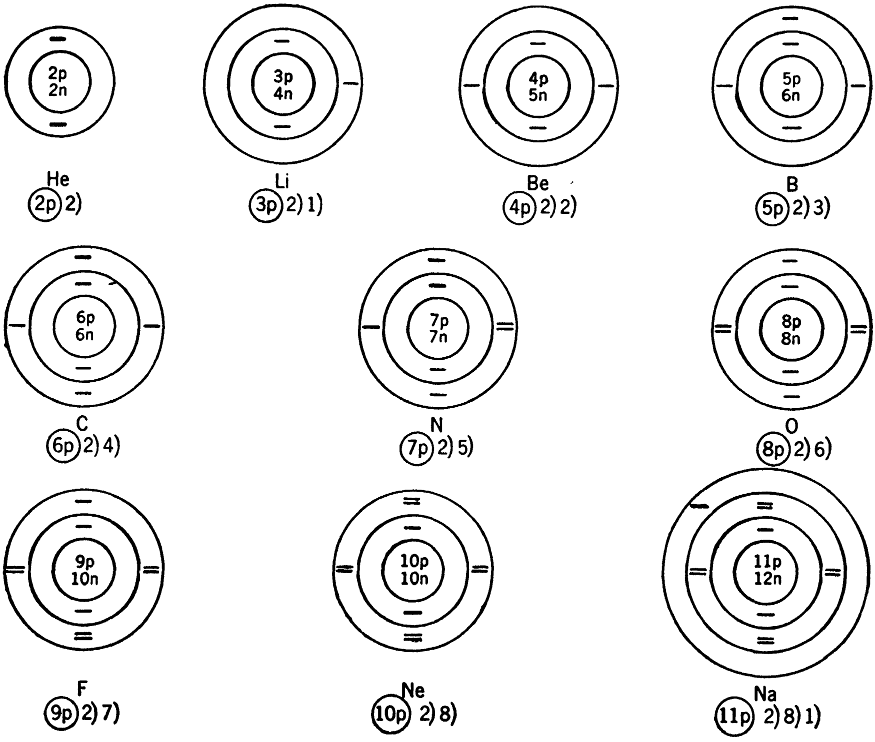


FIG. 11-8.—Electron structures of atoms.

Arrangement of Electrons. Helium and the other inert gases are key elements in one respect. Helium has no chemical action; nor have its related elements. We assume, therefore, that two electrons in the outer part of the helium atom make a complete and stable arrangement. Elements of slightly higher atomic weight, which have more than two electrons, have an additional shell. Lithium, with atomic number 3 and therefore three planetary electrons, has the first, or helium, shell filled with two electrons and just one electron left over for the next shell. (See Fig. 11-7.) Carbon has a filled inner shell and four electrons left for the next shell. Nitrogen has five, oxygen six, and fluorine seven electrons in this second shell. The next element, neon, an inert gas, has no chemical action. Its outer shell holds eight electrons, and here again evidence suggests that the inertness of the gas is due to the fact that this second shell is filled. (See Fig. 11-8.)

To summarize, the first shell of an atom can hold only 2 electrons. The second shell can hold as many as 8. The third can hold as many as 18, although 8 forms a stable arrangement. The inner shells are always filled for the 20 lightest elements before electrons are present in outer shells. The fourth layer may hold even more electrons, but atoms with such a complex structure are beyond our scope at present.

Atom Diagrams. We have gone far enough to enable us to make diagrams of the 20 atoms of lower atomic weight. These are not true pictures of atoms, but they help us understand chemical reactions. Take chlorine for example. Its most abundant isotope has atomic number 17 and atomic weight 35. Consequently, there are 18 neutrons in the nucleus and 17 protons. In the outer shells are 17 planetary electrons, arranged as follows: 2 in the filled inner shell; 8 in the next shell, also filled; and 7 in the outermost shell.

The abundant oxygen isotope with atomic number 8 and atomic weight 16 has 8 neutrons and 8 protons in the nucleus. The 8 planetary electrons have filled the first shell with 2, and the other 6 are in the outer shell.

SUGGESTION: Try making diagrams of a sodium atom (at. wt. 23, at. no. 12); a magnesium atom (at. wt. 24, at. no. 12); an aluminum atom (at. wt. 27, at. no. 13); and a phosphorus atom (at. wt. 31, at. no. 15).

Completed Shells. Eight is the magic number for atoms of light elements! Somehow the atoms favor a shell full of electrons. The first shell is filled when it holds 2, but the next two shells of electrons are apparently filled when they hold 8 (unless electrons are present in a fourth shell; in this case the third shell may hold up to 18 electrons). Chemical inactivity is associated with a shell of 8 electrons, an arrangement with staying power. Let us recall the complete inactivity of neon and argon. Both these elements have their outermost shells filled with 8 electrons, a stable arrangement because neither of these gases unites with any other substance. Let us also look ahead and note that the first period of the periodic table has two elements, the second eight, and the third eight.

Salts. Common salt (NaCl) is a crystalline substance well known to everyone. It has characteristic cubical crystals, which are worth investigating with a magnifying glass. (See Fig. 11-9.) It has a high melting point (801°C). When salt is a liquid, it is a conductor of electricity. Further experiments show that liquids conduct electricity only if charged particles (ions) are present. This with other evidence leads us to conclude that its building units are ***ions.*** Other similar salts include magnesium oxide (MgO—m.p. 2500°C), potassium sulfate (K_2SO_4—m.p. 1076°C), and sodium hydroxide (NaOH—m.p. 318°C). The arrangement of the ions in the crystal can be revealed by studies with X rays.

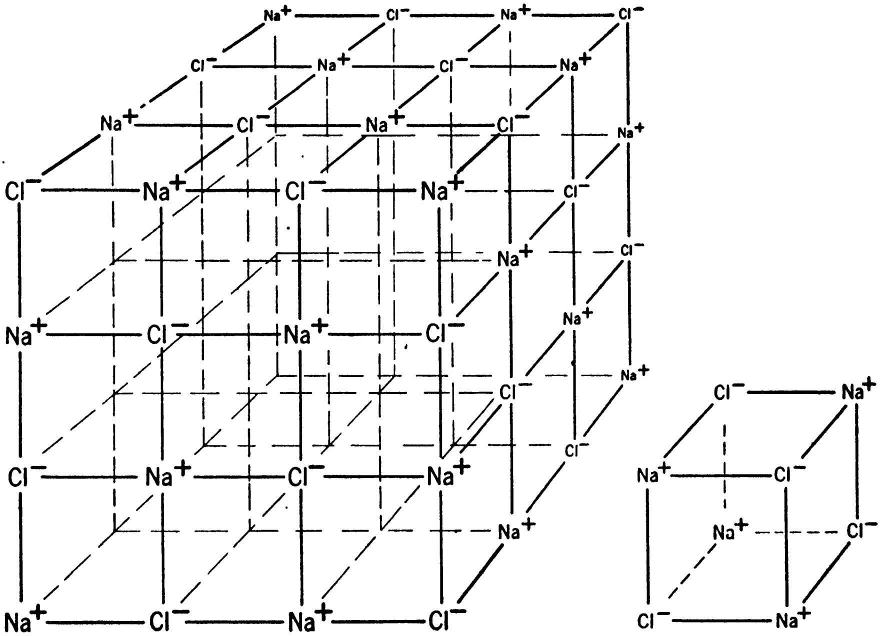


FIG. 11-9.—We believe that a crystal of common salt is a lattice of ions, or electrically charged particles.

On the other hand, many compounds like carbon dioxide (CO_2), ammonia (NH_3), hydrogen chloride (HCl), water (H_2O), and methane (CH_4) have low melting points and are readily changed to a gas. Indeed, many are gases at room temperature. These compounds form true molecules, quite different from salts. When liquefied, they do not conduct electricity. X-ray examination of crystals of these compounds shows that the building blocks are molecules.

It is reasonable to assume that the forces that hold the atoms in the two types of compounds are different. We call the first sort an ***ionic,*** or ***electrovalent,*** bond and the second a ***covalent*** bond.

These can be explained by reference to atomic structure.

How Atoms Join. ***1. Electrovalence.*** The third shell of sodium contains just one electron, $11p\ \ 2)8)1)$.[1] If this electron should become lost, the outer arrangement would resemble that of neon. The third outer shell of chlorine, $17p\ \ 2)8)7)$, contains seven electrons. If its atom should gain one electron, say the one sodium has to offer, its outer arrangement would resemble that of the stably arranged element, argon, and the sodium would resemble neon. These two atoms are suited to be partners. Sodium gives up its electron, and chlorine gladly accepts it. To celebrate the transfer some heat is given off, and common salt is formed.

$$Na + Cl \rightarrow Na^+Cl^-$$

Now the sodium atom has lost an electron. Since the number of protons is greater than the number of electrons, its charge must be expressed in our sign language with a + sign (the sign of lack of electrons), Na^+. The chlorine atom has gained an electron, and therefore we add a − sign to it, Cl^-. The total number of planetary electrons now becomes 10 for sodium and 18 for chlorine. Their nuclei still have the charges due to 11 and 17 protons, respectively. Each atom has become an electrically charged ion with one unit of electricity, and of an opposite sort. Hence they attract each other in common salt.

$11p\ \ 2)8)^+$	$17p\ \ 2)8)8)^-$
sodium ion	chloride ion

Let us consider another example for the union between a metal and a nonmetal, magnesium and sulfur. The magnesium loses its two outermost planetary electrons, and the sulfur fills its two spaces by complete transfer of the electrons to its own outer shell. The magnesium now has acquired a charge of ++ and the sulfur a charge of − −. The two attract each other.

$$Mg + S \rightarrow Mg^{++}S^{--}$$

Such joining of elements in which electrons are completely transferred from one element to another is called ***salt formation,*** since such compounds have the properties of salts.

Let us recall that the combining number of both sodium and chlorine is 1. For magnesium and sulfur the combining number of each element is 2. The combining number in these cases corresponds to the number of electrons transferred. The combining number is the same as the ***ionic***

---

[1] The $11p$ represents the number of positive charges, or protons, in the nucleus, and $2)8)1)$ represents the number of electrons in each shell.

valence, or ***electrovalence,*** number. No molecules of an ionic compound exist in solution, in the liquid state, or in the solid salt.

2. ***Covalence.*** Another type of bond between atoms is well illustrated if we consider the link that holds either chlorine atoms or oxygen atoms together in a molecule. The chlorine atom has seven planetary electrons, 17*p* 2)8)7). A pair of these atoms gets together in such a way that one electron from each does double duty, that is, helps to complete the outer orbit of each atom. The sketch shows how this is possible. (See Fig. 11-10.)

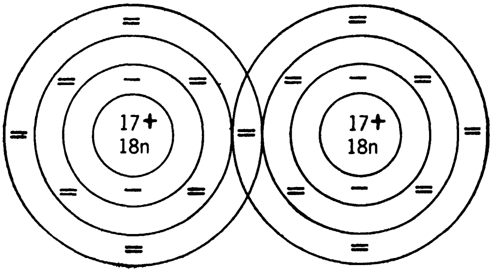


FIG. 11-10.—A chlorine molecule is composed of two atoms held together by the force of a shared pair of electrons—a covalent bond.

The curious fact that two like charges apparently attract each other has been explained by assuming that they are spinning on their axes in opposite directions. By experiment it has been found that two like charges rotating oppositely can attract each other. This attraction between two oppositely spinning electrons is one of the most important forces in nature.

In the case of oxygen atoms, two such pairs of shared electrons are the active force in the formation of an oxygen molecule, O_2. (See Fig. 11-11.) The combining number is the same as the number of these pairs of electrons.

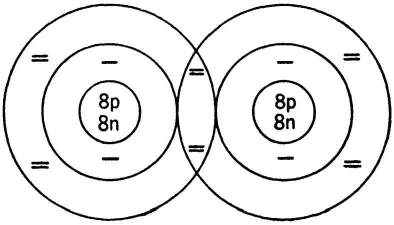
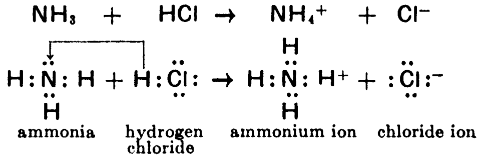


FIG. 11-11.—An oxygen molecule is composed of two atoms, held together by two shared pairs of electrons—covalent bonds.

Such bonds are called ***covalent*** bonds (***co-*** means "together"). It is thought that every hydrogen compound is held together by this sort of bond. Ammonia may be represented as $\mathrm{H}:\underset{\cdot\cdot}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\mathrm{H}$; hydrogen chloride, $\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$. In these diagrams the dots represent electrons. Both types of valence bonds, covalent and electrovalent, agree in number with the combining number of the element.

3. ***Coordinate Covalence.*** The compound ammonium chloride (NH_4Cl) suggests a third possibility. Nitrogen joins three hydrogen atoms with covalent bonds, forming ammonia. Hydrogen also joins chlorine with a single covalent bond. When hydrogen chloride (HCl) and ammonia (NH_3) are brought together, a solid salt, ammonium chloride (NH_4Cl), is formed.

This reaction is thought to occur through the pair of electrons on the nitrogen atom to which no hydrogen is attached. The hydrogen ion (proton) in the hydrogen chloride leaves the chloride ion and becomes attached to the "lone" pair of electrons of the nitrogen atom, forming an ammonium ion $(NH_4)^+$. The product, ammonium chloride, is a true ionized salt.



$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

Such a bond in which both electrons are furnished by one element only is called a ***coordinate covalent*** bond. This type of bond is very common.

To summarize, atoms may join by (1) transfer of one or more electrons completely, (***ionic valence,*** or ***electrovalence***)***;*** by (2) sharing pairs of electrons, each atom furnishing one of the pair (***covalence***)***;*** or by (3) sharing a pair that was provided by one atom only (***coordinate covalence***).

QUESTIONS

11. Define *isotope.*

12. How does heavy water differ from ordinary water: (*a*) in density; (*b*) in composition?

13. Ninety-two natural elements are known. Is it correct to say that only 92 different sorts of atoms exist?

14. What is the maximum number of electrons possible in the innermost shell of an atom? In the next outermost shell? In the third shell?

15. Make atomic structure diagrams to represent: (*a*) lithium (at. wt. 7, at. no. 3); (*b*) boron (at. wt. 11, at. no. 5); (*c*) nitrogen (at. wt. 14, at. no. 7).

16. How many electrons are in the outermost orbit of the neutral atoms of the elements in group I*a*, -II*a*, -VI*b*, and -VII*b*? (See periodic table, page 329.)

17. No element in group 0 (periodic table) forms compounds. Account for this in terms of electrons.

18. From the table in the Appendix, select three salts and list their melting points.

19. From the table of data about common gases (Appendix) select three typical molecular compounds, and list their melting points.

20. Distinguish *ionic valence*, or *electrovalence*, from *covalence*. Give an example of each.

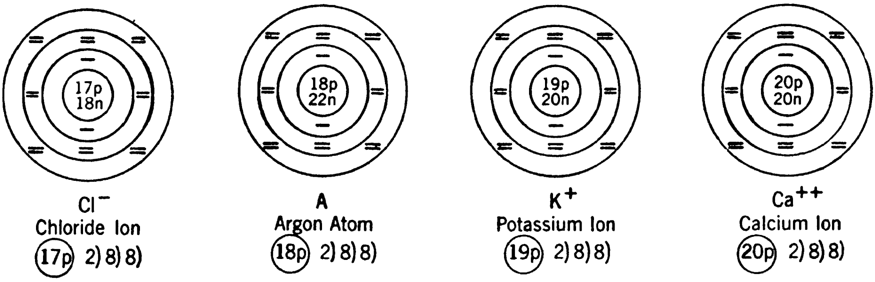
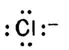
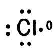


FIG. 11-12.—All three substances represented above have identical outer orbits. They differ only in respect to nuclear arrangement.

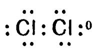
Distinction between an Atom and an Ion. If a chlorine atom gains an electron, it has an outer shell filled. It now has the stable arrangement of a rare gas like argon. Its electrical condition becomes changed, also. The gained electron gives it one extra unit of negative electricity. We represent this in our sign language writing as Cl^- and call it a chloride ion. (See Fig. 11-12.)


$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^-$

chloride ion

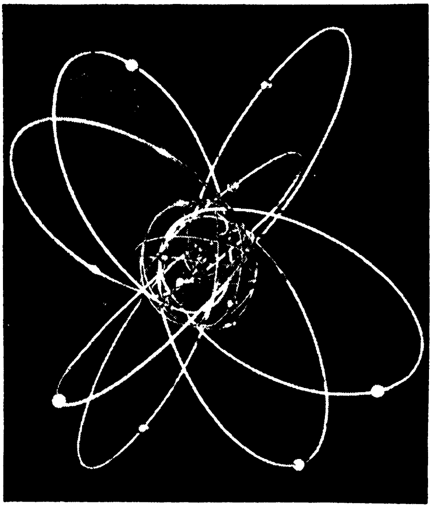

$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot^0$

chlorine atom


$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^0$

chlorine molecule

Chlorine atoms (see Fig. 11-13) in molecular pairs comprise chlorine gas, a green, poisonous substance, extremely active chemically. Chloride ions are present in common salt. They are good to eat in moderation. They are not especially active chemically. Truly a great difference is accomplished by a single electron per atom.



Courtesy of Pennsylvania Salt Manufacturing Company, Photo by Gladys Müller

FIG. 11-13.—This model of the chlorine atom is now on display at the Franklin Institute, Philadelphia. The model represents the structure of an atom according to some of the best current conceptions. It is based on the magnification of two and one-half thousand million times.

Radicals Form Ions. Not only do atoms form ions, but radicals may also have electric charges. The number of positive or negative charges that is to be written above any given ion is the same as its combining number. Here are some examples that illustrate the ions present in some common compounds:

Compound	Formula	Positive ion	Negative ion
Sodium chloride	$NaCl$	Na^+	Cl^-
Potassium nitrate	KNO_3	K^+	NO_3^-
Ammonium sulfate	$(NH_4)_2SO_4$	$2NH_4^+$	SO_4^{--}
Calcium carbonate	$CaCO_3$	Ca^{++}	CO_3^{--}
Magnesium oxide	MgO	Mg^{++}	O^{--}
Copper sulfate	$CuSO_4$	Cu^{++}	SO_4^{--}
Aluminum sulfate	$Al_2(SO_4)_3$	$2Al^{+++}$	$3SO_4^{--}$
Calcium phosphate	$Ca_3(PO_4)_2$	$3Ca^{++}$	$2PO_4^{---}$

Electron Transfer. In many chemical changes one or more electrons per atom take part. The burning of magnesium is a familiar example.

$$\begin{array}{cccccc} & 2Mg & +\ O_2 & \rightarrow & 2MgO & \\ & \text{magnesium} & \text{oxygen} & & \text{magnesium} \quad \text{oxide} & \\ \begin{array}{c}\text{Combining number}\\ \text{before change}\end{array} & 0 & 0 & \rightarrow & \text{ion } 2+ \quad \text{ion } 2- & \begin{array}{c}\text{Combining number}\\ \text{after change}\end{array} \end{array}$$

$$12p\ 2)8)2) + 8p\ 2)6) \rightarrow 12p\ 2)8)^{++}\quad 8p\ 2)8)^{--}$$

In this case it is easy to see that the free elements with valence zero have become part of a compound and hence have acquired ionic valence. The change in charge is due to the transfer of electrons. The magnesium has been ***oxidized,*** gaining in valence by two units positive. This means a loss of two electrons per atom. The oxygen atoms, on the other hand, have become negative in charge by two units, or, more definitely, they have gained two electrons each.

$$\begin{array}{lll} 2Mg \text{ (atoms)} & \text{lose 2 electrons each} & \rightarrow 2Mg^{++} \\ 2O \text{ (atoms)} & \text{gain 2 electrons each} & \rightarrow 2O^{--} \end{array}$$

The oxygen atoms in this case have gained negative valence, or gained electrons, and are said to have been ***reduced.***

In the case of the chemical change,

$$2Na + MgBr_2 \rightarrow 2NaBr + Mg \qquad \text{(formula equation)}$$

$$2Na^0 + Mg^{++} + 2Br^- \rightarrow 2Na^+ + 2Br^- + Mg^0 \qquad \text{(ionic equation)}$$

or

$$2Na^0 + Mg^{++} \rightarrow 2Na^+ + Mg^0$$

the valences are as marked in the ionic equation. The bromine atom remains at valence -1 and therefore has no real part in the change. The magnesium atom changes from valence $+2$ to zero, a move in the negative direction. It has gained two electrons per atom. Hence it is ***reduced.*** $Mg^{++} + 2e^- \rightarrow Mg^0$. The sodium atoms have each lost one electron to become sodium ions, Na^+, a gain in positive valence. $Na^0 \rightarrow Na^+ + e^-$. The sodium atoms are said to be ***oxidized***. These are more general meanings of the terms reduced and oxidized.

Other examples of electron transfer are seen in the chemical changes

$$Cu + 2AgNO_3 \rightarrow 2Ag + Cu(NO_3)_2$$

or, more directly,

$$Cu^0 + 2Ag^+ \rightarrow 2Ag^0 + Cu^{++}$$

The copper is oxidized, and the silver is reduced.

Common Salt, an Ionic Lattice. In forming salt (NaCl) from its elements, an electrically charged atom of sodium, called a sodium ion, Na^+, has been produced from a sodium atom by removal of its outer electron. A charged atom of chlorine, called a chloride ion, Cl^-, has been produced from a chlorine atom by gain of an extra electron. Each now has a quota of eight electrons in its outermost shell.

These two kinds of ions have opposite charges and attract each other with a force sufficient to hold them together as a solid crystal. The ions are arranged alternately in the cubic crystal of salt so that no two ions of the same kind are adjacent. (See Fig. 11-9.) In any visible salt crystal many millions of cubical units are joined together. Each ion is surrounded in space by six of the opposite kind. (See Fig. 11-9.) No sodium ion is attached to any particular chloride ion, although the total number of each is the same. Rather, the whole crystal forms a latticelike pattern. Because of this regular arrangement of particles within the crystal, they can be examined by X rays and the location of the ions determined. The unit sometimes called a "sodium chloride molecule" is merely a convenient name for a pair of ions. Strictly speaking, sodium chloride does not exist as molecules. We should represent it as Na^+Cl^-. Table salt, like potassium nitrate or sodium hydroxide, is an example of an ionic compound.

Within the Atom. An assortment of other atom-dust particles has been announced, and others have been predicted. Now we stand at a new

CHARACTERISTICS OF PARTICLES

	Symbol	Charge	Mass (weight) (in terms of H atom)
Positron	e^+	+1	0.00054
Electron	e^-	−1	0.00054
Proton (H^+)	p^+	+1	1
Neutron	n	0	1
Deuteron (D^+)	d	+1	2
Alpha particle (He^{++})*	α	+2	4

* This particle will be discussed in Chap. 37.

frontier. As our tools, skill, and knowledge improve, we shall penetrate more and more into the secrets of nature. The number of investigators who are interested in this problem is increasing steadily. Teachers and writers are equally busy consolidating the results of research and interpreting them.

SUMMARY

The electron was discovered by Sir J. J. Thomson by passing an electric current through glass tubes containing gas at very low pressure. An electron is a unit particle of negative electricity. It is very light and movable; easily shifting from one atom to another. Electrons are not always attached to atoms but can exist as independent particles. Electrons are attracted to positively (+) charged places, where electrons are lacking; they repel each other. An ordinary atom is electrically neutral because it has a balance of + and − electrical charges. When one or more electrons become attached to or detached from a gas molecule, the molecule becomes an electrically charged ion; + if electrons have left and − if electrons have become attached.

The hydrogen atom has the simplest structure. Its nucleus, or center, consists of a single positively (+) charged proton. Spinning about the nucleus is a single electron (e^-). If the outer electron becomes detached, the remainder is a hydrogen ion (H^+) or a proton (p^+).

Protons are very dense and have one unit of positive (+) electric charge, and they readily attach themselves to other particles.

A neutron (n) is a close combination of a proton and an electron, and it is electrically neutral. Positrons (e^+) are short-lived, lightweight, positively charged units.

The helium atom has a nucleus consisting of two neutrons and two protons. The outer orbit has two electrons. Since this atom exhibits no chemical activity, we believe that the outer orbit is filled. If the helium atom loses its two outer, or planetary, electrons, it becomes a helium ion (He^{++}). The nucleus of an atom is exceedingly dense, and it always bears a positive charge. The number of units of positive charge in the nucleus, that is, the number of protons, is equal to the atomic number.

Isotopes are atoms of the same element that have identical chemical actions but differ in atomic weight. They have the same electron pattern but differ in the nucleus.

The electrons of an element are located in outer orbits or shells. When completely filled, these shells may hold 2, 8, 18, . . . electrons in successive layers.

Salts are compounds that have high melting points, conduct electricity when melted, and have ionic structures. An example is common salt (Na^+Cl^-). This is a typical ionic compound. The number of charges on an ion is equal to its combining number and it is called its ionic valence or electrovalence.

Compounds that contain molecules usually have low melting points. They are nonconductors of electricity when liquid, and the atoms in the molecules are joined by covalent bonds consisting of shared pairs of electrons. The number of covalent bonds of an atom in such a molecule corresponds to the combining number. An example is methane (CH_4).

Coordinate covalence is involved in compounds formed from two molecules that combine, using otherwise unused electrons. It is met less frequently than ionic or covalence bonds.

QUESTIONS

21. List five salts other than those given on page 194, and write after each the ions from which they are formed.

22. Write an equation for the burning of calcium. Under it show the electron structure and electron transfer by simplified diagrams, following the pattern of page 194.

23. Write an equation for the replacement reaction that takes place when a steel knife blade (iron) is dipped into copper sulfate solution. Below the equation show the electron transfer as in question 22.

24. Of what units is a crystal of table salt (sodium chloride) composed?

25. Which sort of valence is exhibited in: (*a*) ammonia (NH_3); (*b*) phosphorus pentoxide (P_2O_5); (*c*) sulfur dioxide (SO_2)?

MORE CHALLENGING QUESTIONS

26. What percentage of the weight of a regular hydrogen atom is due to the electron?

27. Make atom-structure diagrams for the atoms of three metals.

28. Show in terms of atom-structure diagrams the union of lithium with fluorine.

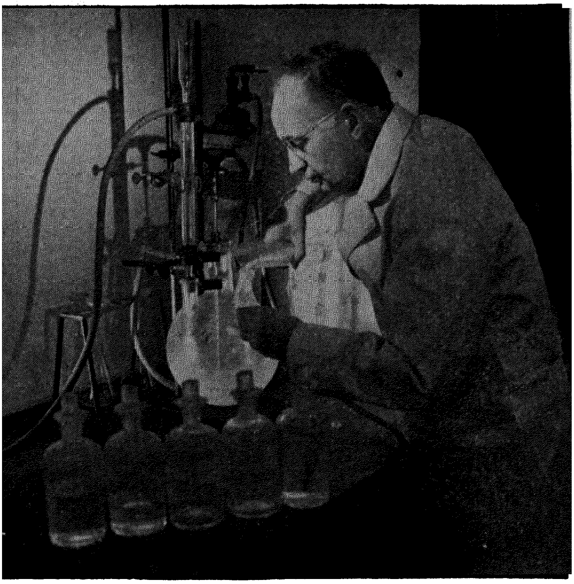
29. How many (*a*) electrons, (*b*) neutrons, and (*c*) protons are present in a molecule of (1) ordinary water (dihydrogen oxide) and (2) heavy water (dideuterium oxide)?

REVIEW—DENSITY

All gases are measured at standard conditions. One liter of oxygen weighs 1.43 grams; of hydrogen, 0.09 gram; of air, 1.29 grams; of liquid water, 1000 grams.

Find the weight of: (1) 1 milliliter (or 1 cubic centimeter) of water; (2) 1 milliliter of oxygen; (3) 25 milliliters of hydrogen; (4) 100 liters of air. Find the volume occupied by: (5) 50 grams of water; (6) 50 grams of oxygen; (7) 51.6 grams of air; (8) 72 grams of hydrogen. (9) Find the density in grams per liter and grams per milliliter of a gas 500 milliliters of which weighs 1.55 grams. (10) The weight of 120 milliliters of a certain liquid is 1.632 kilograms. Find its density.

UNIT THREE



Courtesy of General Electric Company

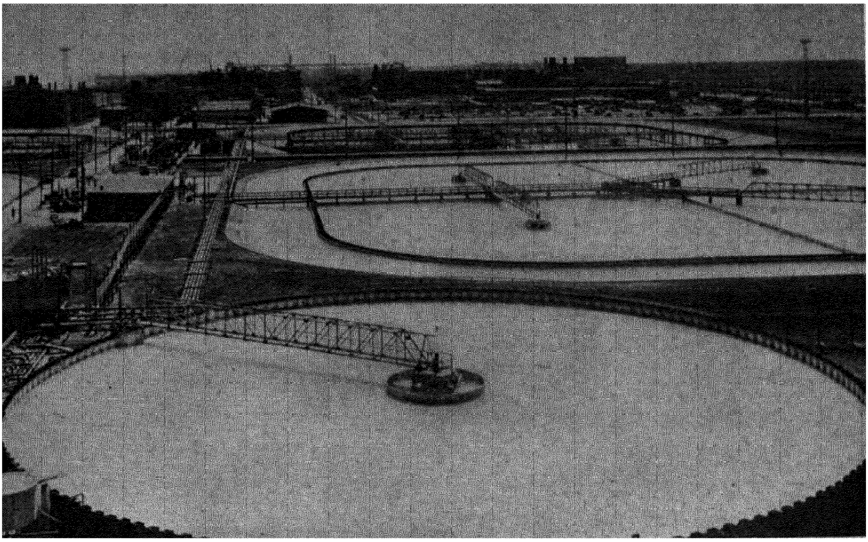
DISPERSIONS OF MATTER

We have studied water and have learned something about its commonplace yet remarkable property of being a solvent. We are now to investigate this property in detail. Water easily dissolves many substances, forming solutions.

Common salt (sodium chloride) dissolves in water, as does sugar. However, a solution of salt conducts electricity, but a solution of sugar does not. We believe that a salt solution contains electrically charged particles called ***ions,*** meaning "wanderers," while a sugar solution contains only uncharged molecules. The ions carry the electric current.

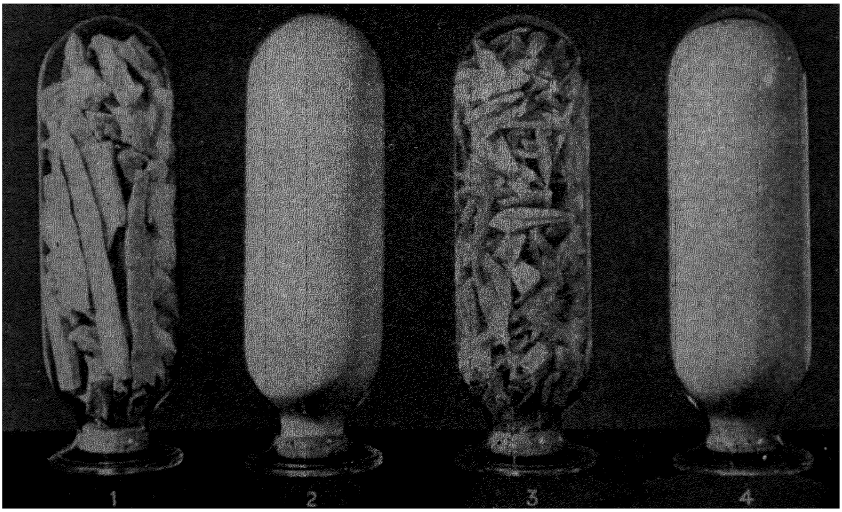
If we alter the electrical condition of the ions, new substances will be formed. This process, called ***electrolysis,*** consists in passing an electric current through a solution. Chemical changes invariably occur. Interesting and useful products are made in this way, and cheaply, too. Such needed chemicals as chlorine and lye are made by electrolysis of a solution of common salt.

Also, we have those near solutions, called ***colloidal dispersions***, formed particularly by gluelike materials. Jelly, foam, smoke, fog, rubber, textiles, and most foods are colloidal dispersions.



Courtesy of Dow Magnesium Corporation and the Austin Company.

These huge tanks show the large scale in which solutions and precipitates are used in industrial processes.



Courtesy of Charles B. Knox Gelatine Company, Inc.

Selected bones (1), 75 per cent mineral and 25 per cent collagen (the organic part of the bone), are separated into dicalcium phosphate (2) and collagen (3). From collagen is made gelatin (4), the colloidal substance that is the basis for prepared gelatin desserts.

UNIT THREE - - - - - - - - - - - - - CHAPTER XII

SOLUTIONS

A bottle of ordinary soda water is an example of a solution. A uniform and attractive color is often imparted to it by adding a bit of harmless dye to the water; a pleasant taste is given by the addition of fruit flavoring, real or artificial; the sweetening is done by adding sugar. The sirup containing these substances is mixed with carbonated water and capped immediately. The result is an agreeable thirst-quenching beverage.

Carbonated water consists of clear water with carbon dioxide gas added to it under a pressure greater than that of the atmosphere. The carbon dioxide dissolves in the water, part of it joining chemically with the water, forming a weak acid (carbonic acid).

$$H_2O + CO_2 \rightarrow H_2CO_3$$

A number of interesting experiments may be made with these beverages. The presence of the dye may be shown by boiling in the liquid a piece of white woolen cloth, which absorbs the dye; the cloth becomes colored and the soda water almost colorless. Or the bottle may be shaken or warmed (with care) before it is opened. Then, if the cap is removed, the gas will escape with so much force that some of the contents will forcibly spout up like a miniature geyser. To prevent this the soda is ordinarily served cold. The fluid loses the gas in the warm mouth, giving a tingling sensation on the tongue.

Common Solutions. The bottle of soda water, physically considered, is a solution of several solids and one gas in the same solvent, water. Liquids that absorb substances into themselves, as water does sugar, are called ***solvents.*** The substance that is dissolved, the sugar in this case, is called the ***solute.*** Together the water and sugar make a clear ***solution,*** composed of solute and solvent.

We are familiar with many solutions. Brine consists of a solution of table salt in water. Sea water is composed of many solutes in the nearly

---

New Terms

solvent
solute
tincture
solubility
effervescence
endothermic
exothermic
anhydrous
molar solution
fractional distillation
supersaturated

universal solvent, water. The druggist provides us with many fluids. Some of them, for example iodine solution used as an antiseptic, are called tinctures or spirits. Tincture of iodine is a solution of the element iodine (I_2) in common, or grain, alcohol (C_2H_5OH). "Spirits of camphor" is made from the compound camphor dissolved in alcohol. Other liquids besides alcohol are good solvents for substances that do not dissolve readily in water. A mechanic uses gasoline to clean his hands because this material dissolves grease.

Importance of Solutions. Solutions are important in photography, dry cleaning, medicine, painting, and many other processes. Our digestive system is a complicated arrangement for getting our food into a solution, for undissolved food does not nourish the body. Plants get their food from solutions, too.

In chemical work solutions are used extensively. They are useful because (1) they provide a convenient way of handling substances; (2) a very small amount of material may be uniformly spread out when it is used in solution; and (3) many chemical actions, especially ionic actions, proceed readily when substances are brought together in solutions.

How to Make a Solution. If we wish to dissolve sugar in water rapidly, we select fine sugar crystals or for quicker action grind up the crystals and stir them in water vigorously, using warm water rather than cold. The same directions hold true for most solids. Since it is evident that dissolving must proceed at the surface of a substance, the more surface of solute in contact with the solvent, the more rapidly the solution will be formed. To dissolve much gas in water, on the other hand, we cool the water, and exert pressure greater than that of the atmosphere on the gas.

A substance that dissolves easily in water, Epsom salts ($MgSO_4 \cdot 7H_2O$) for example, is said to be ***soluble*** in water. Road rock and concrete do not dissolve noticeably in water and are said to be ***insoluble*** in water. Nothing is absolutely insoluble, however.

The amount of solute that can be dissolved in a specified amount of solvent at a given temperature is called the ***solubility*** of a substance. The units must be stated, as for example, the number of grams in 100 grams of solvent. Most solid substances dissolve more readily when the temperature of the solvent is raised (that is, the number of grams of solute which can be dissolved in 100 g of solvent becomes greater). For example, about twice as much saltpeter (KNO_3) can be dissolved in 100 g of water at 40°C as can be dissolved in the same amount of water at room temperature (20°C). Some exceptions should be mentioned, however. Ordinary salt ($NaCl$), which is moderately soluble in cold water, does not change much in solubility with changes in temperature; also, a few substances, especially calcium hydroxide [$Ca(OH)_2$] and calcium sulfate ($CaSO_4$), are less soluble in very hot water than in water at room temperature.

Contrary to the general rule for solids, gases decrease rapidly in solubility as the temperature is raised. In fact, a suitable way to free water of dissolved gas is to heat the water to the boiling point. For this reason, distilled water, lacking dissolved air, tastes flat, and unstoppered bottles of household ammonia (essentially a solution of ammonia gas in water) lose their strength if heated.

Opening a bottle of soda water causes an escape of the dissolved gas as the pressure is reduced. Stirred in a glass, it fizzes. This fizzing is called ***effervescence.*** Reducing the pressure or heating a solution containing any gas causes effervescence.

Heat and Solutions. Let us pour 100 g of water from some melting ice into a thin glass beaker and place the beaker on a moistened piece of wood. Now we add 50 g of ammonium nitrate to the water and stir rapidly. In a very short time we find that the beaker is frozen to the wood. The temperature of the solution in the beaker falls to 10 or 12° below 0°C. The dissolving of the ammonium nitrate in water thus absorbs heat. This, like all changes that take in heat, is called an ***endothermic process.***

In general, substances like ammonium nitrate (NH_4NO_3) and sodium thiosulfate ($Na_2S_2O_3$), also called "hypo," that are more soluble in water when the temperature is raised take in heat when they dissolve. On the other hand, substances like calcium sulfate ($CaSO_4$) that are less soluble in water when the temperature is raised give off heat when they dissolve. A salt that shows decreasing solubility with temperature rise more markedly than most is cerium sulfate [$Ce_2(SO_4)_3$], and it is recommended for a demonstration of this behavior.

Let us prepare a supersaturated solution of sodium thiosulfate, or "hypo," and allow it to crystallize, observing its temperature during the process (see page 207). This, like all changes that give out heat, is called an ***exothermic process.*** The act of crystallizing will raise the temperature several degrees.

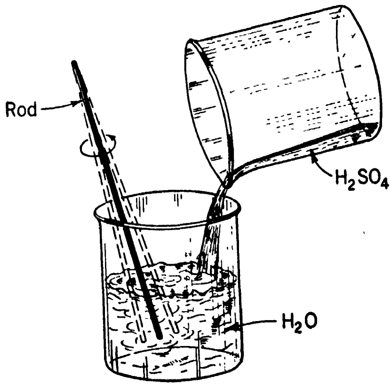


FIG. 12-1.—Pour sulfuric acid into water, *not* water into sulfuric acid. Only a few drops of sulfuric acid should be added to water at one time, and the mixture should be stirred after each addition.

A heat change due to another cause may be noticed when solutions form. Let us pour 20 ml of water into a large test tube, then add 10 ml of concentrated sulfuric acid, 1 ml at a time, stirring briefly with a thermometer after each addition. (See Fig. 12-1.) A temperature well over 100°C may soon be reached. The great increase in heat from this mixing is thought to be caused by adding water (hydration) to the hydrogen ions of the sulfuric acid, forming hydronium ions.

$$H^+ + H_2O \rightarrow H_3O^+ \text{ (+ heat)}$$

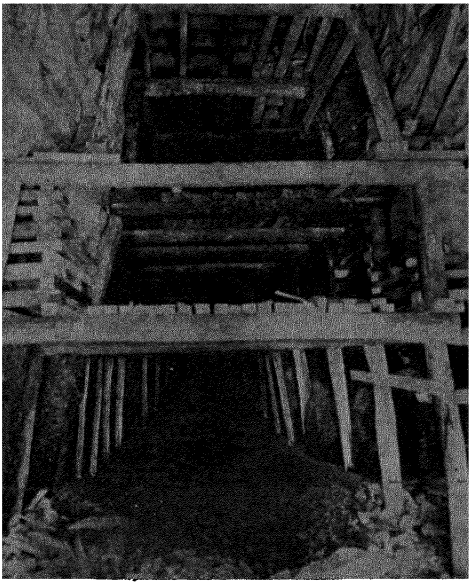
In addition to illustrating one source of heat, this experiment also shows how an accident may sometimes be caused in shops, battery service stations, dyehouses, and laboratories. When sulfuric acid and water are mixed, ***the denser acid should always be poured into the water while stirring it vigorously.*** Then the acid goes down through the water, mixing in as it falls. The entire mixture becomes hot. If this procedure is reversed and the water is poured onto the acid, the less dense water tends to float on the acid, forming a zone of intense heat where the two liquids meet. Often the temperature is high enough to cause so much steam that the liquids are thrown out violently. In laboratory work it is often necessary to mix sulfuric acid and water. Obviously, this should be done with care.

Another case of heat transfer is interesting. If we gently heat some copper sulfate, or blue vitriol, crystals ($CuSO_4 \cdot 5H_2O$) (see page 113) until all the blue color is gone, an almost colorless powder remains ($CuSO_4$). If the powder is to be kept in this dry, or anhydrous, condition, it must be placed in a desiccator. (See Fig. 6-2.)

Continuing the experiment, let us place the vessel containing the ***anhydrous*** (without water) powder on the hand of someone who is willing to investigate the temperature change. As we add water to the powder from a medicine dropper, not only will the blue color begin to return, but the investigator will soon need to take the vessel from his hand to avoid being burned by the heat from the vessel. When more water is added to the blue crystals, a blue solution is formed. The copper ion is thought to be ***hydrated*** in this solution, actually $[Cu(H_2O)_4]^{++}$, although we customarily write Cu^{++} to represent the ion.

Our picture of the action that takes place when a crystal is dissolved in water is something like this. The water molecules add themselves to the positive, or metal, ions, weakening the force of their attraction for the negative ions in the crystal. This causes a breakdown of the crystal lattice, and the highly nonconducting water molecules separate the two sorts of ions, which are now swimming around in the water. Ordinary salt (sodium chloride) in solution has sodium ions surrounded by at least six molecules of water and chloride ions surrounded by another cluster of water molecules. Heat is taken in when the ions are separated from one another and is liberated when the molecules of water attach themselves to the ions. Whether heat is absorbed or evolved when a salt is dissolved in water thus depends upon which of these processes predominates—that in which heat is absorbed or that in which heat is evolved.

Concentration of Solutions. When we boil potatoes, we add a pinch of salt to the water in which the potatoes are to be cooked. The salt crystals dissolve in the water. The sodium and chloride ions have separated from each other, and between them has come a large number of water molecules. In cases where there is little solute we say that the solution is ***dilute***. Solutions that have much solute with relatively little solvent, such as honey or molasses, are called ***concentrated*** solutions. The terms dilute and concentrated are relative terms and have no exact meaning.



Courtesy of Koppers Company, Inc.

FIG. 12-2.—These mine timbers are treated with a solution of zinc chloride in order to preserve them.

QUESTIONS

1. Name three solvents for grease.

2. Name three substances for which water is a good solvent. Can all three dissolve in water together?

3. How could you show that tincture of iodine is a solution?

4. 'A certain solution has 100 grams of solute in 1 liter of water. When 999 liters of pure water is added, what is the amount of solute in each liter?

5. Give directions for making quickly a solution of potassium nitrate (KNO_3).

6. Name a substance which increases in solubility with increase in temperature; one which decreases in solubility with increase in temperature; one for which a temperature change has little effect on solubility.

7. Define *solubility.*

8. Explain the cooling effect noticed when ammonium nitrate (NH_4NO_3) solution is formed.

9. Explain the temperature rise that is observed when concentrated sulfuric acid is diluted.

10. Explain the temperature rise that takes place when a little water is added to anhydrous barium chloride ($BaCl_2$).

Solutions of Definite Concentration. ***Molar solutions,*** on the other hand, have a known concentration. They hold a gram-formula weight (1 mole) of solute in 1 liter of solution. A molar solution of common salt contains 1 mole, 58.5 g of salt with enough water to make 1 liter

$$\begin{array}{c} Na + Cl \rightarrow NaCl \\ 23 + 35.5 = 58.5 \end{array}$$

of solution; a molar sugar solution contains 1 mole, 342 g of sugar ($C_{12}H_{22}O_{11}$) in enough water to make 1 liter of solution.

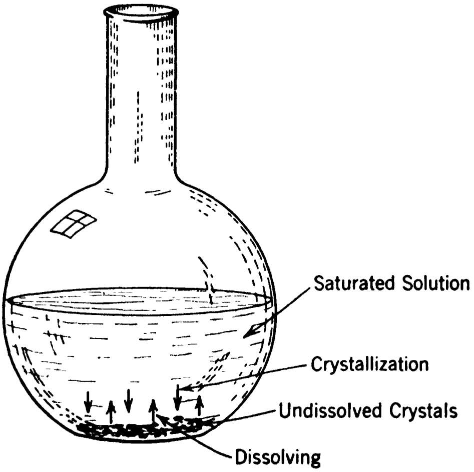


FIG. 12-3.—In a saturated solution in contact with undissolved solute, the processes of dissolving and crystallizing are both going on at the same time.

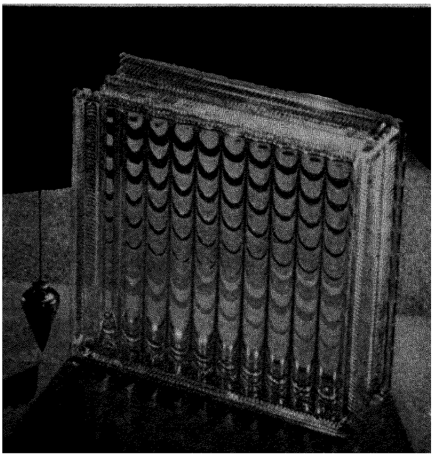
Some solutions hold all the solute that they can absorb at that temperature. Such solutions are called ***saturated*** solutions. If a solution has been shaken but some of the solute still remains undissolved in the bottom of the vessel indefinitely, then we may be sure that the solution is saturated.

Substances Leaving Solutions. During a storm, sea water dashed up on a high rock. Some of the water remained in a shallow natural basin. Afterward the sun came out, and the water dried up. A white deposit was observed around the rim and in the bottom of the rock basin. Some of the deposit was readily recognized by its cubical form as crystals of common salt. The conditions necessary for the obtaining of crystals from a solution are illustrated in this example.

A solution becomes saturated if enough of the solvent is evaporated from it. If still more of the solvent is removed by evaporation, some of the solute separates out in the form of crystals. If the solvent is removed slowly by gradual evaporation, the molecules or ions have time to arrange themselves on crystals already present, forming larger crystals. The making of sizable crystals (as large as several pounds for a single crystal) is a fascinating hobby. Projecting crystal formation on a screen is a valuable demonstration, for it shows the unsuspected beauty in natural formations.

Separating Liquids. Gases usually leave solutions when the solutions are heated, but the separation of two liquids that are mutually dissolved is not always a simple matter. Petroleum contains several mutually soluble liquids, each of which has considerable vapor pressure at the boiling points of the others. It is extremely difficult to separate these compounds by distillation. For this reason the individual compounds in petroleum are not separated for ordinary fuel use. Instead of selecting the distillate at one boiling point, it is customary to collect all the substances (gasoline, kerosene, fuel oil) that leave the mixture between a given range of boiling points. The process of heating a mixture and collecting the distillate that boils over between two given temperatures is called ***fractional distillation.*** The gasoline fraction separates out from petroleum in the boiling-point range of 40 to 225°C, and it is a mixture of several compounds.

Supersaturation. When a saturated solution evaporates, crystals usually form about the edge of the vessel. But we should remember that the formation of crystals depends on the arranging of ions or molecules into definite patterns, for crystals of each kind of substance are always definite in their shape, in the angles between surfaces, and in appearance. Sometimes, when a saturated solution cools, the conditions necessary for crystallization are not reached immediately, especially if the solution is left undisturbed and kept free of dust. The solution may cool to room temperature without change. Under these conditions, crystallization can be brought on at a rapid rate throughout the vessel if the solution is now stirred, if the vessel is scratched on the inside surface in contact with the solution, or, best of all, if a seed crystal is dropped into the solution. Sometimes the material forms a solid mass of crystals almost immediately, and much heat is liberated. Such an unstable solution formed by cooling a saturated solution in which no crystallization has taken place is called a ***supersaturated solution*** because it holds more solute than the liquid is normally able to absorb at the low temperature it has reached. Solutions of sodium acetate ($NaC_2H_3O_2$), borax ($Na_2B_4O_7$), and photographer's "hypo" ($Na_2S_2O_3$) show this effect. It must be emphasized that the condition of supersaturation is easily upset. Normally, when solutions are cooled and become saturated, crystals begin to form at once.



Courtesy of Corning Glass Works

FIG. 12-4.—Shown here is a glass building block. Glass keeps its useful properties only as long as it remains an undercooled liquid. If crystals form in glass, it is worthless.

Glass is an example of a supersaturated solution, or an undercooled liquid. (See Fig. 12-4.) Useful glass has not crystallized but has formed an apparently solid mass at a temperature that is far below the normal freezing point of the compounds in it.

Owing to the fact that some liquids form supersaturated solutions, we must be careful in our definition of freezing point. ***The freezing point is the temperature at which the solid and liquid conditions of the same substance may be mixed without a change in the temperature of either.***

Effects of Dissolved Materials. Let us examine the following laboratory information about a solution of sodium chloride.

SOME PROPERTIES OF SODIUM CHLORIDE SOLUTION

Grams of NaCl/liter	Moles/liter (58.5 g is one formula weight or one mole)	Vapor pressure observed at 100°C, mm.	Vapor pressure of water at 100°C, mm	Drop in vapor pressure due to salt, mm
58.5	1	734.8	760	25.2
117	2	707.9	760	52.1

We notice that doubling the amount of salt in solution in this case practically doubles the drop in vapor pressure.

Considering substances that do not ionize, we shall find that one mole in 1000 g of solvent (*molal* solution)[1] on the average raises the boiling point 0.52°C. The boiling point of a solution containing 342 g of sugar

---

[1] Not to be confused with molar solutions. See Glossary.

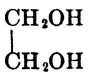
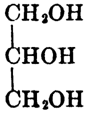
(one mole) in 1 kg of water is actually 100.55°C (760 mm); for 171 g (one-half mole), 100.27°C. Sugar has the formula $C_{12}H_{22}O_{11}$.

Let us consider a solution of sugar and water in which is contained one molecule of sugar for every nine molecules of water. At the surface of the solution the tendency for the vapor of the water molecules (sugar does not vaporize) to escape from the solution is nine-tenths that of a similar amount of pure water. We may say, therefore, that in general the addition of a dissolved solid material to a liquid decreases the vapor pressure of the liquid. Consequently, the temperature at which boiling occurs must be higher than that of the pure solvent alone, since boiling takes place when the vapor pressure of the liquid just exceeds the pressure of the gases above the liquid. If molecules or ions of a nonvolatile dissolved material hinder the escape of solvent molecules, it is evident that the temperature must be raised above the usual boiling temperature before sufficient vapor pressure is obtained to overcome the air pressure above. In this manner we explain the fact that the boiling point of salt water is higher than that of pure water.

In similar manner, formation of crystals is hindered by molecules of the solute. Fresh-water ice freezes out from sea water, but an extremely cold day is needed to freeze over an arm of the sea. Experiments show that a gram-molecular weight (one mole) of a nonionizing substance [32 g of wood alcohol (CH_3OH), for example] lowers the freezing point of 1000 g of water by −1.81°C. On the average, the lowering caused by a mole of all nonionized substances is 1.86°C.

Antifreeze Mixture. The formulas of four commonly used antifreeze liquids and some information about them is given in the following table. This information applies to the pure compounds only.

PROPERTIES OF ANTIFREEZE COMPOUNDS

Name	Formula	Molecular weight	Boiling point, deg C
Methanol, or wood alcohol (poison)	CH_3OH	32	64.7
Ethanol, or ethyl alcohol (sold denatured) (poison)	C_2H_5OH	46	78.5
Ethylene glycol	 $\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH\end{array}$	62	197.2
Glycerol, or glycerin	 $\begin{array}{l}CH_2OH\\ \vert\\ CHOH\\ \vert\\ CH_2OH\end{array}$	92	290

Let us compare alcohol with glycerin as an antifreeze. One gram of ethyl alcohol is twice as effective as 1 g of glycerin in lowering the freezing point, for alcohol has one-half the molecular weight of glycerin. On the other hand, alcohol has a boiling point below that of water and hence evaporates readily. There is no loss of glycerin by evaporation in the ordinary car, but glycerin solution is much more viscous (thick) at low temperatures and does not flow well through radiator tubes.

For the same amount of protection, loss of ethyl alcohol by evaporation is greater than loss of methyl alcohol, since much less methyl alcohol is needed. Also, the boiling point of methyl alcohol–water is lower than that of an ethyl alcohol–water mixture of the same freezing point.

A mixture of water 70 per cent, glycerin 15 per cent, and ethyl alcohol 15 per cent by volume has a freezing point of −20°C (−4°F) and a higher boiling point than an equivalent alcohol–water mixture.

Ethylene glycol is considered by many people to be the most reliable and effective antifreeze, but it is quite expensive. If it is saved from one winter to the next, however, the expense becomes a factor of less importance. Some antifreeze solutions also contain materials that prevent corrosion of the engine block. Such considerations as well as price should be weighed in selecting an antifreeze liquid.

Freezing mixtures containing ionized substances give very large freezing-point lowerings. This is to be expected, for ionized solutions have a larger number of particles than nonionized solutions. Icemaker's brine contains a large amount of dissolved calcium chloride ($CaCl_2$), and its freezing point is so low it can be kept very cold. Cans of pure water are frozen to ice rapidly when immersed in the cold brine. Solutions of salts have not been found satisfactory for automobile radiators and are not generally used.

Equilibrium. A pupil in the chemistry laboratory has made a solution of sugar and water. Sugar has been added to a given weight of water at room temperature and the mixture shaken until apparently no more sugar will dissolve, for some remains in the bottom of the vessel undissolved. Has the process by which sugar dissolves stopped functioning? The answer is "no."

That this answer is correct can be demonstrated by the "repair" of crystals. If small or fractured crystals are allowed to remain in contact with a saturated solution, the small crystals disappear and large ones are formed; the imperfections are filled in; and the crystals develop more perfect edges. This is a result of the continuous dissolving and recrystallizing of the solution.

Experiments show that dissolving proceeds continuously at the surface of the sugar crystals. This is to be expected, for in the haphazard molecular turmoil within a solution a condition of unsaturation must exist at some places here and there. Also, the condition for crystallization to take place must exist at other places within the liquid. In fact, when the solution is saturated and in contact with undissolved solute, the two processes of dissolving and crystallizing are each proceeding at equal rates, each producing the opposite effect. A balance, or equilibrium, of actions is the result.

$$\text{Water} + \text{undissolved sugar} \underset{\text{dissolving}}{\overset{\text{crystallizing}}{\rightleftarrows}} \text{sugar solution}$$

Another example of equilibrium is found in a closed bottle of household ammonia. This solution consists essentially of water and ammonia gas. The free space above the liquid contains air, water vapor, and ammonia molecules. Ammonia and water molecules are continually leaving and returning to the solution. When a bottle has stood a while at a given temperature, the rates of leaving and returning of the molecules are just equal. Since the effects of the two are opposite, an equilibrium is established. (See Fig. 12-5.)

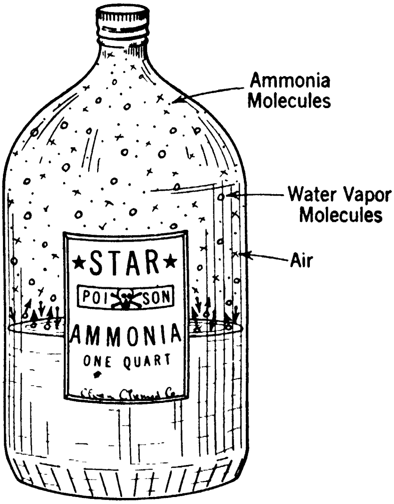


Fig. 12-5.—An equilibrium between moving molecules is illustrated in a closed bottle of household ammonia. The rate of evaporation is balanced by the rate of condensation.

Summarizing, we can readily tell whether a solution of a solid in a liquid is unsaturated, saturated, or supersaturated by adding a crystal of the solute. If the crystal dissolves, the solution is unsaturated. If the crystal remains unchanged, the solution is saturated at that temperature. If the addition of the crystal causes immediate crystallization, then the solution is supersaturated.

SUMMARY

Solutions consist of solvent and solute. Although water is the most common solvent, many others are used. Solutions are used extensively because (1) they are convenient, (2) they have uniform distribution of solute, and (3) chemical actions take place readily in them.

The solubility of a substance is the amount of substance that can be dissolved in a given amount of solvent at a given temperature. We commonly express it as the number of grams of solute in 100 g of solvent. For most solid solutes, solubility of a substance increases with an increase of temperature. Gases are less soluble at increased temperature but more soluble with increased pressure.

Temperature changes affect solubility. Substances that increase in solubility as the temperature rises absorb heat when they dissolve (endothermic change).

Substances that decrease in solubility as the temperature rises liberate heat when they dissolve (exothermic change). Temperature changes may be due in part to addition of H^+ ions to solvent water molecules. Mixing sulfuric acid and water is dangerous because of the heat evolved. The hydration of an anhydrous substance also liberates heat.

$$CuSO_4 + 5H_2O \rightarrow CuSO_4\,5H_2O \text{ (+ heat)}$$

The concentration of solutions used in chemical work is often given in terms of molecular units. A molar solution holds one gram-molecular weight (one mole) of solute in 1 liter of solution.

Saturated solutions hold a maximum amount of dissolved solute in the presence of excess solute at a given temperature.

Crystallization is the process of separating a solute from a solution in the form of crystals. Supersaturation results when crystals do not form from a saturated solution under special conditions.

The freezing point of a solution is the temperature at which the liquid and solid forms of a substance can be mixed without change in temperature.

The addition of solid solute lowers the vapor pressure and freezing point of a solution. The boiling point of a solution is the temperature at which its vapor pressure just exceeds the pressure above the liquid. The addition of a solid nonvolatile solute raises the boiling point of a solution.

The ideal automobile antifreeze liquid has low freezing point, high boiling point, low vapor pressure, low cost, and does not cause deterioration of rubber connections or corrode metal.

Excess solute in contact with a saturated solution is continually dissolving and recrystallizing at the same rate at a given temperature. This is an example of a dynamic equilibrium.

QUESTIONS

11. Distinguish a dilute from a concentrated solution.

12. How many grams of solute per liter are contained in molar solutions of each of the following compounds: NH_4NO_3; KNO_3; dextrose ($C_6H_{12}O_6$); $MgSO_4$; $CuSO_4$?

13. Of what can we be sure when undissolved solute remains in a solution after shaking?

14. The solubility of potassium nitrate is 31.6 grams in 100 grams of water at 20°C and 247 grams at 100°C. What happens when a saturated solution of potassium nitrate at 100°C is cooled to 20°C?

15. What conditions usually produce a saturated solution? A supersaturated solution?

16. What conditions disturb a supersaturated solution?

17. Define *freezing point; boiling point.*

18. What is the effect on freezing point, boiling point, and vapor pressure of a solution of a nonvolatile solute in water of: (*a*) adding more solute; (*b*) adding more solvent; (*c*) lowering the temperature?

19. What is the expected boiling point of a solution containing 1000 grams of water and 360 grams of dextrose ($C_6H_{12}O_6$)?

20. How much glycerin in 1000 grams of water will produce the same freezing point lowering as 32 grams of methyl alcohol (CH_3OH)?

MORE CHALLENGING QUESTIONS

21. One of the lowest temperatures that can be reached by mixing substances (−55°C) is obtained by mixing 1 pint of $CaCl_2 \cdot 6H_2O$ with 0.7 pint of snow in a vacuum bottle. Account for this very low temperature.

22. Calcium chloride solution has a low freezing point. Is this solution a satisfactory antifreeze liquid for automobile radiators? Is kerosene a satisfactory antifreeze liquid for radiators?

23. Examine or make some large crystals of sugar (rock candy), and tell how they were made.

24. Crystals sometimes form in jelly. As the jelly continues to stand, will the crystals change in size?

25. What happens to a liquid left standing in the open if: (*a*) it has a high vapor pressure; (*b*) it has a very low vapor pressure; (*c*) the circulation of air over the top increases?

26. Describe an experiment by which you can find the freezing point of glacia acetic acid. Demonstrate the experiment.

REVIEW

1. What is the percentage composition of dextrose ($C_6H_{12}O_6$)?

2. What is the density of phosphine gas (PH_3) at STP?

3. Find the molecular weight of a compound if 500 milliliters of its vapor weighs 1.03 grams.

4. Balance the following equations (*do not write in this book*):

(*a*) $Zn + H_3PO_4 \rightarrow Zn_3(PO_4)_2 + H_2$
(*b*) $Al(OH)_3 + HCl \rightarrow AlCl_3 + H_2O$
(*c*) NH_4NO_3 (heated) $\rightarrow H_2O + N_2O$
(*d*) $NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$
(*e*) $AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + Ag$

5. A $\left\{\begin{matrix}\text{sheep}\\ \text{cow}\end{matrix}\right.$ drinks $\left\{\begin{matrix}1\\ 2\end{matrix}\right.$ quarts of water $\left(\left\{\begin{matrix}950\\ 1900\end{matrix}\right.\text{grams}\right)$ from a tub in which ice is floating. How many calories does she supply to raise the temperature of this water to her body temperature $\left\{\begin{matrix}40\\ 37\end{matrix}\right.$ °C?

6. A solution is made by using 250 grams of $CuSO_4 \cdot 5H_2O$ in enough water to make 1 liter. What is the concentration of the solution in moles per liter?

UNIT THREE............CHAPTER XIII

ACID AND ALKALINE SOLUTIONS: NEUTRALIZATION

The sour taste of vinegar, pickled pigs' feet, sauerkraut, or pickles is due to an *acid*, acetic acid ($H \cdot C_2H_3O_2$). Unripe fruits, such as green apples, contain free acid. Some weeds, for example sour grass, taste sour because they contain free acid. Sour milk contains lactic acid ($H \cdot C_3H_5O_3$), and rancid butter develops the unpleasant taste of butyric acid ($H \cdot C_4H_7O_2$). The odorous reputation of male goats is said to be due to acids that are present in their perspiration.

The acids commonly used in chemical laboratories, however, are frequently much more active substances than those found in natural sources. They include hydrochloric acid (HCl), nitric acid (HNO_3), and sulfuric acid (H_2SO_4). Sulfuric acid is commonly used in industries; for example, it is used in one step of the process of making nails.

Opposed to the group of acid compounds is another group of compounds called ***bases*** or alkalies. Their water solutions have a bitter taste and a soapy feeling. Many such bases contain the hydroxyl group (OH) combined with a metal and are therefore represented by metallic ***hydroxides.*** The mild metallic hydroxides, limewater [$Ca(OH)_2$] and milk of magnesia [$Mg(OH)_2$], are sometimes used for internal medicine; but, like the strong acids, the strong hydroxides are too caustic to be taken into the mouth. The substance known as lye ($NaOH$) and household ammonia (NH_3 solution) are alkaline substances that are commonly used in the chemical laboratory and in the home. Sodium hydroxide ($NaOH$) and potassium hydroxide (KOH) are most often used in solution. These are soluble bases, called ***alkalies.*** Some parts of the body, the fluid of the small intestine for example, are alkaline.

We have discovered some members of a third group of useful compounds, salts. Common salt ($NaCl$) is the most familiar member of this

---

New Terms

- dissociate
- monobasic acid
- hydronium
- indicator
- alkali
- titration
- burette tubes
- concentration
- precipitation
- exothermic
- completion

class. We shall notice that the formulas for metallic salts do not start with the element hydrogen as do the formulas for acids. These compounds are ionized solids containing a positive metallic ion or its equivalent and another part, such as a negative chloride, nitrate, or sulfate ion.

Salts play many roles in our lives. The salts sometimes used for medicine (a "dose of salts") are indeed salts. Epsom salts ($MgSO_4 \cdot 7H_2O$) is used extensively both inside and outside the body. Rochelle salt was formerly used internally for the same purpose as Epsom salts, as a purgative. Both Epsom and Rochelle salts obtained their names before chemical compounds were named systematically.

Acids. Experiments with strong acids in dilute solution show that they have a sour taste, change a dye called ***litmus*** from blue to red, liberate hydrogen gas when placed with zinc or magnesium, act on carbonates to free carbon dioxide gas, and in general counteract the properties of bases. In water solution we notice that they all produce hydrogen ions.

$HCl \rightarrow H^+ + Cl^-$
hydrochloric acid

$H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$
sulfuric acid

$H_3PO_4 \rightarrow 2H^+ + HPO_4^{--}$
phosphoric acid

$H \cdot C_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^-$
acetic acid (slightly)

These properties, or characteristics, of water solutions of acids are due to the one common factor in these solutions, namely, the hydrogen ion.

We have pointed out that one property of an acid is its ability to counteract the properties of, or ***neutralize,*** a base. So important is this reaction that it can be given as a definition of an acid; that is, ***an acid is a compound that neutralizes a base.***

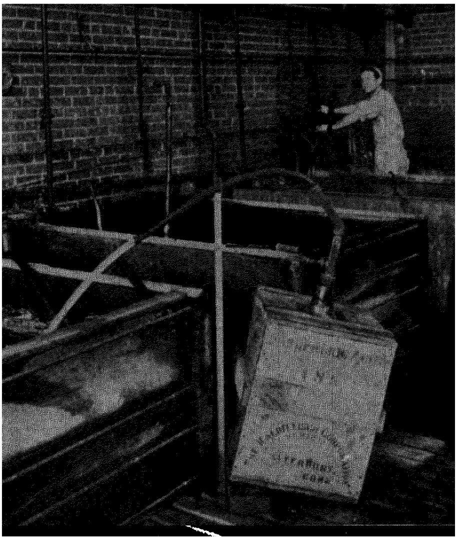
How Acids Are Made. Many acids are found in nature, and sometimes one method of obtaining them is extraction from the original source. Tartaric acid is obtained from grapes indirectly. The alchemists obtained formic acid by grinding up red ants in a mortar with a pestle. The name formic means "pertaining to ants." Formic acid is injected under our skin by such insects as bees, mosquitoes, or hornets when they sting us.

A second method of obtaining acids is by using water and an acidic oxide. The oxides of all nonmetals produce acid solutions of varying strengths. The following equations show how some of these act:

$CO_2 + H_2O \rightarrow H_2CO_3$ carbonic acid
$SO_2 + H_2O \rightarrow H_2SO_3$ sulfurous acid
$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$ phosphoric acid
$SO_3 + H_2O \rightarrow H_2SO_4$ sulfuric acid

These oxides, since they merely lack the water to make them an acid, are often called ***acid anhydrides.*** Nitric pentoxide (N_2O_5) is an anhydride of nitric acid. Sand (SiO_2) is the anhydride of silicic acid (H_2SiO_3), although everyone knows that little chemical action takes place between the sea and the sand of the beach.

A third method of obtaining acids is to mix sulfuric acid with a salt of another acid. Sulfuric acid, a stable, cheap compound, has a boiling point higher than that of any other common acid. Consequently, the other acid may be changed to a vapor by heating and distilled out of the reaction mixture. Nitric and hydrochloric acids are manufactured in this way.



Courtesy of The Travelers Insurance Company

FIG. 13-1.—When compressed air is forced into this carboy of sulfuric acid, the liquid is forced out. Is this method of transfer safer than pouring?

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4 \quad (1)$$

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4 \quad (2)$$

At a higher temperature the sodium hydrogen sulfate acts with more salt,

$$NaCl + NaHSO_4 \rightarrow HCl + Na_2SO_4 \quad (3)$$

and therefore the net result of reactions (2) and (3) is

$$2NaCl + H_2SO_4 \rightarrow 2HCl + Na_2SO_4 \quad (4)$$

Reactions, such as the last two, that proceed in different steps are common in chemistry. Reaction (3) is interesting, for by this means children can make hydrogen chloride in toy chemistry sets without using the hazardous sulfuric acid. Note that this salt, $NaHSO_4$, has the action of a strong acid.

How Acids Dissociate. Some acids, hydrochloric acid for example, form one hydrogen ion or proton, H^+, per formula. $HCl \rightarrow H^+ + Cl^-$. When an acid of this kind acts with sodium hydroxide, a base containing one hydroxyl group or radical per formula, it takes but one formula weight of this metallic hydroxide to act completely with a formula weight of acid. Such an acid is called a ***monobasic*** acid.

Other acids form two hydrogen ions per formula; sulfuric acid is an example. $H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$. When the acid acts on sodium hydroxide, it takes two formula weights of this base to act with one formula weight of the acid.

$$2H^+ + SO_4^{--} + 2Na^+ + 2OH^- \rightarrow 2Na^+ + SO_4^{--} + 2HOH$$

Such an acid is called a ***dibasic*** acid. Dibasic acids dissociate in two steps. (1) $H_2SO_4 \rightarrow H^+ + HSO_4^-$. Then the hydrogen sulfate ion, which as we have already seen can act as an acid itself, dissociates into more simple parts. (2) $HSO_4^- \rightarrow H^+ + SO_4^{--}$.

Strength of Acids. Not all acids dissociate into ions by action with water with equal ease. Those which split off ions well and appear to have split off a large percentage of hydrogen ions or protons when dissolved in a lot of water are called ***strong*** acids; those which split off ions poorly, producing a small percentage of hydrogen ions when dissolved in water, are called ***weak*** acids. In a dilute solution, hydrochloric acid is completely ionized; it is therefore a strong acid. Acetic acid in vinegar and carbonic acid in "soda water" are very weakly ionized and are weak acids.

Further, it is known that the hydrogen ion or proton is a very additive particle; that is, it attaches itself to some substances easily. It is thought to attach itself quite readily to solvent water molecules, making $H^+ + H_2O \rightarrow H_3O^+$ or $H_2O{\cdot}H^+$, called the ***hydronium ion.*** Hence it would be more accurate to use the term hydronium ion instead of hydrogen ion, and in chemical writings both terms are encountered. We shall in general use H^+.

More evidence of the additive nature of the hydrogen ion may be secured from other common substances. If a hydrogen ion attaches itself to an ammonia molecule, an ammonium ion is formed. Two cases will illustrate this point.

$$NH_3 + H^+ \rightarrow NH_4^+$$
$$NH_3 + HCl \text{ (dry)} \rightarrow NH_4^+Cl^- \text{ (solid)}$$

Possibly this added ammonia molecule does not completely neutralize the acid properties of the hydrogen ion. We add concentrated ammonium chloride solution to magnesium and find that hydrogen is liberated just as it would be from any acid, but at a much slower rate.

$$\left.\begin{array}{r} Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow \\ Mg + 2NH_4Cl \rightarrow MgCl_2 + H_2\uparrow + 2NH_3\uparrow \end{array}\right\}\text{(formula equations)}$$

$$\left.\begin{array}{r} Mg + 2H_3O^+ + 2Cl^- \rightarrow Mg^{++} + 2Cl^- + H_2\uparrow + 2H_2O \\ Mg + 2NH_4^+ + 2Cl^- \rightarrow Mg^{++} + 2Cl^- + H_2\uparrow + 2NH_3\uparrow \end{array}\right\}\begin{array}{c}\text{(ionic}\\ \text{equations)}\end{array}$$

The ammonium ion, like the hydronium ion, is capable of giving up a proton and is thus an acid.

QUESTIONS

1. Define *acid.*

2. List four properties of acids.

3. To what common factor are the properties of the acids due?

4. Define and give an example of an acid anhydride.

5. What relationship does the compound $NaHSO_4$ bear to the compounds H_2SO_4 and Na_2SO_4?

6. Complete, write in formulas, and balance the following equations (*do not write in this book*):

Carbon dioxide + water →
Nitrogen pentoxide + water →
Sulfur trioxide + water →

7. (Answer in tabular form.) Write the formulas for three important acids. How many removable hydrogen atoms does each contain? Write the formulas of the ions formed when the acids dissociate. Are the acids strong or weak?

8. Distinguish a strong acid from a weak acid, and give an example of each.

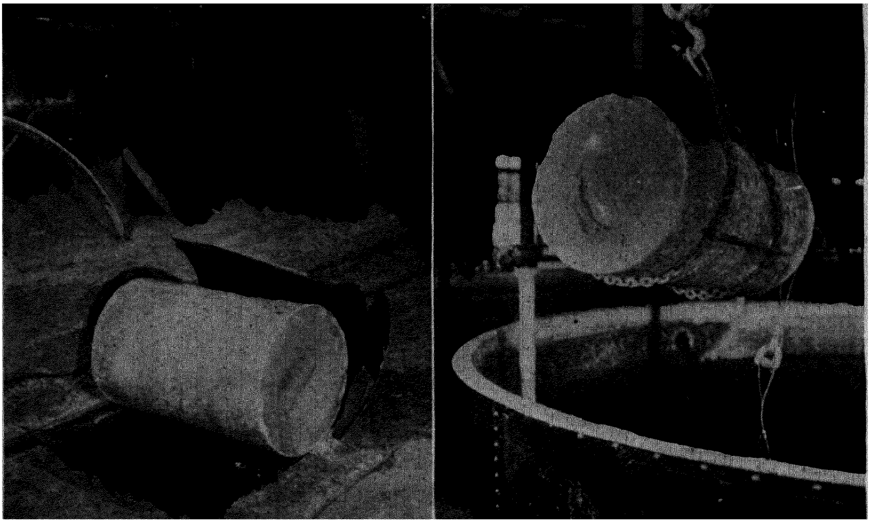
9. Write the formula equation for the action of hydrochloric acid on sodium, calcium, and aluminum, respectively. Beneath each write the ionic equation.

10. Repeat question 9, substituting sulfuric acid for hydrochloric acid.

Soluble Metallic Hydroxides. In testing soluble metallic hydroxides (alkalies), satisfactory personal contact can be made by dipping the finger tips into an alkaline solution of a soluble metallic hydroxide (NaOH, KOH); when rubbed together the fingers feel slippery. Such solutions change red litmus to blue and form a cerise-red color with phenolphthalein, an ***indicator*** of the same general use as litmus dye. They also act with carbon dioxide to form carbonates. If we examine the formulas of several metallic hydroxides, we find that they all contain hydroxyl (hydroxide) ions. When these compounds are soluble in water, the solutions are also found to contain hydroxyl ions

Solid Hydroxide		Solution in Water	Solid Hydroxide		Solution in Water
Na^+OH^-	→	$Na^+ + OH^-$	$Ba^{++}(OH)^-_2$	→	$Ba^{++} + 2OH^-$
K^+OH^-	→	$K^+ + OH^-$	$Ca^{++}(OH)^-_2$	→	$Ca^{++} + 2OH^-$

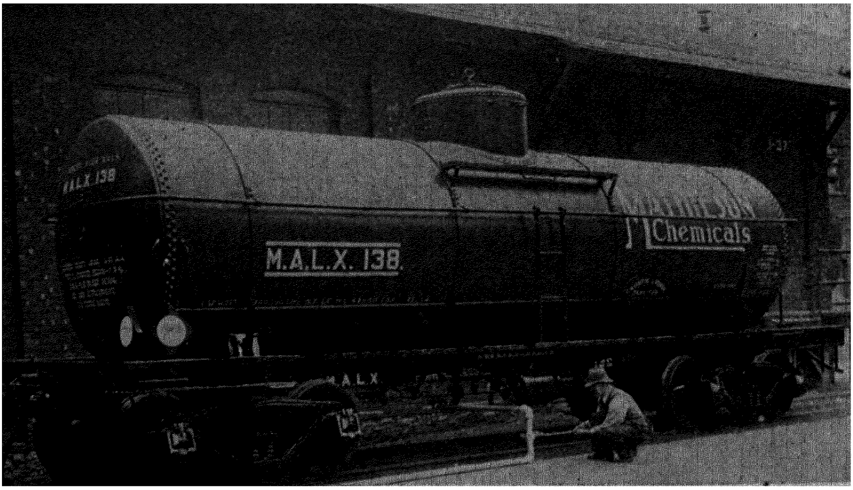
The properties that are common to alkaline solutions of hydroxides must be due to the hydroxyl ions (OH^-) present. The properties char-



Courtesy of The Mathieson Alkali Works, Inc.

(*a*) (*b*)

FIG. 13-2.—(*a*) A drum of solid sodium hydroxide (caustic) must be opened by using an axe. (*b*) Here a solid mass of sodium hydroxide is being lowered into a tank to prepare sodium hydroxide solution.



Courtesy of The Mathieson Alkali Works, Inc.

FIG. 13-3.—Unloading a tank carload of sodium hydroxide solution is a relatively simple matter.

acteristic of the hydroxyl ion are said to be those of a ***base.*** A partial definition of a base is ***a compound that produces hydroxyl ions when dissolved in water.*** Compounds, such as copper hydroxide [$Cu(OH)_2$] and aluminum hydroxide [$Al(OH)_3$], that dissolve very little in water contain hydroxyl ions; they are not considered to be active as bases because they do not dissolve sufficiently in water. The most active bases, caustic soda (NaOH) and caustic potash (KOH), are often called ***alkalies.*** A solution of ammonia in water was called ***volatile alkali*** by the alchemists because the basic properties would entirely disappear when the solution was warmed.

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O\uparrow.$$

This solution is only weakly basic because the reaction

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

does not proceed very far.

$$NH_4^+ + OH^- \underset{1\ \%}{\overset{99\ \%}{\rightleftarrows}} NH_3 + H_2O.$$

The compound NH_4OH does not exist as a solid. Ammonia water is a better name than ammonium hydroxide.

How Metallic Hydroxides Are Made. Many bases of importance are found in nature. These include carbonates and borates, sodium carbonate and borax being common examples. Certain regions are called "alkali country" because of these bases present in the soil.

If soluble metallic hydroxides are exposed to air, they absorb both moisture and carbon dioxide and change to carbonates.

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

Unlike the carbonates, these hydroxides are not found in nature.

A method of making hydroxides is to add one of the highly active metals to water. Hydrogen is replaced and a solution of the hydroxide formed. Evaporating to dryness leaves the hydroxide in the pure condition.

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

This method is interesting from a theoretical standpoint, but it is not used practically except when very pure bases are needed.

Another method of making hydroxides is to add water to a metallic oxide. This has a more practical application. It may be best illustrated by the slaking of lime.

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

Preparation of Insoluble Hydroxides. The two methods just described are somewhat limited. Hydroxides that do not dissolve in water may be made by the same methods by which any insoluble compound is produced; namely, a soluble salt containing the ion of the desired metal and an alkaline hydroxide are put together in solution. The hydroxide ions combine with the metal ion and form an insoluble compound called a ***precipitate,*** which can be removed from the liquid by filtering. For example, zinc chloride solution mixed with a limited amount of sodium hydroxide solution forms a thick gelatinous precipitate of zinc hydroxide.

$$ZnCl_2 + 2NaOH \rightarrow \underset{\text{insoluble}}{Zn(OH)_2\downarrow} + 2NaCl \quad \text{or} \quad Zn^{++} + 2OH^- \rightarrow Zn(OH)_2\downarrow.$$

Actions of Acids and Bases Together; Neutralization. A famous rhyme (Eugene Field, 1850–1895) tells the story of how

> "The gingham dog and the calico cat
> Side by side on the table sat. . . . "

During the night the two toys began to quarrel and then to fight. In the morning, much to the owner's dismay, both had disappeared. The poem concludes with the explanation,

> . . . "They ate each other up."

The action of a strong acid on a strong base is like that. When brought together in the right amounts (formula-weight proportions), such bases and acids destroy each other's characteristic properties. All the properties of the acid disappear, as do all the properties of the base. But in chemistry we cannot, with poetic license, have nothing left; experience stated in the law of conservation of matter tells us that something is left. The products formed are usually a salt and water. For example,

$$\underset{\text{base}}{NaOH} + \underset{\text{acid}}{HCl} \rightarrow \underset{\text{salt}}{NaCl} + \underset{\text{water}}{HOH}$$

$$\text{Sodium hydroxide} + \text{hydrochloric acid} \rightarrow \text{sodium chloride} + \text{water}$$

In terms of ions the same reaction is represented in this way:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + HOH$$

We may consider that the sodium and the chloride ions were present both before and after the action; therefore, they have not changed. The action is essentially

$$H^+ + OH^- \rightarrow HOH \quad \text{or} \quad H_3O^+ + OH^- \rightarrow 2HOH$$

The action between a base and an acid is called ***neutralization.*** In solution, water is formed, and the ions of a salt remain. If solid salt is desired, the water is evaporated.

QUESTIONS

11. Define *base.*

12. To what common ion are the properties of the soluble metallic hydroxides due?

13. Need bases be hydroxides? Need hydroxides be bases?

14. Define *alkali; alkaline solution.*

15. Write equations for the reaction of carbon dioxide on solutions of (*a*) potassium hydroxide, (*b*) calcium hydroxide, (*c*) barium hydroxide, (*d*) lithium hydroxide. (Li has combining number 1.)

16. Show by equation how to prepare by precipitation aluminum hydroxide, copper hydroxide, and zinc hydroxide.

17. Write formula equations for the neutralization of hydrochloric acid by (*a*) sodium hydroxide, (*b*) calcium hydroxide, (*c*) aluminum hydroxide, and (*d*) sodium carbonate. Beneath each write the ionic equation.

18. Repeat question 17, using sulfuric acid in place of hydrochloric acid.

19. What is the only important change that takes place in the process of neutralization of an alkaline solution by an acidic solution?

20. What is the effect of slaked lime [$Ca(OH)_2$] on "sour" soil? Of limestone?

Titration. When an experiment illustrating neutralization is carried out in the laboratory, the pupil selects the proper acid and base. For example, to make potassium sulfate by neutralization, molar solutions of potassium hydroxide and sulfuric acid are selected. About twice as much potassium hydroxide solution as sulfuric acid is required; they are mixed in a suitable vessel. The volume of the two solutions is usually measured in long graduated tubes called ***burettes.*** (See Fig. 13-4.)

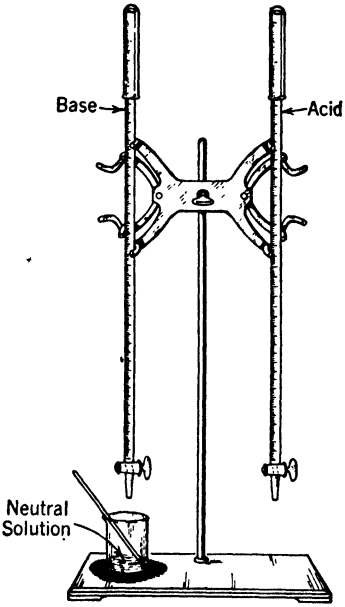


FIG. 13-4.—These burette tubes are used in titrating.

$$2K^+ + 2OH^- + 2H^+ + SO_4^{--} \rightarrow 2K^+ + SO_4^{--} + 2HOH$$

A sample is removed on a stirring rod and a drop placed on pieces of litmus paper of both colors. If the red paper turns blue, the base is in excess and more acid is added. If the blue paper still turns red, then more base is added cautiously, until one drop of the reagent is required to make the litmus indicator change color. The ***end point*** is then said to have been reached, and the salt may now be obtained by evaporation of the water.

An experimenter wishes to use this knowledge about acids and bases to find out the percentage of acetic acid in vinegar; this should be 4 per cent by law. He makes up a solution of a base, sodium hydroxide, of known concentration. He then measures out a definite amount of vinegar. While stirring he adds the base solution slowly to the vinegar until, as evidenced by use of the indicator, the end point, or complete neutralization, is reached. Much base will be needed if the acid in the vinegar is abundant, and little will be needed if the acid concentration is low. After measuring the volumes of vinegar and base solution used, the strength of the vinegar may be calculated.

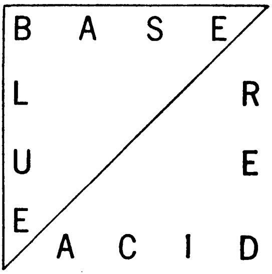
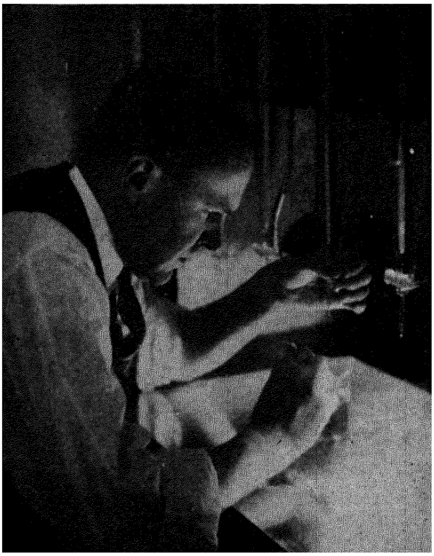


FIG. 13-5.—The litmus color changes are easily remembered by this memory aid.

The Acid-base Measuring Stick. A certain descriptive poem tells of the visit of some blind men to an elephant. Each gained an impression from the portion of the beast that he happened to touch, and each impression was different.

Water (HOH or H^+OH^-), like the elephant, apparently differs according to the angle of approach. Viewed from one end it shows the hydrogen ion, the mark of an acid; viewed from the other end it shows the hydroxyl ion, the sign of a base. Viewed face on, it is both acid and base at the same time—hence, neither.



Courtesy of The Travelers Insurance Company

FIG. 13-6.—Chemist Joseph Ficklen carries out a titration. Experimental work such as this gives facts that can be used to promote better health conditions in factories.

Thus our study of neutralization actions has shown that water is a compound which contains both the hydrogen ion of the acid and the hydroxyl ion of the base, but so nicely balanced that it is neutral. The position of water between acids and bases has given chemists the suggestion that a scale of acid strength and base strength can be made with water included at the middle point. Convenience shows that 14 divisions are needed on this scale, water being placed at the seventh division. A molar solution of hydrochloric acid lies at the 0 (zero) position, and a molar solution of sodium hydroxide lies at the position 14. Thus, pH SCALE

acid strength increasing	*water*	base strength increasing
←		→
0 1 2 3 4 5 6	7	8 9 10 11 12 13 14
	neutral	

The position of a substance in reference to the scale is called its pH, a term widely used today by persons in agriculture and in many industries. The pH of pure water is 7. This is an exact balance between hydroxyl and hydrogen (hydronium) ions. Acid solutions have pH lower than 7, and basic solutions have pH higher than 7. An acid of pH 2 has ten times higher concentration of hydrogen (hydronium) ions than a solution of pH 3.

A set of indicators of standard colors can be made in test tubes, each hue corresponding to a certain pH value. The experimenter follows a definite procedure and finds that the solution in his test tube has a color depending on its pH value. To find the position of the substance being tested on the scale, the experimenter makes a color comparison. The method is rapid, and in the hands of an experienced worker accurate enough results can be obtained for most industrial purposes. Litmus indicator is red in solutions with pH less than 7 and blue in solutions of pH more than 7, the depth of shade of color giving some clue as to how far from neutral the solution is. Many other indicators are known for the different pH ranges. Phenolphthalein is cerise red in solutions more alkaline than approximately pH 9. Test papers that show the approximate pH value of a solution by color changes are available. Hydrion B paper is one example. The paper is dipped into the solution to be tested. The pH value is then estimated by comparing the resulting color of the paper with a chart. The range is pH 1 to 11, and the colors vary from red through green in the same order as in the rainbow.

pH control is used in sugar manufacturing, water purification, paper manufacturing, baking, jelly making, canning, and other food industries, soil testing, bacteriology, and medicine.

	pH Values		pH Values
Apples	2.9–3.3	Milk (cow's)	6.4–6.8
Beans	7.3–7.5	Oranges	3.0–4.0
Blood (human)	7.3–7.5	Peaches	3.4–3.6
Bread, white	5.0–6.0	Pumpkin	4.8–5.2
Blackberries	3.2–3.6	Rhubarb	3.1–3.2
Corn	6.0–6.5	Saliva (human)	6.0–7.6
Flour, wheat	6.0–6.5	Soil, "sweet"	7.0–9.0
Grapes	3.5–4.5	Soil, "sour"	4.0–6.9
Ginger ale	2.0–4.0	Tomatoes	4.1–4.4
Fruit jelly	3.0–3.5	Vinegar	2.4–3.4
Lemons	2.2–2.4	Mineral water	6.2–9.4
Limes	1.8–2.0	Distilled water*	5.2–6.0
Molasses	5.0–5.4	Wines	2.8–3.8

* Due to CO_2 from air.

QUESTIONS

21. In a certain titration experiment twice as much acid as sodium hydroxide solution was required for neutralization. What is known about the relative concentration of the acid and the base?

22. At what point on the pH scale should an indicator change color if it is to show exact neutralization?

23. A certain soil changes blue litmus paper to pink. Suggest a possible pH value for this soil.

24. Is distilled water always exactly neutral (pH 7)?

25. Why is the method of testing with litmus paper by putting a drop of the liquid on the paper better for most purposes than dipping the paper into the solution?

Methods of Preparing Soluble Salts. ***1. Reaction of Acids and Bases.*** The other substances concerned in the examples of neutralization given were salts. Examination shows that these salts are related to both the acid and the base. They have the metallic ion from the hydroxide and all the acid except the hydrogen ion. Calcium nitrate, a salt, can be made by the action of calcium hydroxide on nitric acid and the resulting water removed by evaporation.

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$ (formula equation)

$$Ca^{++} + 2OH^- + 2H^+ + 2NO_3^- \rightarrow Ca^{++} + 2NO_3^- + 2H_2O$$ (ionic equation)

Here again it may be seen that such neutralizations consist in allowing the hydrogen ion and the hydroxyl ion to form water. Many soluble salts may be formed in this way.

2. Reaction of Metal and Acid.

$$Ca + 2HNO_3 \rightarrow H_2 + Ca(NO_3)_2$$ (formula equation)

$$Ca + 2H^+ + 2NO_3^- \rightarrow H_2\uparrow + Ca^{++} + 2NO_3^-$$ (ionic equation)

3. Reaction of Metal Oxide and Acid.

$$CaO + 2HNO_3 \rightarrow H_2O + Ca(NO_3)_2$$ (formula equation)

$$CaO + 2H^+ + 2NO_3^- \rightarrow H_2O + Ca^{++} + 2NO_3^-$$ (ionic equation)

4. Reaction of Metal Carbonate and Acid

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2\uparrow$$ (formula equation)

$$CaCO_3 + 2H^+ + 2NO_3^- \rightarrow Ca^{++} + 2NO_3^- + H_2O + CO_2\uparrow$$ (ionic equation)

5. Special Methods.

$$Ca(NO_2)_2 + O_2 \rightarrow Ca(NO_3)_2 \qquad \textit{(oxidation)}$$

$$\left\{\begin{array}{ll} Zn(NO_3)_2 + Ca \rightarrow Zn + Ca(NO_3)_2 & \text{(formula equation)} \\ Zn^{++} + 2NO_3^{-} + Ca \rightarrow Zn + Ca^{++} + 2NO_3^{--} & \text{(ionic equation)} \end{array}\right.$$

(replacement)

$$\left\{\begin{array}{ll} CaCl_2 + 2AgNO_3 \rightarrow 2AgCl\downarrow + Ca(NO_3)_2 & \text{(formula equation)} \\ Ca^{++} + 2Cl^{-} + 2Ag^{+} + 2NO_3^{-} \rightarrow 2Ag^{+}Cl^{-}\downarrow + Ca^{++} + 2NO_3^{-} & \text{(ionic equation)} \end{array}\right.$$

(precipitation of another compound at the same time)

Which Metallic Compounds Are Soluble? Experiments may be performed to show which compounds dissolve in water. The substances are shaken in water and the results recorded. Summarized, they are as follows:

		Except
Nitrates, chlorates, acetates, bicarbonates	Soluble	
Sodium, potassium, ammonium compounds	Soluble	
Chlorides	Soluble	Ag, Hg^{+}, Pb ($PbCl_2$ soluble in hot H_2O)
Sulfates	Soluble	Ba, Pb, Ca slightly
Carbonates, phosphates	Insoluble	Na, K, NH_4
Sulfides, hydroxides	Insoluble	Na, K, NH_4, Ca, Ba

Kinds of Chemical Changes. Chemical changes are classified according to type or sort. Some common types are combination, decomposition, displacement or replacement, and double replacement or double decomposition.

1. Combination. Two or more substances join to form one substance. This may be the result of a combination of two elements, an element and a compound, or two compounds. One compound is formed.

$$\begin{gathered} 2H_2 + O_2 \rightarrow 2H_2O \\ Zn + S \rightarrow ZnS \\ 2SO_2 + O_2 \rightarrow 2SO_3 \\ CaO + H_2O \rightarrow Ca(OH)_2 \end{gathered}$$

The general type of equation for an addition or combination reaction is

$$A + B \rightarrow AB$$

2. Decomposition. A single compound breaks down into two or more simpler substances. This sort of change is just the opposite of combination. The products formed may be elements, an element and a compound, or simpler compounds. Examples are

$$\begin{gathered} 2H_2O \rightarrow 2H_2 + O_2 \\ 2KClO_3 \rightarrow 2KCl + 3O_2 \\ CaCO_3 \rightarrow CaO + CO_2 \\ NH_4NO_2 \rightarrow 2H_2O + N_2 \end{gathered}$$

The general type of equation for a decomposition reaction is

$$AB \rightarrow A + B$$

Replacement Series
K
Ca
Na
Mg
Al
Zn
Fe
Sn
Pb
H
Cu
Hg
Ag
Pt
Au

3. ***Displacement or Replacement.*** Several examples of exchange reactions have been given in the description of the chemical actions of water with metals. One element, being more active than another in a compound, takes the place of that element. One element and the solution of a compound form a new compound while a different element is liberated. Examples are

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

(sodium replaces part of the hydrogen in water)

$$Fe + CuCO_4 \rightarrow FeSO_4 + Cu$$

(copper is exchanged for iron)

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

(hydrogen in the acid is exchanged for zinc)

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

(chlorine replaces bromine)

The general type of equation for an exchange is

$$AC + B \rightarrow AB + C$$

or

$$AC + B \rightarrow BC + A$$

4. ***Double Replacement, or Double Exchange.*** This sort of chemical change is like an exchange of partners in an old-fashioned square dance. It is also often called ***double decomposition.*** The second part of one compound exchanges with the second part of another compound. The same parts are written first in each compound. For example,

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$

Double-replacement reactions may often be considered as a special case of combination. The last three equations are combination actions when simplified in terms of ions.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$
$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4\downarrow$$
$$H^+ + OH^- \rightarrow H_2O$$

The general type of equation for double replacement is

$$AC + BD \rightarrow AD + BC$$

Reversible Chemical Actions. Nearly all chemical actions are reversible; that is, once the product(s) are formed, they act on each other to a greater or less extent to form the original substances. For example, let us consider the chemical action that takes place in a bottle of soda water as it stands on the grocer's shelf. The dissolved carbon dioxide gas molecules in the water solution are continually colliding with water molecules. The conditions are often just right for these collisions to result in chemical action, forming carbonic acid. $H_2O + CO_2 \rightarrow H_2CO_3$. The unstable carbonic acid is in turn continuously breaking down, again forming water and carbon dioxide. $H_2CO_3 \rightarrow H_2O + CO_2$. Both reactions are proceeding at the same rate, but they have the opposite effect. Under a given set of conditions, an equilibrium is maintained between a liquid and its vapor in the closed space above the liquid. We use the double arrow to represent this situation.

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$

The equilibrium condition means that a mixture of reacting substances and products is formed. In the example just given, a capped bottle of soda water contains water, carbon dioxide, and carbonic acid in solution.

Extent of Chemical Actions. Several factors influence the amount of each reacting substance present in an equilibrium. Important is the effect of ***temperature.*** In the reversible reaction

$$H_2O + CO_2 \rightleftarrows H_2CO_3$$

the carbon dioxide gas is less soluble at higher temperatures. Increasing the temperature, therefore, would favor the decomposition of carbonic acid, or the reaction indicated by the left-pointing arrow. An equilibrium would be established in which a small percentage of carbonic acid was present.

The higher the temperature, the faster the molecules move. Faster motion means more chance for collision and hence more opportunities for chemical reaction. A rise in temperature of 10°C frequently doubles the rate of a chemical reaction. A reaction that requires 20 minutes or 1200 seconds to complete itself at 20°C may be ended in 1 second if the temperature is 120°C.

The effect of ***pressure*** changes may also be noted. Gases are soluble in water in proportion to the pressure applied on them (Henry's law). A bottle of soda is capped under pressure in order to increase the amount of dissolved carbon dioxide in the liquid. The greater the pressure (within limits) with which the bottle is capped, the more carbonic acid is formed. What is the reaction favored when a bottle of soda is uncapped?

Another example of the effect of pressure is seen in the synthesis of ammonia, a reversible action, $N_2 + 3H_2 \rightleftarrows 2NH_3$. One volume of nitrogen and three volumes of hydrogen, four in all, make two volumes of ammonia gas. We should expect that an increase of pressure would favor the change from four volumes to two volumes, as indeed it does. We can say, then, that in reversible reactions temperature or pressure changes may favor one of the reactions more than the other and may thus alter the point at which an equilibrium is established.

A third substance introduced into an equilibrium may ***catalyze*** both actions. The result is that the equilibrium is established more quickly than without it. Even if the pressure is low, the formation of ammonia from its elements is greatly helped by a catalyst and its formation hindered if the catalyst becomes poisoned by impurities. Catalysts cannot start a reaction that does not proceed slowly by itself, and they do not affect the final concentration of products and reactants at the point of equilibrium.

Now let us consider a closed bottle of hydrogen and nitrogen. Nitrogen and hydrogen together act very slowly to form some ammonia. As soon as ammonia is formed, some of it begins to decompose. But meanwhile more nitrogen and hydrogen combine. Eventually the rate of formation is equaled by the rate of decomposition, and an equilibrium is established. It has been found that at 500°C and a pressure of 300 times that of normal air about 25 per cent of a proper mixture of nitrogen and hydrogen is changed into ammonia. In the presence of a catalyst this same ratio of nitrogen and hydrogen to ammonia is reached more quickly.

The sign $\rightleftarrows$ represents a chemical "push-of-war" game. Two actions are struggling against each other. If one team (chemical reaction) is to gain the advantage, there are just two possibilities: (1) it must be strengthened or (2) its opponent must be weakened.

A way to strengthen one chemical reaction so that it will gain ground over the other is to have an increased amount of one of the reacting substances crowded into the same space. If the equilibrium reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$ is considered again, it will be seen that, when the percentage of hydrogen is increased, the chances of hydrogen colliding and reacting with nitrogen are improved. It is as if someone in a milling crowd were counting how often he met people wearing eyeglasses. If he secured someone to help him observe, the chances are that the two would observe twice as many bespectacled people. If suddenly twice as many people in the same crowd should put on glasses, the chances of the two observers meeting people wearing eyeglasses would again be doubled. In chemical terms, the general rule is that the speed of a simple chemical action increases as the concentration of the reacting substances is increased. The ***concentration*** is defined as the amount of material in a given volume of space, for example, the number of moles per liter.

In the blast furnace in which pig iron is produced, the iron oxide ore comes in contact with hot carbon monoxide gas. Carbon dioxide and iron are formed. At the high temperature within the furnace, the iron is able to remove oxygen from carbon dioxide; therefore, the reaction is reversible.

$$\underset{\text{ore}}{Fe_2O_3} + 3CO \rightleftarrows 2Fe + 3CO_2$$

But do the smelters of iron allow the hard-won iron to be turned back into ore? No more than they can avoid. They provide such an excess of carbon monoxide that the carbon dioxide molecules are crowded away from the hot iron; they increase the concentration of carbon monoxide and reduce the concentration of carbon dioxide.

The principle involved is called the principle of mass action, and may be stated thus: ***An equilibrium reaction may be made to resemble a nearly completed reaction by increasing the concentration of one of the reacting substances or by decreasing the concentration of the product.***

The chemical way to weaken the opposition is to provide some means of removing one of the products as fast as it is formed. Four cases are worth investigating.

Completed Reversible Chemical Actions. Chemical actions that continue until one or more of the reacting substances is nearly used up are called "completed" actions. In what proportions were the reacting substances present if they are nearly used up at the same time?

1. One Product Is Removed. A completed or nearly completed action can be obtained from a reversible reaction by applying ***the principle of mass action,*** namely, removing one of the products as fast as it is formed and thus reducing its concentration. If we heat ammonia gas, it decomposes and establishes an equilibrium.

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

If the vessel is constructed in part of palladium, the hydrogen may pass through the palladium wall but the larger molecules of both nitrogen and ammonia do not. Removing the hydrogen reduces the extent of the reverse action and favors the decomposition reaction.

2. A Gas Escapes. Often a gas may be removed from the mixture of reacting substances. In the action $CaCO_3 \rightleftarrows CaO + CO_2\uparrow$, the carbon dioxide is a gas at the temperature of the reaction. If it is allowed to escape, limestone changes into lime. There is no chance for the reverse action to occur.

Likewise, in the case $NH_4Cl + NaOH \rightleftarrows NaCl + NH_3\uparrow + H_2O$, the ammonia is allowed to escape as a gas. Substances that leave the reaction as a gas (sometimes when the temperature is raised) are fittingly marked by the upward-pointing arrow ($\uparrow$).

3. A Solid Crystallizes. In the action $AgNO_3$ (solution) + HCl (solution) $\rightarrow$ $AgCl\downarrow$ (solid) + HNO_3 (solution), the silver chloride is a solid that is insoluble in water; it therefore leaves the region of the reaction, taking no more part in it than the container holding the reacting solutions. NH_3 (gas) + HCl (gas) $\rightarrow$ $NH_4Cl\downarrow$ (solid) is a chemical example of a reaction that resembles the physical process of rain condensing from water vapor. Both cases are called ***precipitation,*** a word connected in meaning with the act of falling down. The insoluble substance formed, called a ***precipitate,*** may be marked by the downward-pointing arrow. Barium sulfate precipitates in the following reaction:

$$BaCl_2 \text{ (solution)} + H_2SO_4 \text{ (solution)} \rightarrow BaSO_4\downarrow \text{ (solid)} + 2HCl \text{ (solution)}$$

This is another example of a reaction that goes on nearly to completion. It is obvious here that the reacting substances must be somewhat soluble in water and one product, possibly more, insoluble. The barium sulfate formed in the example is a very insoluble substance. The rules for the insolubility of common compounds have already been given (page 227). When insoluble substances separate, the reversible reaction proceeds nearly to completion.

4. An Un-ionized Product Is Formed. Whenever an un-ionized or slightly ionized product is formed, a reaction goes to completion. Water is a familiar example of a slightly ionized compound. When water is formed from the hydrogen ion of an acid and the hydroxyl ion of a base, the reaction is carried to completion.

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

is an illustration. The details of this reaction have already been described (page 222).

Hydrolysis. The experiment of neutralization (page 223) shows that when sodium hydroxide neutralizes hydrochloric acid the resulting solution is neutral and has pH 7. A solution of sodium chloride was prepared by mixing the acid and the alkaline solutions in the exact proportions to form sodium chloride and water. Sodium hydroxide is a highly dissociated basic substance, and in solution hydrochloric acid is a highly dissociated acid.

Suppose we substitute acetic acid, a weakly dissociated compound, for the hydrochloric acid and attempt to neutralize it with sodium hydroxide. We find that, when we have added the acid and the base in equivalent reacting quantities, the solution is still quite strongly alkaline. We can accomplish the same result by dissolving crystals of pure sodium acetate in distilled water and testing the solution with litmus. The red litmus turns blue since the solution is alkaline and not neutral. Since acetic acid is weakly dissociated, it does not release as many hydrogen ions to the solution as does hydrochloric acid, and hydroxyl ions from sodium hydroxide are in excess. The acetate ion in sodium acetate actually takes up hydrogen ions from the water, thus:

$$Na^+ + C_2H_3O_2^- + H_2O \rightleftarrows Na^+ + HC_2H_3O_2 + OH^-$$

Sodium carbonate solution is also basic. This is due to the weak dissociation of carbonic acid or even of the hydrogen carbonate ion.

$$2Na^+ + CO_3^{--} + H_2O \rightleftarrows 2Na^+ + HCO_3^- + OH^-$$
$$Na^+ + HCO_3^- + H_2O \rightleftarrows Na^+ + H_2CO_3 + OH^-$$

Hydrolysis is defined as the ***action of an ion with water.*** It is a very common type of reversible reaction and is the reason why solutions of many salts are alkaline. For example, trisodium phosphate (Na_3PO_4), borax ($Na_2B_4O_7 \cdot 10H_2O$), sodium sulfite (Na_2SO_3), sodium sulfide (Na_2S), and potassium cyanide (KCN) are all salts containing an ion derived from a weak acid.

A solution of ammonium chloride in distilled water is acidic, as can readily be determined by testing. This is due to the fact that the ammonium ion is an acid in itself (page 218).

$$NH_4^+ + Cl^- + H_2O \rightleftarrows NH_3 + H_3O^+ + Cl^-$$

A solution of ammonium chloride is sufficiently acid to release hydrogen when placed on carefully cleaned magnesium.

Salts like copper sulfate ($CuSO_4$), aluminum chloride ($AlCl_3$), and zinc chloride ($ZnCl_2$) also form acid solutions. Their positive ions react with water, and hydrogen ions are produced in the solution. The following equation in part explains the complicated type of reaction that occurs:

$$Cu^{++} + H_2O \rightarrow [Cu(OH)]^+ + H^+$$

Copper hydroxide [$Cu(OH)_2$] is insoluble; but since no precipitate forms when copper sulfate is dissolved in distilled water, it would not be correct to say that copper hydroxide is a product of the reversible reaction of copper sulfate with water. Because the acidity can be traced to the action of the positive ion (Cu^{++} in this case) with water, it is an example of hydrolysis.

In some instances an insoluble product of hydrolysis does form. This product can be separated and analyzed.

$$BiCl_3 + H_2O \rightarrow BiOCl\downarrow + 2HCl \qquad \text{(formula equation)}$$
$$Bi^{+++} + 3Cl^- + 3H_2O \rightarrow (BiO^+Cl^-) + 2H_3O^+ + 2Cl^- \qquad \text{(ionic equation)}$$

Complete hydrolysis may occur.

$$TiCl_4 + 4H_2O \rightarrow Ti(OH)_4 + 4HCl$$

The titanium hydroxide immediately decomposes.

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$$

The hydrolysis of titanium tetrachloride is a reaction used in making smoke screens; for titanium dioxide is a dense white material, and hydrogen chloride forms a fog in moist air.

Energy Changes in Chemical Changes. If a firecracker is set off, a boisterous explosion results. The compounds formed by the chemical change have less energy than those which went into the change. The energy liberated heated the products and their surroundings so quickly that they expanded forcibly, chiefly in the gaseous state.

If we strike a match so that it catches fire, heat and light are produced in the rapid combustion. The compounds formed by the burning have less energy than those on the original match. The extra energy is converted into heat and light energy. The production of electrical energy may be the result of chemical changes, such as those which occur inside the battery of a hand flashlight. Let us recall that reactions which liberate energy are called ***exothermic.***

In the electrolysis of water, energy is absorbed; therefore, it must be provided by the battery or generator. Frequently chemical changes must have energy supplied by outside means in order to maintain the reaction. Heating is necessary to maintain the reaction of steam on coke. $H_2O + C \rightarrow H_2 + CO$. These substances do not react when they are cold; and since heat is absorbed during the reaction, the mixture will cool unless heating is continued. Again we should remember that reactions which absorb heat are called ***endothermic.***

Starting Chemical Reactions. Sometimes a high temperature is required for a chemical change to start. Thereafter the reaction furnishes its own heat, maintaining the temperature necessary to keep it going. When gasoline vapor and air are raised to a high temperature by a very hot spark jumping across a spark-plug gap on the cylinder of an automobile motor, the mixture explodes. The expanding gas furnishes the power to drive the car. Hydrogen and oxygen can be mixed safely when they are cold; but when a lighted match is applied to the mixture, the spread of the flame throughout the gas is so rapid that it cannot be readily measured. Hydrogen passed over copper oxide gives no reaction unless the oxide is warmed. When, however, the chemical action occurs readily, enough heat comes from it to cause a glow to spread throughout the mass. When finely divided iron and sulfur are heated together in the right proportions, the heat liberated by their reaction maintains the high temperature. $Fe + S \rightarrow FeS$ (+ heat).

A balance between chemical changes giving out heat and physical changes taking in heat (evaporation in this case) may be illustrated by an experiment.

Equal volumes of carbon tetrachloride (CCl_4) and carbon disulfide (CS_2) are mixed in a dish. The mixture is set on fire by applying a lighted match. The flame is not uncomfortably warm, as may be demonstrated by dipping the hand into the burning liquid and bringing it out covered with flames. This experiment must be performed in a well-ventilated hood, for ill-smelling and poisonous gases are formed by the chemical change.

The general principle relating energy changes to chemical changes may be expressed as follows: Compounds that liberate much energy when they are formed are stable. This energy is called the heat of formation.

Unstable compounds give out little energy or even take in energy when they are formed.

HEAT OF FORMATION
(For a gram formula weight at 18°C)

Name	Symbol	Kcal
Aluminum chloride	$AlCl_3$	166.8
Ammonium nitrate	NH_4NO_3	87.9
Ammonium nitrite	NH_4NO_2	62.2
Calcium carbide	CaC_2	14.6
Calcium oxide	CaO	151.7
Carbon dioxide	CO_2	94.4
Carbon disulfide (liquid)	CS_2	−22.0*
Copper oxide	CuO	34.9
Dihydrogen oxide (water)	H_2O	68.4
Hydrogen peroxide	H_2O_2	44.5
Lead azide (detonator)	$Pb(N_3)_2$	−100.6*
Mercury fulminate (detonator)	$HgC_2N_2O_2$	−64.5*
Mercury oxide	HgO	21.7
Phosphorus oxide	P_2O_5	365.8
Sodium chloride	$NaCl$	98.4
Sodium bromide	$NaBr$	86.3
Sodium iodide	NaI	69.5

* Endothermic.

So important are the energy changes of chemical reactions that chemists learn many of the facts of chemistry by their study. Other practical people are also much interested in the energy that comes from chemical changes. Every fuel is valued because of the energy it produces when burned, not for the products of combustion alone.

Theories Change. As we shall see, Mendeleyev's first great generalization of the periodic law was later improved by Moseley. Moseley's addition in no way lessens the value of Mendeleyev's contribution to the progress of science.

The kinetic molecular theory in its original form does not describe exactly the behavior of gases, for it assumes that the gas molecules themselves occupy no space and that they have no forces of attraction for each other. Refinements of measurement, especially at higher pressures than are used in elementary laboratories, show that additions must be made to Boyle's law. Then the behavior of gas volumes is described more precisely. The more exact statement of the law is used, for example, by the designers of Diesel engines.

The fact that Boyle's law is limited in its description of the behavior of gases does not detract from its great usefulness.

In a similar fashion, the theory of ion formation and of the actions of solutions has been developed further. We live in a world in which the chemistry is chiefly a chemistry of water solutions. Certainly all life processes are tied up with the chemistry of water solutions. In describing his theory of ionization in 1887, Svante August Arrhenius (1859–1927) of Sweden did not have the benefit of the knowledge of atomic structure that we possess today. Also, he limited his consideration to the chemistry of water solutions, naturally enough.

Since the time his theory of ionization was stated, other developments have taken into account the knowledge of atomic structure and have broadened the theory to include all types of solutions. These theories have been stated by P. Debye, E. Hückel, J. N. Brønsted, T. M. Lowry, M. Usanovich, G. N. Lewis, and many others. The details of their experiments and theories are beyond the scope of an elementary book on chemistry.

SUMMARY

Acids have the following general properties: They taste sour; change blue litmus paper to red; act with active metals, liberating hydrogen; act with carbonates, liberating carbon dioxide; and neutralize alkalies. These properties are all thought to be due to the presence of hydrogen ions (H^+), or protons, in water solutions of acids.

Some acids are found in nature in plant or animal bodies. Acids can be made by the action of an oxide of a nonmetal with water and by the action of sulfuric acid on a salt. Soluble acids dissociate hydrogen ions in water solution; strong acids dissociate well and weak acids poorly. Hydrogen ions, or protons, attach themselves readily to water and to ammonia to form hydronium (H_3O^+) ions or ammonium (NH_4^+) ions.

Soluble metallic hydroxides are alkalies, or bases, but the term base includes other compounds, also. Soluble metallic hydroxides have the following general properties: They have an unpleasant bitter taste; feel slippery to the fingers; form alkaline solutions; change red litmus dye to blue; absorb carbon dioxide to form carbonates; and neutralize acids. These properties are thought to be due very largely to the presence of hydroxyl ions (OH^-) in their solutions in water.

A base has the properties of the hydroxyl ion in solution, and it can neutralize an acid. A substance with marked basic properties is an alkali.

Few metallic hydroxides are found in nature. They are prepared by the action of an active metal on water, liberating hydrogen, and by the interaction of oxides of active metals with water. Insoluble hydroxides are prepared by precipitation.

Neutralization is the interaction of a base and an acid. In water solutions, essentially it is

$$H^+ + OH^- \rightarrow H_2O$$

or

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

Titration is a method of carrying on neutralization or similar reactions and measuring the amounts of solutions used. Titration may be used to find the total concentration of an unknown base or acid.

The pH scale numbers show the relative strength of an acidic or alkaline solution. Water has pH 7, acids less than 7, and bases more than 7. Indicators are sensitive within certain pH ranges. Litmus changes color at almost pH 7.

Salts may be prepared by neutralization; by metal plus acid; by metal oxide plus acid; by metal carbonate and acid; and by special methods. The solubility of salts is summarized in solubility rules.

Chemical changes may be classified according to types:

1. Combination. One product is formed from at least two starting materials.
2. Decomposition. Starting with one substance, at least two products form.
3. Displacement. An element reacts with a compound, liberating a second element and forming a new compound.
4. Double replacement. Two compounds interchange parts.

The replacement, or electromotive, series is a list of elements in order of decreasing chemical activity.

Some reactions are reversible. In reversible reactions, an equilibrium of two opposite chemical reactions is set up, under a given set of conditions of concentrations, temperature, and pressure.

The rate of a chemical reaction is influenced by temperature; by pressure if a gas is among the reacting substances or products; by the presence of a catalyst; and by the concentration.

The principle of mass action may be expressed as follows: A reversible equilibrium reaction can be made to approach a nearly complete reaction by increasing the concentration of one of the reacting substances or by decreasing the concentration of the product.

Without changing the temperature or pressure, a nearly completed chemical reaction results when (1) a gas escapes, (2) a solid crystallizes from solution, or (3) an un-ionized product forms from ions.

Chemical actions that liberate energy are called exothermic. Chemical actions that absorb energy are called endothermic. Compounds that liberate much heat when they form are stable; others are unstable.

Hydrolysis is the action of an ion on water. Owing to hydrolysis, solutions of some salts act alkaline to litmus, and others acidic. If the salt removes hydrogen ions, then its solution is alkaline; if hydroxyl ions are removed, then the solution is acid.

QUESTIONS

26. Write equations showing how the following salts may be prepared by neutralization: KNO_3; $CaCl_2$; $MgSO_4$; $Zn(C_2H_3O_2)_2$; $AlCl_3$.

27. Show by formula equations how to prepare (*a*) copper chloride (cupric) in three ways; (*b*) zinc nitrate in five ways; (*c*) magnesium sulfate in five ways.

28. List four important types of chemical changes, and give an example of each.

29. To what type of chemical changes do neutralization reactions belong? (Form of answer: "Neutralization reactions belong to the double-replacement type."—good. "Double replacement."—not so good. The answer should be in the form of a complete sentence.)

30. List three factors that influence the rate of chemical reactions. State clearly the effect of each.

31. State the principle of mass action.

32. Under what three conditions may the double-replacement type of chemical actions be made to go to completion?

33. Illustrate each type mentioned in question 32 by a balanced formula equation.

34. Which compound is easier to decompose, carbon disulfide or water? (HINT: Use table, and calculate heat of formation in kilocalories per gram.)

MORE CHALLENGING QUESTIONS

35. Concentrated sulfuric acid dissociates one hydrogen ion more readily than two. Write the equation for both dissociations.

36. Look up in the dictionary the definition of the word *alkali*, especially the original meaning. From what language does the word come? List some other terms used in chemistry or elsewhere that come from the same language.

37. Write equations for the reactions of acetic acid, nitric acid, sulfurous acid, and phosphoric acid each on potassium hydroxide, ammonium hydroxide, and calcium hydroxide (12 equations in all). Under each formula equation, write the ionic equation.

38. In a certain titration three times as much acid as base was required for complete neutralization. What is the relative concentration of the acid and the base? In general in a titration, what relationship exists between the volume of liquid used and its concentration?

39. Write equations for the reaction of sulfuric acid on both sodium carbonate and trisodium phosphate, showing in each case the various stages in the process of neutralization.

40. Explain in terms of ions the hydrolysis of solutions of: (*a*) zinc chloride; (*b*) sodium acetate; (*c*) sodium phosphate; (*d*) aluminum sulfate; (*e*) cupric chloride.

UNIT THREE............CHAPTER XIV

ELECTRICITY AND CHEMISTRY

We are all familiar with the many useful services performed by electricity. By harnessing this valuable servant, which Benjamin Franklin first drew down from the skies on a kite string, we can now conveniently sew, sweep, cure the sick, start automobiles, send messages, and shave. Also, we find that interesting results are obtained when the relationships between electricity and chemistry are investigated.

When electricity is passing through any metallic conductor, ***solid*** or ***liquid,*** such as a copper wire or a pool of mercury, it may be noticed (1) that the metal gets warmer than it would be otherwise and (2) that the region around the metal influences a compass needle. We say that a magnetic field is set up. Likewise, when electricity is passing through a water solution of a salt these same two effects may be noted and also a third. The solution becomes changed chemically; new substances are formed. This chemical process of making changes in composition in a liquid by means of electricity we call ***electrolysis.*** These statements refer, in general, to the electric current from a dry cell, a storage battery, a rectifier, or a direct-current generator (one-directional current) (d.c.). The type of electric current supplied to many homes today is called alternating current (a.c.) because it changes its direction rapidly—in most localities sixty times each second.

Chemists are able to produce substances that carry or conduct electricity well. Copper is the most important commercial carrier of electricity. Such metallic carriers of electricity, common metals and carbon in the form of graphite, are good ***conductors.*** Melted salts and solutions of acids, bases, and salts in water are fair electrolytic conductors. All other products of the chemist's art are poor conductors of electricity. These substances, such as hard rubber, glass, porcelain, sulfur, and synthetic resins like Bakelite and Lucite, are called insulators. Obviously

---

New Terms

anode
cathode
conductor
electrolyte

inhibitor
graphite
silicon
abrasive

anodized
cell
electroplating

if we are to control electricity we must have both suitable insulators and suitable conductors.

A Simple Electrolysis Experiment. We can learn the principles of electrolysis by a simple apparatus. (See Fig. 14-1.) It consists of a drinking glass partly filled with copper sulfate solution ($CuSO_4$), the electrolytic solution. Copper sulfate is the ***electrolyte*** in this case. Two rods, one of carbon and the other of copper, hang into the solution without touching each other. The copper strip is connected to the positive (+) post of a dry cell and is called the ***anode.***

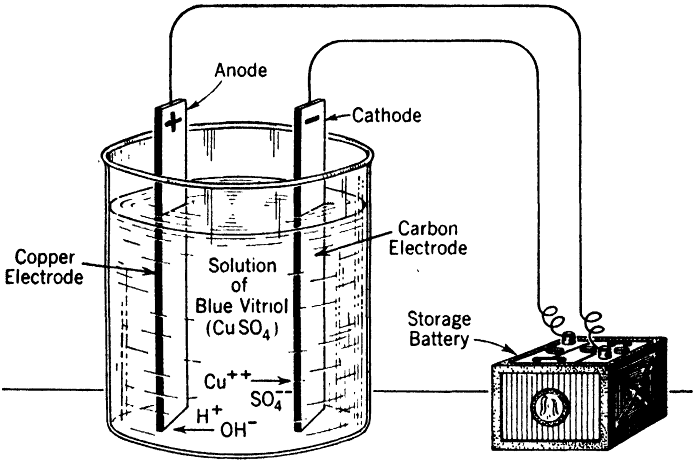


FIG. 14-1.—This apparatus is called a cell. Two general types of cells are used: one, dry cell or storage battery, for example, generates electricity by chemical actions; in the other, as in this case, a chemical change is carried out when electricity is sent through the cell.

The carbon strip is connected to the negative (−) post of the dry cell and is called the ***cathode.*** The copper ions (Cu^{++}) in the copper sulfate solution are attracted to the negative carbon strip and move in the solution to this cathode. There they receive two electrons per ion from the cathode, which is crowded with extra electrons, and become copper atoms.

$$\underset{\text{reduction of copper}}{Cu^{++} + 2e^-} \rightarrow \underset{\text{atom}}{Cu^0} \qquad (e^- = \text{electron})$$

The copper atoms plate out, or deposit themselves, on the carbon rod as metallic copper. A thin layer of pink copper is noticed on the carbon cathode soon after the wires are connected to the apparatus. This apparatus does simple copper-plating! It can be shown that the amount of deposit on the carbon rod depends upon the amount of current flowing and also upon the length of time that the current flows.

Meanwhile, at the anode the copper rod is losing weight. The copper atoms are oxidized to copper ions, and these are supplying ions to the solution.

$$Cu^0 \rightarrow Cu^{++} + 2e^-$$

If we desire to clean the carbon strip after the experiment, we can immerse it in nitric acid, which attacks the copper but not the carbon. A more appropriate method, however, is to reverse the flow of electrons by changing the connections to the ***dry cell.*** The copper ions now deposit on the copper strip, which becomes the cathode, and copper atoms are taken off the inactive carbon anode, leaving it black and uncoated as it was at the start.

Commercial electroplating processes use the principles brought out in the previous experiment. If, for example, an electroplater wishes to coat silver over a spoon of less expensive metal, the spoon is first scrupulously cleaned. Then, without touching it by hand, the spoon is made the cathode in a solution that contains silver ions (commercially, silver and cyanide ions). The anode is a bar of pure silver. When the current is turned on, a deposit of silver forms on the spoon. This may be polished to give a fine luster. The evenness of the plating, the strength with which the coat is bonded to the spoon, and its cost depend on the skill of the worker.

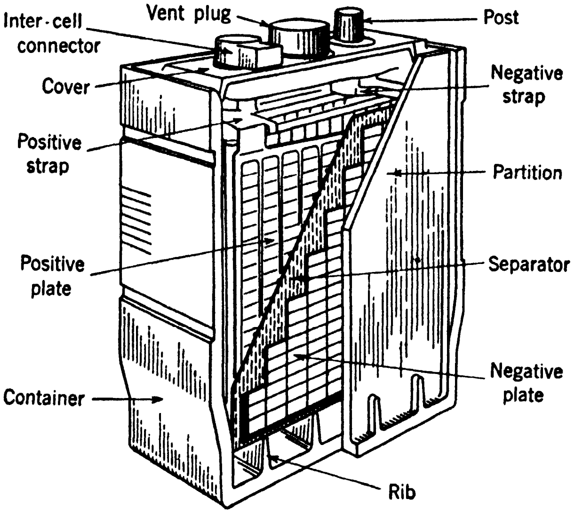


FIG. 14-2.—A complete storage battery cell (without acid) is cut away in order to show details.

Depositing copper and zinc together on a cathode produces a plate of brass. Even rubber latex particles can be deposited by the electrolytic process to produce rubber-coated articles. The metalwork on automobiles and hundreds of articles of household hardware and office machinery are electroplated with metals, chromium, nickel, brass, or cadmium, often with copper plating beneath. Some jewelry is gold-plated; even inexpensive containers for lipstick and other cosmetics are sometimes covered with a thin layer of pure gold, applied by electroplating.

We have examined a chemical change brought about by passing an electric current through a solution. Now let us investigate the reverse process, namely, the chemical actions occurring in a cell by which electricity is generated.

Producing Electricity. Many chemical actions, burning for example, produce heat. Most oxidation-reduction reactions can be made to liberate electrical energy as well. The chemical action in a storage battery is a good example of an oxidation-reduction reaction that produces electricity. The charged battery has two sorts of plates immersed in dilute sulfuric acid. The gray lead plates are the negative (−) plates, and the chocolate-colored lead dioxide (PbO_2) plates are the positive (+) ones. (See Fig. 14-2.)

At the cathode of a discharging storage battery the lead becomes lead sulfate. The lead loses two electrons per atom, or is oxidized to form lead ions. These join sulfate ions, precipitating as insoluble lead sulfate.

$$Pb^0 \rightarrow Pb^{++} + 2e^-$$
$$Pb^{++} + SO_4^{--} \rightarrow Pb^{++}SO_4^{--}\downarrow$$

The two electrons (accompanied by millions more) run around the circuit outside the battery, possibly lighting a headlight on the way, and arrive at the lead dioxide anode. Here they reduce lead dioxide to lead ions, which also precipitate as lead sulfate.

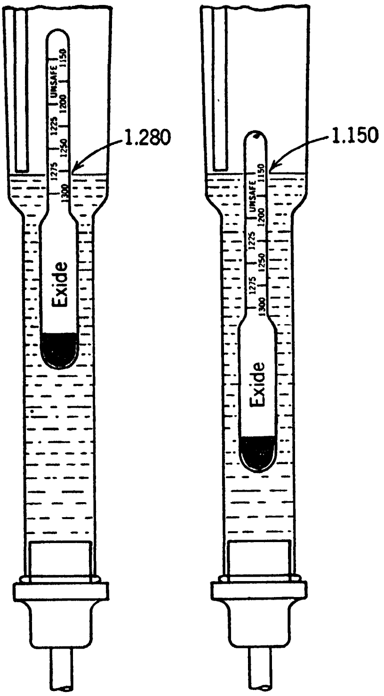
$$2e^- + PbO_2 + 4H^+ \rightarrow Pb^{++} + 2H_2O$$
$$Pb^{++} + SO_4^{--} \rightarrow Pb^{++}SO_4^{--}\downarrow$$

The total reaction is

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4\downarrow + 2H_2O$$

when the battery furnishes current.

As this chemical action goes on, both plates gradually become changed to lead sulfate, sulfuric acid is used up, and the liquid becomes diluted with water. The density of the liquid falls to 1.150 g per ml, almost that of water, 1.00. (See Fig. 14-3.) The supply of electrons rushes through the starting motor of a car over wires when we push the starting button. We say that an electric current is "flowing." More chemical action takes place to maintain the supply of electrons. There is a limit to this action, however, for after a while the battery will "go dead."



Courtesy of Exide Battery Company

FIG. 14-3.—The float rides higher in the hydrometer when the sample of liquid is taken from a fully charged battery than it does when the acid is taken from a discharged battery. The hydrometer reading to the left is 1.280 for a charged battery and to the right 1.150 for a discharged battery.

After the car is operating, the engine of the car runs a generator that supplies electricity to the battery, charging it again for future startings. In the battery, the chemical action is reversed, and the plates restored to their original composition—one to lead and the other to lead dioxide. Meanwhile, the liquid becomes more concentrated with sulfuric acid and more dense because the acid is exchanged for water. A fully charged battery should have a sulfuric acid–water mixture of density about 1.280 g per ml, or "twelve-eighty."

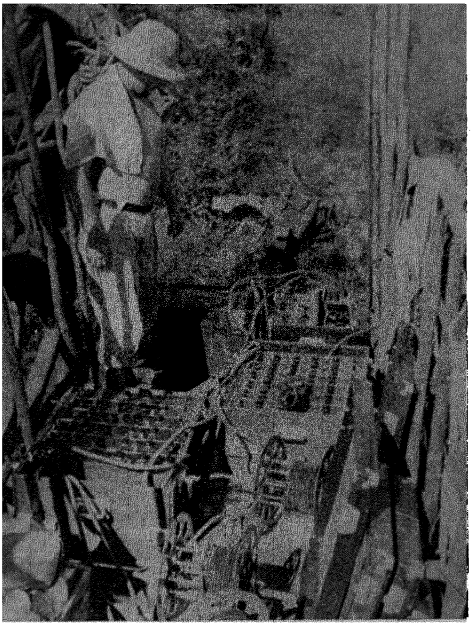


FIG. 14-4.—A chemical change in the storage battery here sends an electric current through some dynamite. The violent chemical change that follows sets up vibrations in the earth. The seismograph records these earth vibrations, and by them the explorer locates oil—maybe.

In charging the battery the following equation applies:

$$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$$

Electrons are restored to some lead ions of the lead sulfate at one electrode and removed from an equal number at the other electrode.

$$2Pb^{++} \rightarrow Pb^0 + Pb^{++++}$$

The storage battery, then, is a specialized chemical device designed to carry out a chemical change that produces electricity. The battery stores "chemicals," not electricity.

The Dry Cell. The "dry" cell with which we light our flashlight and operate bells and buzzers is wet inside. Contained in the zinc cup that forms the outer metal case is a paste consisting of the following: graphite; an oxidizing agent, usually manganese dioxide (MnO_2); and the acid, ammonium chloride (sal ammoniac, NH_4Cl). In the center is a carbon rod, which is sometimes labeled positive (+). (See Fig. 14-5.) Chemical action proceeds rapidly in the cell when the + and − terminals are connected by wires to form a circuit as is the case when a person lights a flashlight. The zinc is oxidized, releasing electrons and placing them on the zinc cup itself, which becomes the negative (−) terminal.

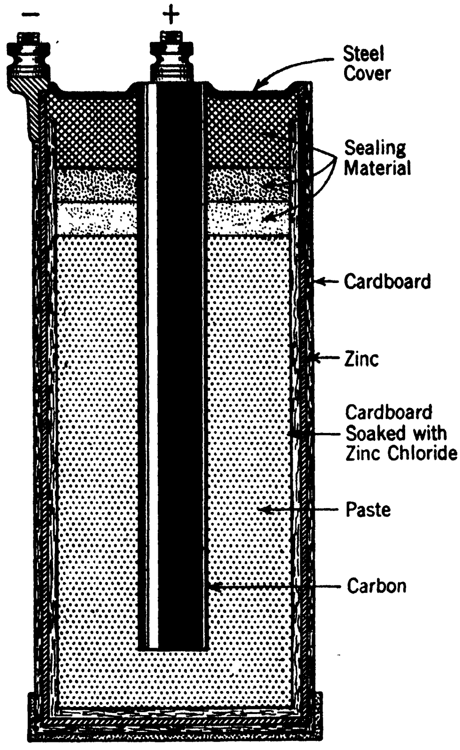


FIG. 14-5.—This cross section of a dry cell shows that it is actually wet inside.

$$Zn^0 \rightarrow Zn^{++} + 2e^-$$

Zinc ions (Zn^{++}) are formed in the solution. At the anode manganese dioxide is reduced in a rather complicated action.

$$2e^- + 2MnO_2 + 2NH_4^+ \rightarrow Mn_2O_3 + H_2O + 2NH_3\uparrow$$

When either the zinc cup or the paste becomes used up, the cell is worthless. No way has yet been discovered to reverse this action satisfactorily, but dry cells may be partly recharged if not allowed to run down too far.

QUESTIONS

1. Distinguish a conductor from an insulator of electricity.

2. Make a labeled diagram of a cell for the electrolysis of silver nitrate solution, using a silver anode and a platinum cathode.

3. Trace the path of silver from anode to cathode in silver plating.

4. Name three electroplated articles on an automobile or at home; name both the foundation metal and the coating metal in each case.

5. Rhodium is a precious metal about twice as expensive as gold. Account for the fact that rhodium-plated articles can be purchased at a five-and-ten-cent store.

6. Distinguish a storage cell from a dry cell.

7. List three "dos" and three "don'ts" in taking care of a storage battery.

8. Why should pure water be added to a storage battery from time to time?

9. What is the most satisfactory method of testing the condition of charge of a storage cell?

10. Does any useful metal remain in a worn-out storage battery? In a worn-out dry cell?

Producing Metals by Electricity. Chemists are faced with a challenge today. There is a steady demand for light metals, but such metals are also active chemically and hard to extract from the natural materials in which they are discovered in the earth. Heating them with powerful reducing agents, such as coke, hydrogen, or carbon monoxide, is not a vigorous enough treatment to free them. In 1807 Sir Humphry Davy (1778–1829) first used electricity to liberate these very active metals.

Sodium is one of these metals. There is plenty of this element on the earth, but it is locked tightly in a chemical compound with chlorine, in the form of sodium chloride, or common salt. To unlock the element sodium from the salt, we first melt the salt by heating it carefully. An anode and a cathode are placed in the molten or fused liquid in a Downs cell, but no water is present. The sodium ions respond when the current is turned on and move to the cathode.

$$\text{Na}^+ \text{ (ion)} + e^- \rightarrow \text{Na}^0 \text{ (atom)}$$

In a similar manner the chloride ions carry electrons to the anode, lose their burden at the anode, become free chlorine atoms, seek a partner, and escape as chlorine molecules.

$$\text{2Cl}^- \text{ lose } 1e^- \text{ per atom} \rightarrow \text{2Cl}^0 \text{ (atoms)}$$
$$\text{2Cl (atoms)} \rightarrow \text{Cl}_2 \text{ (molecule, a package of two atoms)}$$

This experiment must be done with care if the sodium is to be obtained. When this was first accomplished, Sir Humphrey Davy, who used melted sodium hydroxide instead of melted salt, soon discovered that the shiny metal, sodium, had to be protected from contact with substances that attack it. These include air, water, and the substances formed at the anode.

Davy describes his product from the electrolysis of potassium hydroxide (KOH), a previous experiment in 1807, thus:

> . . . small globules, having a high metallic lustre, and being precisely similar in visible characteristics to quicksilver, appeared; some of which burned with explosion, and bright flame, as soon as they were formed, others remained, and were merely tarnished, and finally covered with a film, which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash.

Sodium metal is soft and silverlike when fresh. Care must be taken to avoid contact between this metal and water, and for this reason it is shipped in vacuum-sealed tin cans and kept immersed in kerosene in the laboratory. In contact with water, sodium liberates hydrogen by replacing it from the water so vigorously that the gas may catch fire. The gas escapes so quickly that an explosion may be caused and hot lye spattered around the neighborhood.

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

The element sodium is too active for the purposes to which ordinary metals are put. It is too soft for hardware. Most of the sodium produced is used in the making of sodium cyanide (NaCN) and tetraethyl lead for gasolines. Sodium finds many special uses in chemical laboratories; and we may find it inside sodium-vapor lights—the road lights that give out a yellow glow. In these lights the sodium and the inert gas neon are enclosed together in a sealed glass tube. No chemical action takes place in the sodium-vapor light; the sodium vapor glows. The same yellow glow can be duplicated easily by throwing salt in a fire. A sensitive test for sodium is to clap one's hands near a colorless flame of a Bunsen burner. The dust will give a yellow flash in the flame.

Compounds made from the element sodium include sodium cyanide (NaCN) used in electroplating, hardening steel, and in obtaining gold; and sodium peroxide (Na_2O_2) used in bleaching.

The method for making potassium is similar to that for making sodium. Magnesium, calcium, beryllium, and the important metal aluminum are also made by electrolysis of fused salts. In each instance the fused compounds of the metals are used for the electrolyte, water, which would prevent the formation of the metal, being avoided.

Purifying Metals by Electricity. Ordinary copper in wires for carrying electricity is remarkably pure, 99.8 per cent. Impure copper not only carries electricity poorly but in addition wastes it by converting it to heat. An electrolytic method is employed in making this exceptionally pure commercial product cheaply. Slabs of cast impure (blister) copper to serve as anodes are hung in a tank of copper sulfate solution. Sandwiched between these, but not touching them, are cathodes of thin pure copper sheets. (See Fig. 14-6.) An enormous surge of electrons at a low voltage is used. When the current is turned on, the cathodes grow at the expense of the anodes. (See Fig. 14-7.) Impurities drop out and settle to the bottom of the tank. Among them are metallic silver and gold. These precious metals when recovered from the sludge in the tank may be of sufficient value to pay most of the cost of refining the copper.

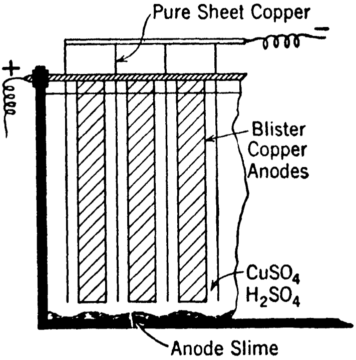
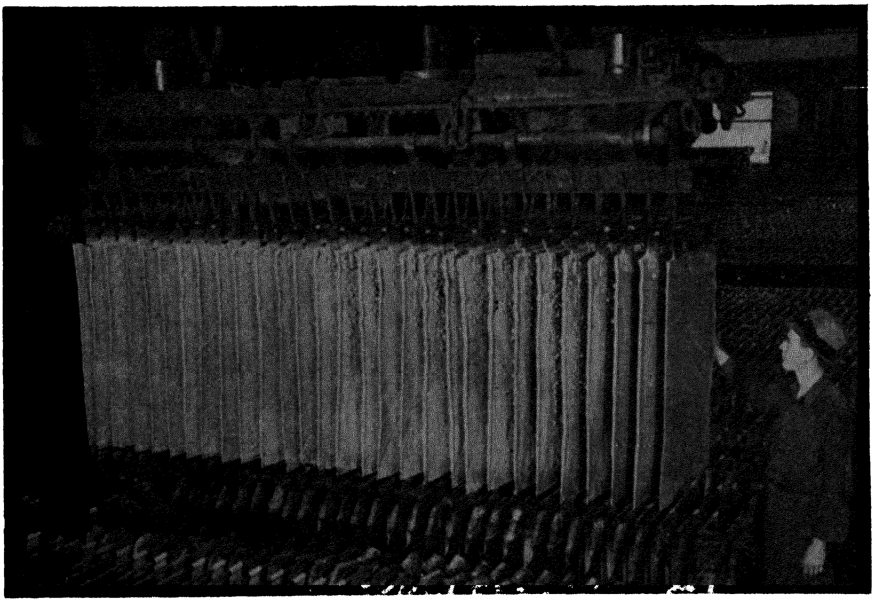


FIG. 14-6.—This type of cell is used for refining copper. The copper forms ions at the anode, and these ions deposit on the cathode. Electrical energy provides the moving force. The impurities in the anode sink to the bottom of the liquid.

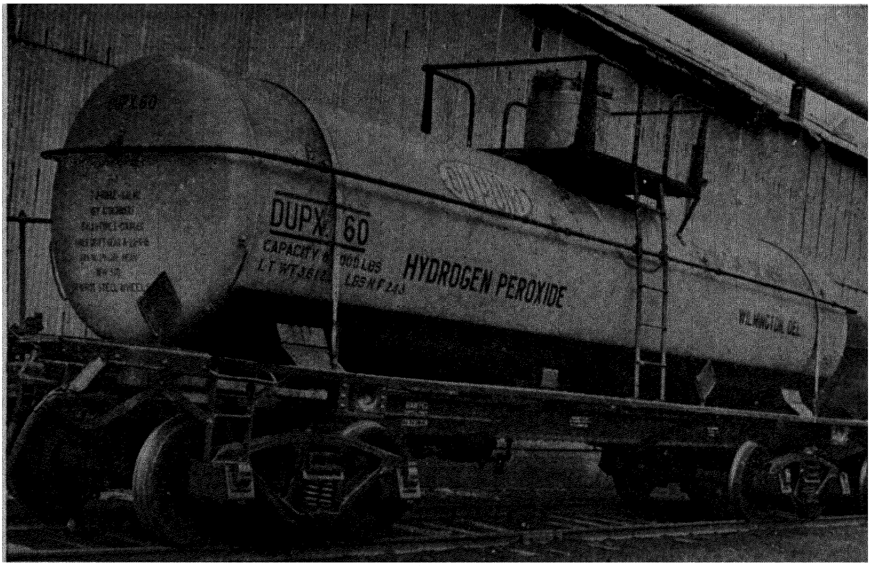


Courtesy of Anaconda Copper Mining Company

FIG. 14-7.—Cathodes of pink pure copper are lifted from the commercial cell after refining. Most of this metal is destined to be used for such electrical purposes as wiring houses for electric lights.

Some lead and zinc are refined by electrolysis, and highly pure iron may also be prepared by this method.

At the Anode. We should not overlook the fact that valuable products come from chemical changes occurring at the anode as well as at the cathode. When a silver spoon is to be replated, all former platings are first removed by making the spoon an anode in an electrolytic bath. Afterward it is ready for an even, fresh coating. Such an "anodizing" process saves silver. Some metals, aluminum for example, are anodized (oxidized at the anode) to give them special finishes and to make them corrosion resistant. The important gas chlorine is collected at the anode. Potassium permanganate is produced commercially by anodic oxidation of manganese ions.



Courtesy of E. I. duPont de Nemours & Company, Inc.

FIG. 14-8.—Highly concentrated hydrogen peroxide is now available in carload lots.

Making Hydrogen Peroxide. Hydrogen peroxide, often used at home as a mild antiseptic or bleaching agent, is made at the anode in a cooled electrolytic cell containing ammonium sulfate [$(NH_4)_2SO_4$] and sulfuric acid. The product is obtained by adding concentrated sulfuric acid to the material obtained at the anode, peroxysulfuric acid, and distilling the hydrogen peroxide under reduced pressure. The 3 per cent solution sold at retail stores is often labeled "10 volume" peroxide. One pint of this liquid will produce 10 pints of oxygen at standard temperature and pressure. Manganese dioxide (MnO_2) serves as a catalyst, or promoter, of the decomposition of hydrogen peroxide; acetanilide ($C_6H_5NHCOCH_3$), as a retarder.

The compound is unstable, especially if impure. It breaks down easily, even explosively, into water and oxygen.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

As prepared for the market, an inhibitor like acetanilide is usually included to retard decomposition. Hydrogen peroxide is used commercially for bleaching animal products—silk, hair, wool, and feathers—and to make other peroxides. When it is poured slowly on a wound, oxygen bubbles are released from the blood and this helps cleanse the wound. Peroxides have an oxygen-to-oxygen valence bond. In hydrogen peroxide we may represent it as $\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$ or H—O—O—H.

QUESTIONS

11. In what part of the replacement series are the metals that are produced by electrolysis of fused salts located?

12. Write formula equations for (*a*) decomposition of sodium hydroxide into elements by electrolysis; (*b*) burning of sodium to form sodium peroxide; (*c*) action of sodium on water; (*d*) action of sodium on melted aluminum chloride.

13. What test is used to identify the presence of sodium in a compound?

14. Why must water be avoided in the preparation of metallic calcium?

15. Point out an advantage gained by the electrolytic refining of copper.

16. Make a labeled diagram of a cell for the refining of copper, (*a*) at the start of the process and (*b*) at the close of the process.

17. For what purpose are aluminum airplane parts *anodized?*

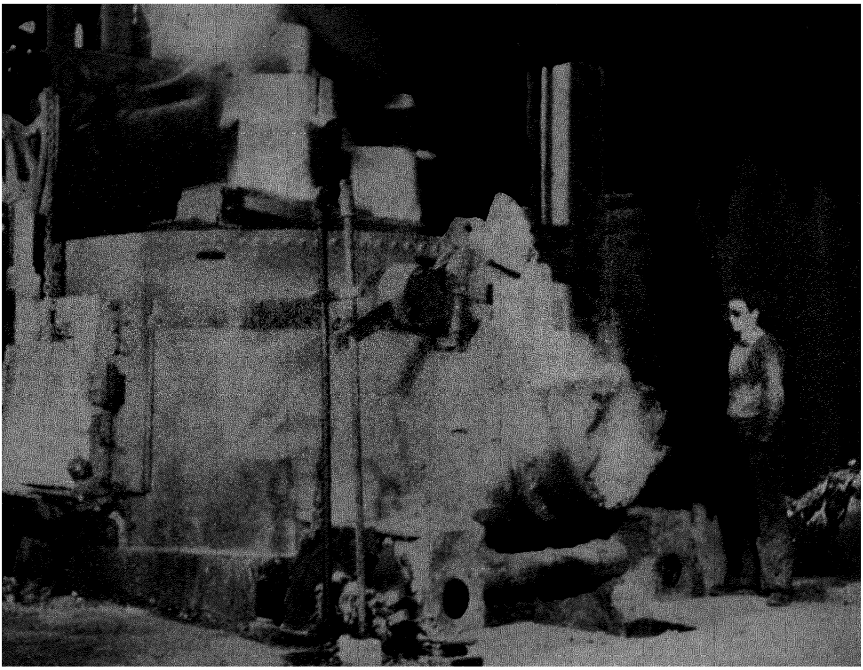
18. Why should we not represent hydrogen peroxide (H_2O_2) by the formula HO?

19. Give three uses for hydrogen peroxide.

20. Write formula equations for (*a*) the decomposition of hydrogen peroxide when heated; (*b*) the action of hydrogen peroxide on sulfurous acid; (*c*) the action of sodium peroxide on potassium nitrite solution; (*d*) the action of hydrogen peroxide on sodium sulfite solution; (*e*) the action when hydrogen sulfide is bubbled into hydrogen peroxide (free sulfur is one product).

Chemical Changes Brought About by Electric Heat. The modern electric light bulb is a light source of reasonably high efficiency. But it is also an electric furnace of a sort, for part of the electricity produces heat. The changing of electricity into heat has some advantages, namely: (1) A very high temperature can be obtained. (2) The heat can be directed where it will do the most good. (3) Very little energy is wasted in the change from electricity to heat.

Two chief types of furnaces are in use today for changing electricity into heat: (1) the arc furnace; (2) the resistance furnace. The arc furnace (see Fig. 14-9), first developed by Henri Moissan (1852–1907), a French scientist of great ingenuity, consists essentially of two carbon rods that are allowed to touch and then are drawn slightly apart. When connected to a source of electricity, an arc, or spark, of carbon vapor at an exceedingly high temperature will enable the electricity to jump the gap. This electric arc is one of the hottest spots on earth. Its temperature is estimated at 4100°C. That of the sun's surface is thought to be 6200°C. A crucible placed directly beneath the arc becomes heated intensely.



Courtesy of American Iron and Steel Institute

FIG. 14-9.—In this large electric arc furnace for refining steel, the entire furnace serves as a crucible. Three white-hot electrodes are seen at the top. The liquid metal pours out over the cup-shaped lip in the foreground when the furnace is tipped.

The other type of furnace depends upon the resistance, or opposition, that certain substances offer to the passage of electricity through them. A flatiron contains a high-resistance unit that becomes warm when electricity is turned on. A toaster or hair curler contains nichrome (an alloy of nickel and chromium) wires or other wires that do not oxidize easily but glow red-hot when they carry the current. Heating elements of this sort embedded in the walls of a furnace make a convenient and concentrated source of heat used for steel analysis, hardening metals, and annealing.

Graphite. Graphite occurs naturally as a mineral, but it is also manufactured in electric-resistance furnaces. To make graphite, a bed of hard coal is placed between two huge conductors of electricity. The coal offers great resistance to the passage of the current, and little arcs, or sparks, jump between the lumps of coal. The heat converts the coal into crystalline carbon, or graphite. Most of the impurities are vaporized.

Graphite (plumbago) is a suitable material for making crucibles because it melts at a very high temperature. It is a good lubricant, for the crystals are thin plates that slide over one another easily. Graphite with more or less clay is the writing substance in so-called "lead" pencils. Powdered graphite dusted over objects makes them conducting so that they may be electroplated.

Silicon. If we wish to produce silicon to use in preparing special steels, a furnace similar to the graphite furnace is loaded with mixed sand and coke. A sand covering over the top of the charge shuts out air as in the graphite furnace. A core of carbon through the charge in the furnace ensures a conducting path of high resistance. A great surge of current rushes through the furnace when the power is turned on. Great heat is produced, and the sand and coke act on each other.

$$\underset{\text{sand}}{SiO_2} + \underset{\text{coke}}{2C} \rightarrow \underset{\substack{\text{carbon}\\\text{monoxide}}}{2CO\uparrow} + \underset{\text{silicon}}{Si}$$

The carbon monoxide gas escapes through the loose walls of the furnace and burns as soon as it reaches the air.

Silicon Carbide. Useful silicon carbide can be made by a process similar to that of making silicon except that a larger proportion of powdered coke is used in the mixture. In practical work some sawdust and salt are mixed with the sand and coke in order that the mass may be somewhat porous.

The extra coke this time reacts with the silicon to form silicon carbide (SiC).

$$Si + C \rightarrow SiC$$

Silicon carbide is crystalline, shiny, and so extremely hard that it will scratch glass; it is used extensively at home and in factories for grinding steel. Such hard substances are called ***abrasives.*** Many carbides are very hard. Masses of iridescent crystals are found near the core of the silicon carbide furnace, glistening and handsome. Prepared for market, the crystals are crushed, graded according to size, and bonded with clay, rubber, Bakelite or other plastics to form a whetstone, or grinding wheel. Trade names for silicon carbide include Carborundum and Crystolon.

Phosphorus. In another application of the electric-resistance furnace elementary phosphorus is produced. The furnace is loaded with quarried rock phosphate [$Ca_3(PO_4)_2$], sand, and coke. Let us call calcium phosphate [$Ca_3(PO_4)_2$] equivalent to 3CaO and P_2O_5. The action that occurs may be described by the following equations:

$$6CaO + 6SiO_2 \rightarrow 6CaSiO_3$$
$$2P_2O_5 + 10C \rightarrow 10CO\uparrow + P_4\uparrow$$

The phosphorus vapor leaves the furnace with the carbon monoxide gas, and both are run through cold water. The phosphorus condenses to a white, waxlike solid, but the carbon monoxide continues through as a gas. The calcium silicate is a liquid at the temperature of the furnace and is allowed to run off from time to time.

Carbon Disulfide. Another useful substance prepared by electric heat is carbon disulfide. The furnace is charged (loaded) with mixed coke and sulfur. The sulfur is a nonconductor, but the carbon carries the electricity and produces heat in so doing. At a high temperature the sulfur vaporizes. The sulfur vapor passes through the arc between the carbon electrodes and joins with the carbon.

$$C + 2S \rightarrow CS_2$$

The carbon disulfide formed in the furnace is a gas. It is led off through an opening near the top and cooled; a clear, sparkling liquid is formed. Pure carbon disulfide is reported to have no objectionable odor. The material used in most laboratories, however, has a disagreeable odor. The odor may be endured to some degree, but no more than is necessary, for it is poisonous. The liquid is very useful as a solvent; it dissolves rubber, sulfur, phosphorus, and many other materials insoluble in water. Also, it is used to make another solvent, carbon tetrachloride.

$$\underset{\text{carbon disulfide}}{CS_2} + \underset{\text{chlorine}}{3Cl_2} \rightarrow \underset{\text{carbon tetrachloride}}{CCl_4} + \underset{\text{sulfur chloride}}{S_2Cl_2}$$

Chloroform, used as an anesthetic and a solvent, can be obtained by reduction of carbon tetrachloride.

$$\underset{\text{carbon tetrachloride}}{CCl_4} + \underset{\text{hydrogen}}{H_2} \rightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{hydrogen chloride}}{HCl}$$

"Carbide" and Aluminum Oxide. The electric furnace led to the discovery of calcium carbide. Lime and coke were heated together in an arc-type furnace at an exceedingly high temperature. The new substance formed, calcium carbide (CaC_2), was gray-brown, and it liberated much gas when thrown into a pail of water. The gas, which was found to burn readily with a sooty flame, was recognized as acetylene ($H—C\equiv C—H$). In the furnace the reaction is

$$\underset{\text{lime}}{CaO} + \underset{\text{coke}}{3C} \rightarrow \underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} + \underset{\substack{\text{carbon}\\\text{monoxide}}}{CO\uparrow}$$

In water the action is

$$\underset{\substack{\text{calcium}\\\text{carbide}}}{CaC_2} + \underset{\text{water}}{2H_2O} \rightarrow \underset{\substack{\text{slaked}\\\text{lime}}}{Ca(OH)_2} + \underset{\text{acetylene}}{C_2H_2}$$

Aluminum oxide melted in an electric furnace (see Fig. 14-10) and then cooled and crushed makes an excellent abrasive. It is hard and has sharp edges. Many tons of this material, called corundum, are used to make emery wheels for grinding steel.

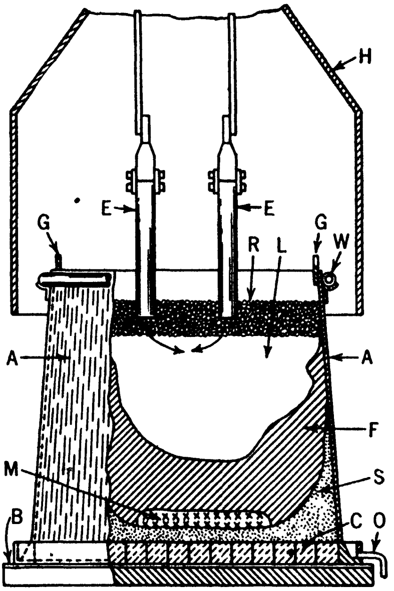


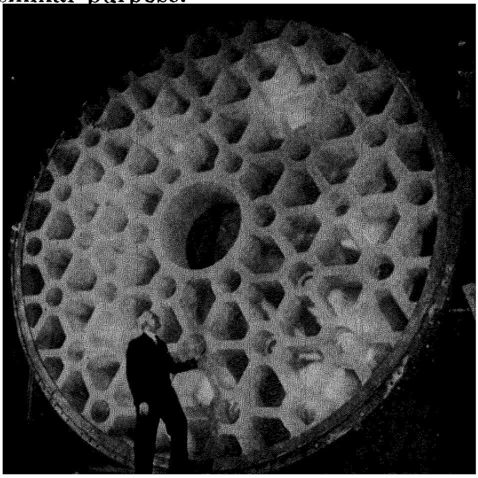
FIG. 14-10.—The cure for toothache starts in an electric furnace. A hard fused aluminum oxide abrasive is manufactured by electric heat. Fine grains of abrasive are made into grinding tools for dentists. The rest of the story is left to the reader's imagination.

Making Mirrors by Evaporation of Metals. Electric light bulbs that have been used for a long while become darkened by a deposit of tungsten on the inside of the glass. This metal comes from the glowing hot-filament wire, which is made of tungsten. The filament has evaporated some of its metal; the metal has then condensed on the glass. A miniature distillation has occurred inside the bulb.

The evaporation of tungsten can be retarded by filling the bulb with some inactive gas, argon or nitrogen. Conversely, the evaporation is hastened if as much gas as possible is drawn out of the bulb. By hanging other metals on the tungsten filament, a mirror can be made. The metal and the substance to be coated are placed parallel in a high vacuum. Then electricity heats the tungsten filament, which in turn melts the metal. Evaporation of the metal and the depositing of a mirrorlike metallic film follow. In this fashion many large astronomical reflectors are coated, the famous 200-in. mirror for the telescope in the observatory on Palomar Mountain, for example. (See Fig. 14-11.)

Flash Bulbs. A bulb like an electric light bulb is filled with oxygen and with metal foil or wire of aluminum or magnesium. Also included is a filament that becomes hot when an electric current runs through it. This arrangement produces the photographer's flash bulb. At present, such bulbs can be used only once.

A radio tube, on the other hand, does not have oxygen in it; it is, in fact, as nearly a perfect vacuum as can be obtained. Magnesium metal, a silvery dense metal, has remarkable ability to absorb gases. This "getter" metal is included in some radio tubes to remove traces of gas not taken out by the vacuum pump when the bulbs are made. Barium is also used for a similar purpose.



Courtesy of Corning Glass Works

FIG. 14-11.—The curious ribbed back structure of the 200-in. telescope mirror was designed to decrease weight and to stiffen the mirror. The mirroi surface will be on the opposite side.

Opportunities in Electrochemistry. The application of electricity to chemistry has merely started. New and purer chemical compounds may be made in the future by electrical means. New types of cells, changes at both the anode and the cathode, and electrolysis in various solvents all offer possibilities.

In the induction type of electric furnace, the furnace itself does not become very hot. Only certain heavy metals placed within its powerful and rapidly changing magnetic field become heated. If the hand is held in the furnace, it will not be affected unless a metal ring is being worn. The ring, however, would become so hot that a painful burn would result. It is possible to reach 2500°C or even higher with such equipment.

Economical ways of producing electricity should be further investigated. In a dry cell, zinc is used up, and the quantity of electrical power produced is small. Larger amounts of electrical power are produced by burning coal: The heat of the fire boils water; the steam formed passes through a turbine, causing the turbine to turn an electric generator. Each step in the process suffers a loss of energy, and as a result we waste more of the coal than we utilize. Fame, fortune, and the gratitude of the world await the person who can show how to transform coal directly into electricity in an economical manner.

SUMMARY

Electrolysis is the process of causing chemical changes in a liquid by passing a direct electric current through it. The liquid may be a solution or a melted salt. The positive (+) plate is called the anode, the negative (−) plate the cathode, and the liquid the electrolyte.

Metallic ions are positive and are discharged at the cathode. Electroplating is an application of simple electrolysis, depositing metal on a cathode.

Two common cells for producing electricity are the storage cell and the dry cell. The storage cell has lead, lead dioxide, and dilute sulfuric acid as the electrolyte. Charging the battery increases the density of electrolyte; discharging the battery decreases its density. The dry cell has zinc (−), carbon (+), and sal ammoniac (NH_4Cl) solution in paste form. Manganese dioxide is also present to oxidize liberated hydrogen to water.

Active metals are prepared by electrolysis of fused salts. Sodium collects at the cathode from melted sodium chloride. The metal must be protected from air and water. Sodium is a soft, silvery metal that tarnishes easily. It reacts explosively with water. Sodium is used for the preparation of tetraethyl lead and to make sodium compounds, such as sodium cyanide ($NaCN$) and sodium peroxide (Na_2O_2). Potassium, magnesium, calcium, and aluminum are made similarly.

Refining metals by electrolysis is an important industry. The impure metal is placed at the anode, pure sheet at the cathode; metal ions in electrolyte are discharged at the cathode and deposited.

Electric heating is convenient. In an arc furnace a very high temperature is reached. The resistance furnace is extensively used.

Products of electric furnaces include graphite (crystallized carbon), used for a lubricant and a refractory; silicon, used in steelmaking; carbides, such as silicon carbide (SiC), used as an abrasive because it is a very hard substance; white phosphorus, used for making phosphorus sesquisulfide (P_4S_3) for matches; carbon disulfide (CS_2), a solvent, also used to prepare carbon tetrachloride (CCl_4); calcium carbide (CaC_2), used to make acetylene (C_2H_2); and cyanamide ($CaCN_2$); and aluminum oxide (fused Al_2O_3), an important commercial abrasive.

Sputtering is a process of depositing a metallic mirror by the evaporation of a metal heated electrically in high vacuum.

Flash bulbs contain magnesium or aluminum foil or wire and oxygen.

QUESTIONS

21. Give at least two advantages and two disadvantages of electric heating compared with heating by burning a fuel.

22. Which type of electric furnace does an ordinary electric light bulb resemble?

23. Cite one advantage and one disadvantage of graphite when compared with oil as a lubricant.

24. What property of graphite accounts for its use as an ingredient of the paste within a dry cell?

25. In an electric furnace for producing silicon, the reaction mixture contains salt and sawdust in addition to sand and coke. Suggest a reason for using the extra materials.

26. Write an equation for the burning of the carbon monoxide outside a silicon-producing furnace in action.

27. List five useful products of electric-resistance furnaces.

28. Why is air generally excluded from an electric-resistance furnace?

29. Write formula equations for (*a*) burning carbon disulfide; (*b*) chlorination of carbon disulfide; (*c*) reduction of carbon tetrachloride by hydrogen.

30. A few drops of carbon disulfide are poured into a large, tall glass jar. A warmed glass rod is brought to the mouth of the jar. Then a sheet of blue flame starts near the mouth and burns downward. The walls of the jar become coated with a light yellow deposit. Explain these observations.

31. When nitrogen is passed over calcium carbide in an electric furnace, calcium cyanamide ($CaCN_2$) is formed. Carbon is the other product. Write the equation to represent this change.

32. What properties has carbon tetrachloride that make it (*a*) a good extinguisher for small fires; (*b*) a good clothes cleaner?

33. What is the percentage of chlorine in carbon tetrachloride?

34. What type of valence bonding is exhibited in chloroform ($CHCl_3$)?

MORE CHALLENGING QUESTIONS

35. What is the difference between an 80-ampere-hour storage battery and a 100-ampere-hour battery?

36. Make a labeled diagram of a Downs cell. Consult a book on industrial chemistry, for example, the one by Reigel.[1]

37. A certain compound contains 10.05 per cent carbon, 0.84 per cent hydrogen, and 89.1 per cent chlorine. Find its simplest formula. Also, 100 ml of its vapor at STP weighs 0.538 g. Find its molecular formula.

38. The following equations are taken from a publication of the American Chemical Society.[2] In summarizing three electrolytic processes for making hydrogen peroxide, J. S. Reichert gives these equations. Balance each (*do not write in this book*).

1. Cell reaction	H_2SO_4		$\rightarrow H_2S_2O_8$	$+ H_2$
Steam distillation	$H_2S_2O_8$	$+ H_2O$	$\rightarrow H_2SO_4$	$+ H_2O_2$
Over-all balance		H_2O	$\rightarrow H_2$	$+ H_2O_2$

---

[1] Reinhold Publishing Corporation, New York.

[2] *Chemical and Engineering News*, vol. 21, No. 7.

$$\begin{array}{llllll}
\text{2. Cell reaction} & NH_4HSO_4 & & \rightarrow & (NH_4)_2S_2O_8 & + H_2 \\
\quad\text{Steam distillation} & (NH_4)_2S_2O_8 & + H_2O & \rightarrow & NH_4HSO_4 & + H_2O_2 \\
\cline{2-6}
\quad\text{Over-all balance} & & H_2O & \rightarrow & H_2 & + H_2O_2
\end{array}$$

$$\begin{array}{llllll}
\text{3. Cell reaction} & NH_4HSO_4 & & \rightarrow & (NH_4)_2S_2O_8 & + H_2 \\
\quad\text{Conversion} & (NH_4)_2S_2O_8 & + KHSO_4 & \rightarrow & NH_4HSO_4 & + K_2S_2O_8 \\
\quad\text{Steam distillation} & K_2S_2O_8 & + H_2O & \rightarrow & 2KHSO_4 & + H_2O_2 \\
\cline{2-6}
\quad\text{Over-all balance} & & H_2O & \rightarrow & H_2 & + H_2O_2
\end{array}$$

39. The tank car pictured in Fig. 14-8 holds 8000 lb of hydrogen peroxide solution, of which 27.6 per cent by weight is hydrogen peroxide. What is the weight of the actual hydrogen peroxide in the car? What weight of oxygen is available from the peroxide when it is all decomposed?

40. Balance the following equation (*do not write in this book*).

$$KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$$

41. What is meant by 10-volume and by 100-volume hydrogen peroxide?

42. Trace the flow of electrons through a circuit consisting of a charged lead storage battery connected by means of copper wires to a cell consisting of two copper electrodes dipping into a solution of copper bromide ($CuBr_2$).

UNIT THREE .... CHAPTER XV

COLLOIDS

Many of us may have wondered why scum forms on hot milk or cocoa while it cools or why a cake of soap is sometimes surrounded by a jelly-like slush. We may have noticed that sometimes jelly does not "jell," that the petal of a white lily has no white substance in it, or that hot water at first is not always best for washing clothes. We may have found ice crystals in ice cream and wondered why frozen desserts and puddings are usually so "smooth" to the taste. Questions like these and many more were investigated by Thomas Graham (1805–1869), a Scottish scientist. He studied various liquids and the way in which they soaked through parchment paper and animal membranes. He found that solutions of salt and sugar, true solutions, diffuse through these thin, skin-like sheets readily but that liquids such as gelatin and glue in water do not go through so quickly. He called the second group of materials "glue-like" or ***colloids.*** Although Graham is called the "father of colloid chemistry" for his work, several other workers of the generation before him prepared and studied colloids also. Since Graham's time, numerous investigators have worked with colloids.

Up to this point in this book we have been investigating pure substances and have thus developed several principles of chemistry. Some of these principles have been described by laws. Now we depart for a while from the study of pure substances and investigate natural materials, substances just as they are found in nature to a great extent. This is practical chemistry indeed, applied chemistry. But it is not a new chemistry. The story of colloid chemistry is told by applying known principles to a special condition of matter.

What is Colloidal Dispersion? Following Prof. Graham's investigations, it was found that "colloids" differ from true solutions in respect to the size of the dispersed particles. We can see large chips of material with the unaided eye. We can also see smaller bits of substances when we use a microscope. Atoms and molecules are very much smaller still,

---

New Terms

absorb
adsorb
coagulation
protective colloid
diffuse
Tyndall effect

most of them too small to be seen even under an electron microscope, The particles in a colloidal dispersion are intermediate in size; that is. they are too small to be seen by the ordinary microscope but too large to be true atoms or simple molecules. Some of the larger molecules are of colloidal size; the size range is thus general rather than precise.

Colloids are like true solutions in many respects. It is possible, therefore, to think of each of the three states of matter mixed into each of the three states acting as solvents. Here are some examples:

Substance suspended	Suspended	Example
Gaseous bubbles	In a gas	Impossible
	In a liquid	A foam—whipped cream
	In a solid	Air in certain porous minerals—meerschaum, pumice-or in floating soap
Liquid droplets	In a gas	A mist or a fog—clouds
	In a liquid	An emulsion—salad dressing
	In a solid	Water in butterfat
Solid particles	In a gas	A smoke
	In a liquid	Colloidal metals in water; house paint
	In a solid	Wings of butterflies; some alloys

However, colloids differ from true solutions in many respects. They do not pass readily through parchment membranes, as Graham found, and they show the path of a beam of light. Just as an automobile headlight sends many streamers of light beams out into the fog, so a light beam shows its path in a colloidal suspension. This effect, called the Faraday-Tyndall effect, sometimes serves to distinguish colloids from true solutions.

How Colloids Are Made. Some colloids occur naturally. Nature makes starch particles colloidal in size. In fact, it is well known that starch does not make a true clear solution with warm water. Glue, gums, flesh, and many plant parts are already in colloidal-size particles. Soap put into water makes, not a true solution, but a colloidal suspension of soap in water. Milk is a colloid of casein and butterfat suspended in water. Rubber latex resembles milk in appearance and contains tiny particles of rubber hydrocarbon.

Since colloidal particles are a matter of size, there are only two general ways of making them: (1) making extremely small particles larger; (2) making large particles smaller.

1. Let us start with a solution in the molecular or in the ionic condition. Then let us cause a precipitation to take place in this solution in such a fashion that the particles formed are of colloidal size. Here we can be guided by a principle well known to the druggist. Concentrated or extremely dilute solu-

tions and rapid precipitation cause small-sized crystals. Moderately concentrated solutions and slow separation of the material produce large-sized particles. A delayed precipitation is startling to watch and illustrates the point under discussion.

If we put hydrochloric acid into a solution of photographer's "hypo," colloidal sulfur forms in the solution after a short while. It is white and opalescent but does not settle out completely.

$$\underset{\text{hypo}}{Na_2S_2O_3} + \underset{\substack{\text{hydrochloric}\\ \text{acid}}}{2HCl} \rightarrow \underset{\text{salt}}{2NaCl} + \underset{\substack{\text{sulfurous}\\ \text{acid}}}{H_2SO_3} + \underset{\text{sulfur}}{S\downarrow}$$

Let us shake a small amount of solid ferric-chloride with cold water. A yellow-brown solution forms that contains Fe^{+++} ions and Cl^- ions. Using the same amount of the chloride, let us add it to a similar amount of water that is boiling vigorously. This time a garnet-red colloid is produced, ferric hydroxide suspension.

$$FeCl_3 + 3HOH \rightarrow Fe(OH)_3\downarrow + 3HCl$$

Colloidal arsenic sulfide is formed when hydrogen sulfide acts on arsenious acid (H_3AsO_3), and sometimes silver ions and chloride ions together form silver chloride, which becomes suspended in the solution in colloidal-sized particles. Gold chloride solution treated with a reducing agent, fresh tannic acid solution for example, forms metallic gold colloids, red when heated, violet or blue when cooled and diluted. The color depends on the size of the particle, not its composition.

2. Let some potato starch and water be stirred together. Then let the solution be poured into a folded filter paper and the filtrate tested for starch. A drop of iodine solution produces a blue color if starch is present. No color is produced at first. Now let the starch be ground vigorously in a chemist's mortar with a pestle and the experiment repeated. This time some of the starch has been made small enough to pass through a piece of filter paper. This is finely divided, or colloidal, starch.

Mechanical grinding by means of mills produces powders that are colloidal in size. These mills are used to prepare paints, medicines, insecticides, and mayonnaise dressing. In one type of mill, the grinding is done between two parallel, horizontal, hard steel plates that are so close together that a page of this book could not be placed between them without touching.

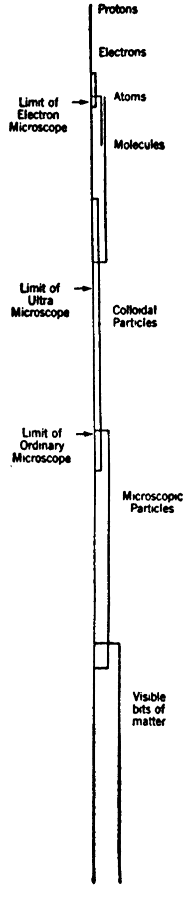


FIG. 15-1.—The size scale of particles.

A trace of washing soda is added to some water and two silver wires or coins are connected to a 115-volt direct-current source that can deliver 6 to 12 amperes in series with an adjustable resistor. (See Fig. 15-2.) Dark-brown colloidal silver suspension forms in the water when the silver wires are touched and then separated a bit. Again, when mercury is poured in the funnel of the apparatus shown in Fig. 15-3 the metal drops form an electric spark across the gap in the level bulb that contains ordinary water. It is thought that the metal vaporizes and then is condensed in the cold water to gray-green colloidal particles of elementary mercury.

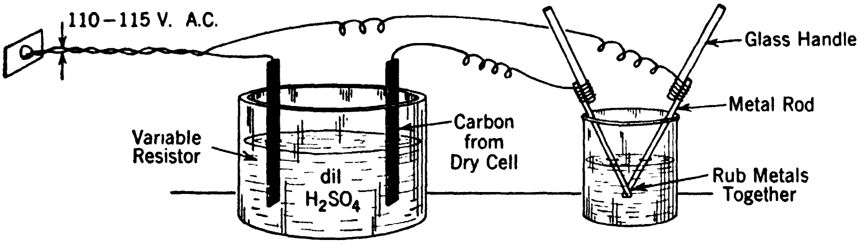


FIG. 15-2.—This apparatus produces a colloidal dispersion by the Bredig arc method. A spark is caused to jump between two metals that are immersed in a liquid.

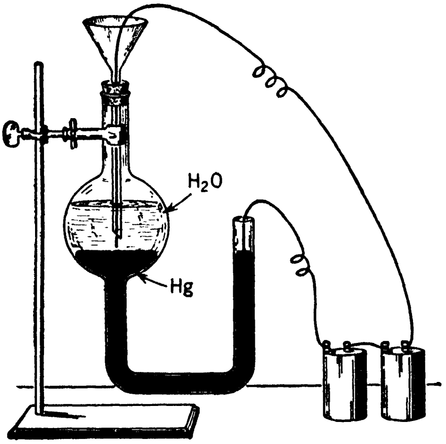


FIG. 15-3.—The Bredig arc method may be applied to a liquid metal by using the apparatus above.

Properties of Colloids. Many colloids have attractive colors. Colloidal gold suspended in glass is purple or red. Oil films of colloidal thickness give opalescent, peacock colors when spread out on water. In fact, the color of some flower blossoms and birds' feathers is thought to be caused by air bubbles of colloidal size or thin plates, for we can discover no colored material (pigment) in them. Nor is any blue substance found in blue eyes. The colloidal substances in the eye break up light and reflect only blue.

Colloidal suspensions in liquids show the path of a beam of light. They pass through an ordinary filter paper. Just as a dog runs through a forest, so a colloidal particle finds its way through the mat of fibers that compose paper.

Let us find out a few things about the effect of surface. To use a homely example, any housekeeper knows that dust gathers on furniture surfaces. The greater the amount of surface, the greater the amount of dust.

Now suppose that we have a cube of cheese one centimeter on an edge. It has six square centimeters of surface. If we slice it parallel to any face, the surface is increased by the area of both sides of the cut, or two square centimeters more. (See Fig. 15-4.) Many thin slices or, better still, grinding will give much more surface, as the table below shows.

EFFECT OF CUTTING A 1-CM³ LUMP OF SUGAR INTO SMALLER CUBES

Length of edge, cm	Number of cubes	Total surface	Comparable area
1	1	6 cm²	A large postage stamp
0.001	1,000,000,000 (1 × 10⁹)	6000 cm²	A small rug
0.000,001	1 × 10¹⁸	600 meters²	A home-size building lot
0.000,000,01	1 × 10²⁴	15 acres	A city block

That is, the surface from a lump of sugar, fine pulverized, is more than all the floor space in a large high school. Any surface effect, then, is brought out in colloids to a remarkable extent.

Colloids ***adsorb*** many substances readily; that is, substances cling to the surface of a colloid. Notable in this respect is activated charcoal, made by charring selected vegetable material. Brown sugar solution is boiled with activated charcoal, and the coloring materials are adsorbed. The sugar becomes colorless. Bone black also shows the same property, but not so much as activated charcoal. Activated charcoal is used as an adsorbing agent in general military defensive gas masks and for purifying water. Ordinary charcoal spread over vile-smelling, putrid organic matter will make it tolerable for a while. From a bottle full of freshly heated and air-cooled activated charcoal, several bottles full of air may be collected by pouring in water. This is because the charcoal has adsorbed so much air. (See Fig. 15-5.)

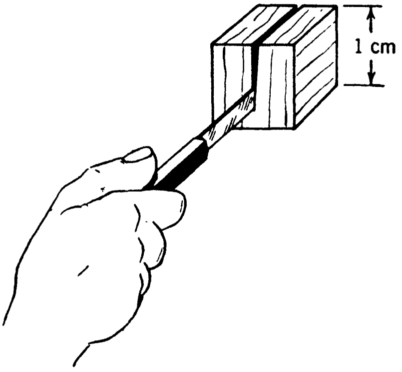


FIG. 15-4.—Cutting or grinding a material exposes new surface.

Experiments also show that particles in a colloid are usually charged electrically. In ferric hydroxide, for example, all the particles are charged with the same kind of electricity, positive. Hence, the colloidal particles repel each other and tend to stay suspended and apart. Colloidal arsenic sulfide has a negative charge. The electric charge on colloidal mist is thought to be connected with thunderstorms.

The fact that colloids are usually electrically charged accounts for some of their most interesting properties. Indeed, colloidal particles behave quite like ions at times. Rubber colloids may be electrically plated onto metal articles, producing adhering coatings.

To summarize, colloidal particles (1) give color effects, (2) show the path of a strong beam of light, (3) adsorb gases or impurities from liquids because of their large surface, and (4) carry an electric charge.

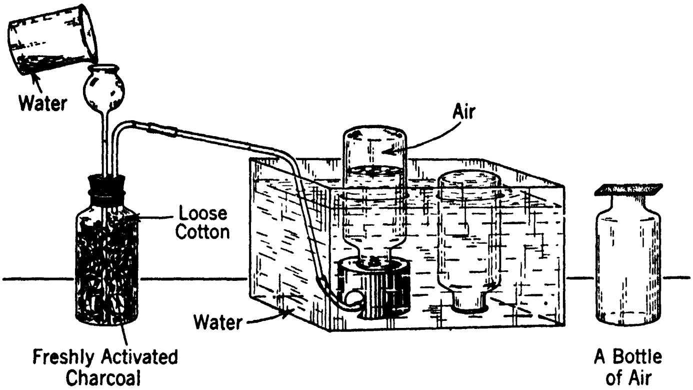


FIG. 15-5.—Interesting and true: More than one bottle of air can be displaced from a bottle of freshly activated charcoal.

QUESTIONS

1. What is the meaning of the word *colloid?*

2. How did Graham distinguish colloidal dispersions from true solutions?

3. Mention the state of matter of both the dispersed material and the dispersing medium in each of the following: beaten egg white; cigar smoke; bentonite clay used as drilling mud in an oil well; atmospheric dust; slippery soil; mayonnaise salad dressing; cold cream.

4. Account for the fact that darkened crankcase oil cannot be restored to its former clear, amber condition by filtering through newspaper.

5. Ordinary gold is yellow, but gold precipitated from gold chloride solution by tannin solution is purple. Account for the difference in color.

6. Name three types of industries that a salesman for colloid mills should visit.

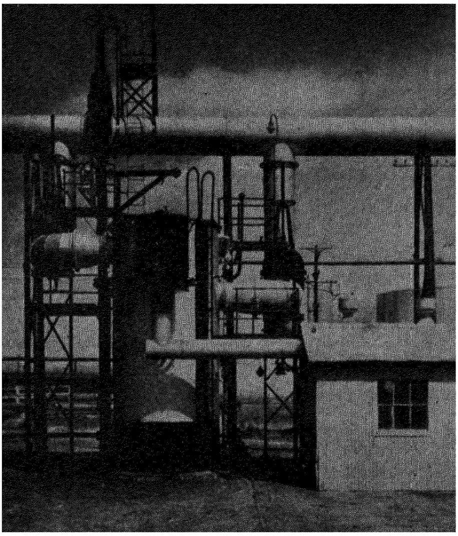
7. Some samples of coal have iridescent surfaces. Explain this appearance.

8. A druggist finds that a certain caramel solution is too dark for his needs. How can he lighten the color?

9. Some of the colloidal gold dispersions prepared by Faraday in 1857 are still preserved in the Royal Institute. They show no tendency to settle out. What property of colloidal dispersions is illustrated by their behavior?

10. Point out a similarity between a colloidal particle and an ion.

Causing Colloidal Particles to Come Together. Frying or boiling an egg causes a change, familiar to all of us, in the appearance of the egg yellow and egg white. After heating, we obtain a lumping of all the little colloidal particles, a ***coagulation.*** Heating or souring milk likewise causes a coagulation of the casein. Cooling and even exposing to sunlight may help jellies to "set"; hence, a change in temperature may cause coagulation of colloids. Blood stains, for example, must first be washed from clothing with cold water to remove the protein material. Very hot water on soiled clothes causes the colloidal proteins in the dirt to coagulate, or "set," and then wash out clean with difficulty.

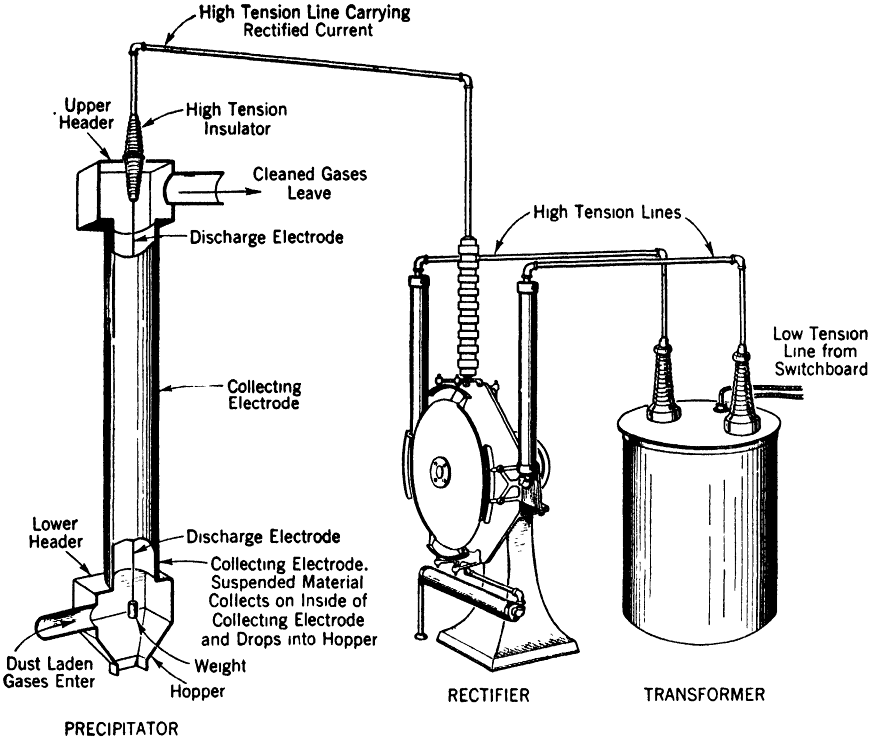


Courtesy of Western Precipitation Corporation

FIG. 15-6.—A dust precipitator installation looks like this.

The opposite electric charge will neutralize the charge already on a colloid and cause it to coagulate. F. G. Cottrell applied this fact to stop the smoke nuisance from smelters and factories. (See Figs. 15-6, 15-7.) He found that by passing the smoke between highly charged plates the charged colloidal particles become discharged and collected. By using the Cottrell method of coagulation of smoke, smelters and factories have become better neighbors; purer and cleaner chemical products, such as sulfuric acid and fertilizers, can be made; potash is recovered from the stack of cement kilns; zinc oxide is recovered from brass foundries; and precious metals are no longer lost from refineries. Household dust is reduced by use of small model electric precipitators. In general, wastes and nuisances have been turned into a source of profit, and our natural resources have been saved.

Soap when first made sometimes forms a colloidal jellylike mass that



Courtesy of Western Precipitation Corporation

FIG. 15-7.—Cottrell precipitator.

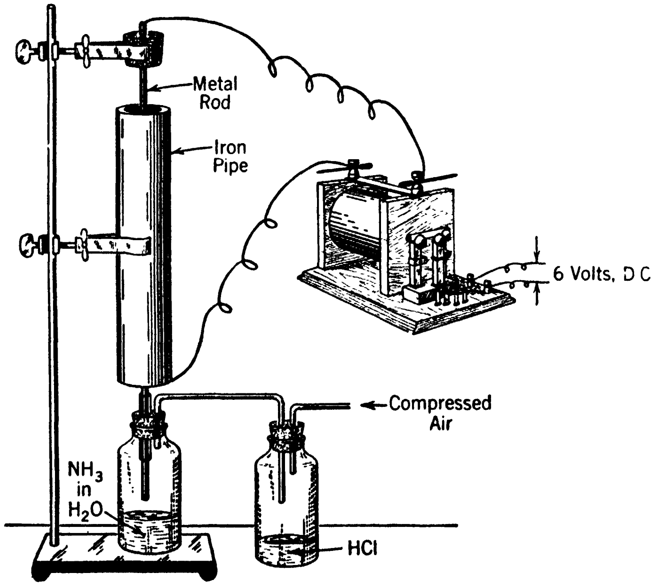
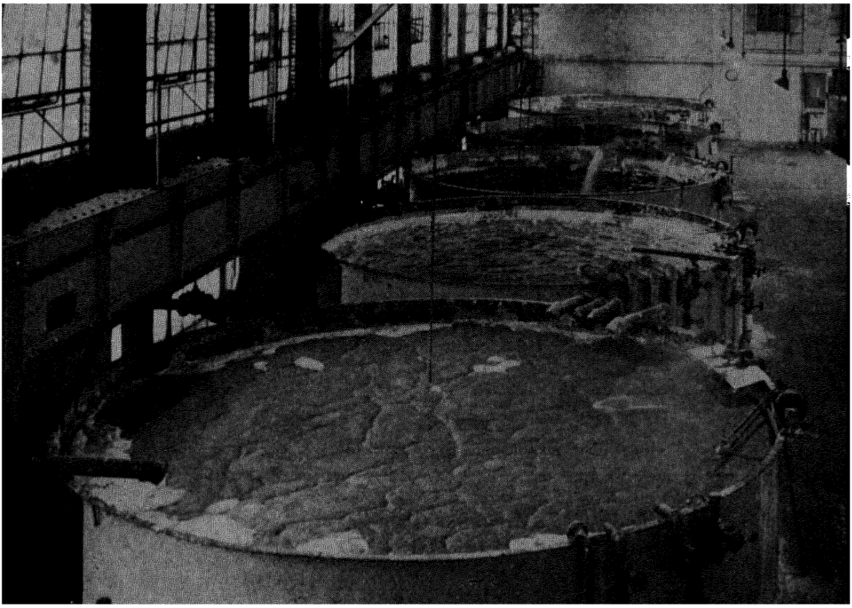


FIG. 15-8.—How a demonstration dust precipitator may be built for the laboratory.

cannot be sold in cake form. (See Fig. 15-9.) The soapmaker avoids this condition by "salting out" his soap with a saturated solution of salt. In so doing he copies a process seen in nature. Clay and mud in a river settle near its mouth, not only because the river slows up there, but also because the colloidal-size particles are coagulated by the action of the salt in the sea water. Witness the enormous deltas the Mississippi and Nile rivers have built by this process.



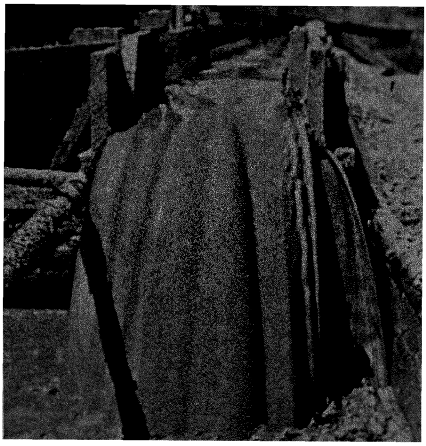
Courtesy of Manhattan Soap Company

FIG. 15-9.—The soapmaker's art uses the principles of colloid chemistry. These huge tanks hold several carloads of soap.

We can tan hides to leather by using common salt, but a more customary way is to precipitate the colloidal skin by means of alum or by tannins from the bark of trees. Both are acid substances. Eskimo women produce the same effect by chewing hides. Latex from a rubber tree is changed into rubber as we know it by means of dilute acetic acid or by smoke, which is slightly acid (smoked Pará rubber). When milk sours, bacteria form lactic acid from milk sugar. The acid changes the colloidal casein into a curd. What happens to milk in the human stomach, which contains 0.2 per cent hydrochloric acid? From these examples it can be seen that adding an acid often coagulates a colloid. Adding a base may also produce the same result.

Mixing two oppositely charged colloids may produce coagulation of both. Ferric hydroxide and arsenic sulfide colloids (previously mentioned) are oppositely charged; put together, both precipitate.

Causing Colloid Particles to Stay Suspended. In a colloid, tiny particles may absorb electrically charged particles, ions, or another colloid and thus form an electrically charged shell. The charged particles serve as a covering, a *protective* colloid. For this reason we add gum to India (drawing) ink to prevent carbon from settling out, gelatin to ice cream to prevent the formation of large crystals, and soap or other detergents to insecticides to make them spread better. Without the tannins present in straw the ancient Hebrews had trouble making bricks for Pharaoh, according to the fifth chapter of Exodus in the Bible. Colloidal graphite suspended in water (Aquadag) is held there by a protective colloid. Oil may also be used for the suspending medium. In both cases an excellent lubricant is formed.



Photographed by La Tour

FIG. 15-10.—Colloidal rotary-drilling mud is flowing into the mud pit at an oil well. This special type mud, developed by petroleum engineers and chemists, is pumped into a drilling well to clear the cuttings from the drill bit and then is forced up the outside of the drill pipe to seal the walls of the hole, to prevent caving, and to maintain gas pressure.

Ordinary washing depends upon a similar action. Grease holds dirt to hands and clothes. If nothing held the dirt, we could blow it off and become clean. Grease and water do not mix, but grease does form a suspension in soapy water. The soap is thought to surround each grease droplet, acting as a protective colloid. The dirt comes off with the grease.

In general, a colloid will remain as a colloid indefinitely if no condition exists to cause it to coagulate. Olive oil and water beaten together do not make a permanent emulsion; but if egg yolk is added to the mixture and it is beaten again, mayonnaise forms and keeps well.

Other Cases of Colloids. Colloids may be droplets or particles. But in some cases the colloidal size may extend in one or two directions but not in the other. That is, threads may be colloidal except in length; sheets may be of colloidal thickness. A web of films or sheets into which much fruit has been adsorbed is a jelly.

We may notice that a jelly sometimes has drops of liquid on it. The colloidal membranes of which it is made are under some tension or pull, apparently, and tend to squeeze out drops of liquid. It is interesting to observe that unripe fruit contains more of the jelly-forming material, pectin, than does ripe fruit. For this reason jellies are sometimes made by using ripe fruit juices and a preparation that "jells" readily, a pectin preparation.

High explosives and photographic films also have a spongelike structure of colloidal webs.

"Canned heat," jelly that has adsorbed alcohol, is easily prepared in the laboratory by adding saturated calcium acetate [$Ca(C_2H_3O_2)_2$] solution to ordinary (95 per cent) alcohol in the volume proportion of 1 to 9. Silica gel is readily made by adding dilute hydrochloric acid to diluted commercial water-glass solution.

Dried silica gel is extensively used as a catalyst and as an adsorbing agent. Agate, flint, and opal are minerals that are essentially dried silica gels.

To prevent rusting during shipment or storage, machine parts, guns, and other equipment are packed in moisture-proof containers, together with a small porous bag containing silica gel. The silica gel adsorbs residual moisture from the air in the enclosed space and checks rusting.

SUMMARY

Colloidal dispersions differ from a true solution in the size of the dispersed particles. Colloids may be classified according to the state of matter of the suspended material, which may be solid, liquid, or gas. Some natural colloids are available.

Colloidal dispersions may be prepared by precipitation under unusual conditions and by grinding or arcing under water.

The properties of colloids are often due to the size of the particles. Some suspensions are colored. They show the path of a beam of light. They pass through ordinary filter paper. Colloids have extensive surface and adsorb some substances. Particles carry an electric charge.

Coagulation of colloids is caused by heat, salt solutions, acid or alkali, electric precipitation, and mixing with an oppositely charged colloid.

The colloidal condition is maintained by a protective colloid surrounding the dispersed particles and by the electric charge possessed by each.

Colloidal dimensions are found in films and filaments. Examples are soap bubbles and spider's silk, respectively.

QUESTIONS

11. If kerosene and water are shaken together, the two liquids separate soon after the mixture comes to rest. If soap is now added and the experiment repeated, the separation is delayed. What part does the soap play in the experiment?

12. What is the effect of (*a*) alum on hides; (*b*) smoke on rubber latex; (*c*) lactic acid on fresh milk; (*d*) tannins from coffee beans or tea leaves on milk?

13. Point out two ways in which the Cottrell process of dust precipitation has proved its value.

14. Explain how a gas mask protects the wearer. Is the wearer protected from all poisonous gases or smokes?

15. Hemoglobin in the blood is in the form of a positively charged colloidal dispersion. How may hemoglobin be precipitated?

16. What purpose is served by the charcoal in some brands of dog-food mixtures?

17. Butter churns more readily from sour cream than from sweet cream. Explain in terms of colloidal chemistry.

18. A cake disturbed while baking in the oven refuses thereafter to "rise." Explain.

19. Why do jellies form better when made from slightly unripe fruit than from completely ripened fruit?

20. Tell how to separate a mixture of starch and salt so that both substances are recovered dry and separated from the other.

21. Investigate and report about the Precipitron.

REVIEW

1. Find the density of methyl chloride vapor (CH_3Cl) in grams per liter.

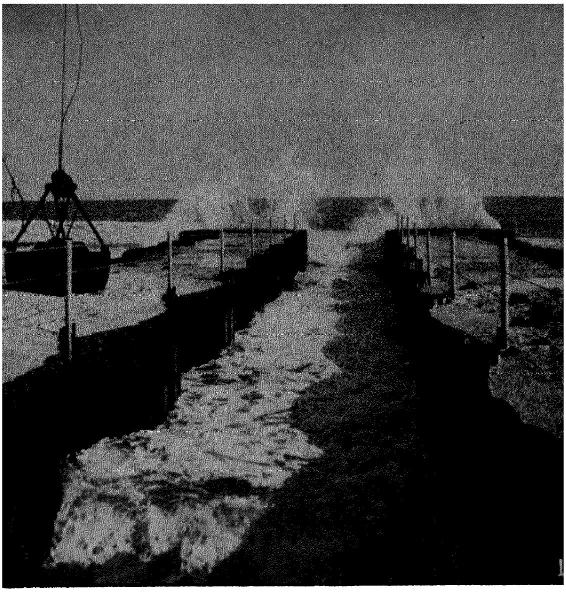
2. What is the percentage of sulfur in "hypo" crystals ($Na_2S_2O_3 \cdot 5H_2O$)?

3. Write formula equations for (*a*) action of zinc on lead acetate solution; (*b*) burning copper in sulfur vapor; (*c*) effect of heating mercuric oxide; (*d*) action of barium chloride solution on sodium sulfate solution. (*e*) Name the type of reaction represented in each case.

4. What is the percentage composition of calcium carbide (CaC_2)?

5. Explain the hydrolysis of zinc sulfate in solution. Use an equation.

UNIT FOUR



CHEMISTRY OF THE EARTH'S CRUST

Man's first important use of sea water as a source of raw materials was the extraction of bromine. Although sea water contains less than 70 parts per million of the element, this has proved a sufficient supply. Now two plants for extracting bromine from sea water are in operation.

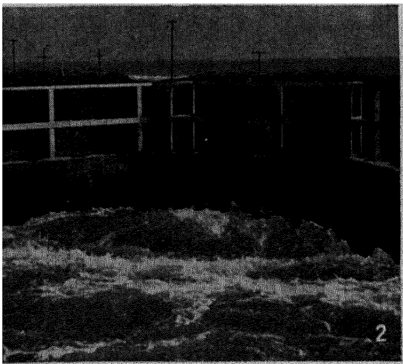
The sea water, bearing bromine in solution, pounds through an intake (1) on its way to the settling basin, where powerful pumps (2) lift 137,000 gal per minute over the dam. The water then flows 4000 ft to a rotary screen (3), where debris is turned aside.

The diagram flow sheet of the process (4) shows the relationship of the operations. Acid and chlorine are added to sea water on its way to the blowing-out tower, where bromine vapor is liberated by a countercurrent of air into the absorption tower.

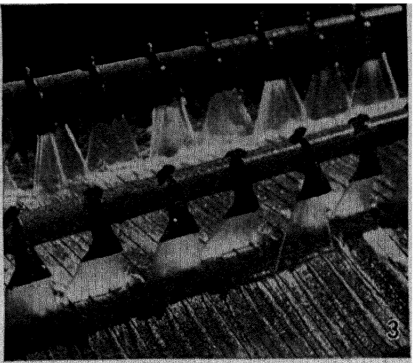
The effluent from the plant (5) presents a challenge. Almost all the bromine has been removed, but tons of other precious elements remain in every cubic mile of it.

In the absorption towers the liberated bromine is captured by passing it into sodium carbonate solution (6). Here a mixture of sodium bromate and sodium bromide forms in solution.

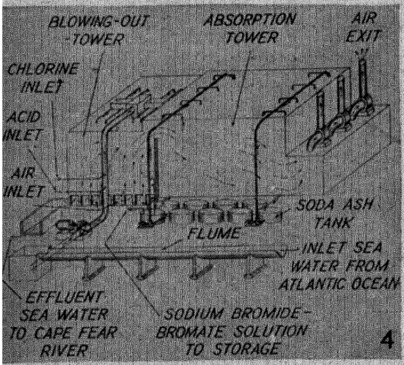
Once more the bromine is set free. This time sulfuric acid is added to the bromate-bromide solution to accomplish the liberation. In this building (7), free concentrated bromine is produced. Later the bromine is collected and made into useful compounds.



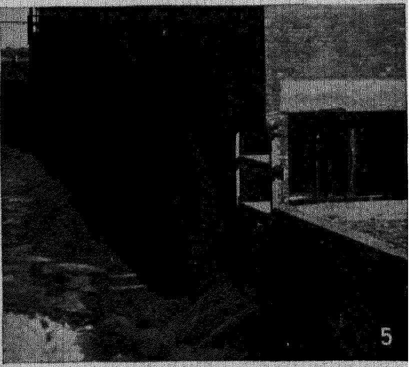
2



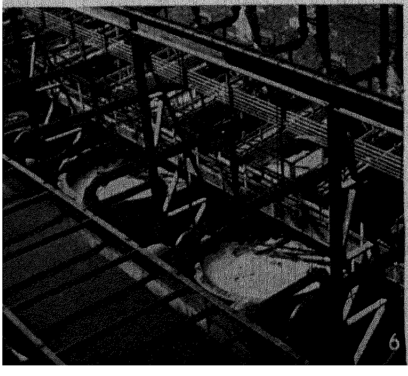
3



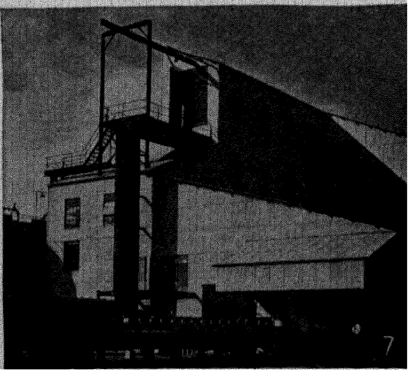
4



5



6



7

Courtesy of Dow Chemical Company

UNIT FOUR - - - - - - - - - - - - CHAPTER XVI

THE EARTH AND ITS ORES

The planet earth, on which we live, is almost a perfect sphere with an 8000-mile diameter. The weight of the earth is known, and its volume can be estimated quite easily. From these facts we find that the average density of the earth is 5.5 times that of water. We do not know definitely of what the earth is made, however, for the pressure and other conditions deep within the earth are not accurately known.

Explorations show that, the deeper we go into the earth, (1) the higher the temperature and (2) the greater the pressure exerted by the weight of material above. The practical use of earth heat and earth pressure is an unsolved problem.

If we represented the earth as the size of an apple, the skin of the apple would be too thick to represent to scale the extent that man has explored the earth, measuring from the deepest boring (about 3 miles) to the highest stratosphere flight into the air. Yet this thin shell is a remarkable region. Here exists life. Here are found 92 elements. Here is a region of ceaseless activity, of chemical and physical changes. Here the great forces of the air, the sea, the earth, and life act on each other. This is our region. The changes in it include our chemistry. Here we must use intelligence to overcome natural obstacles that stand in the way of our gaining food, clothing, and shelter.

In this unit our purpose is to consider the solid and liquid part of earth as it affects our welfare. We shall see how minerals are obtained and put to use. We shall learn how the sea is yielding chemical treasure.

Rocks, Minerals, and Ores. We call almost any hard, dense material a rock. Rocks are found abundantly, even in open fields. They make huge mountains. A very short distance below the soil continuous bedrock is reached.

Rocks that have definite chemical composition are called ***minerals.*** Granite, composed of a mixture of the minerals feldspar and mica ce-

---

New Terms

mineral
rock
gangue
gravity separation
froth flotation
leaching
flux
metallurgy
slag

mented together by mineral silica, is considered a rock, but limestone, chiefly calcium carbonate ($CaCO_3$), and sandstone, chiefly silica (SiO_2), are nearly pure minerals.

Minerals from which a useful substance, metal or compound, can be extracted with profit are called ***ores.*** It follows that an improved or cheapened process for extracting a metal will, in many cases, increase the supply of available ores.

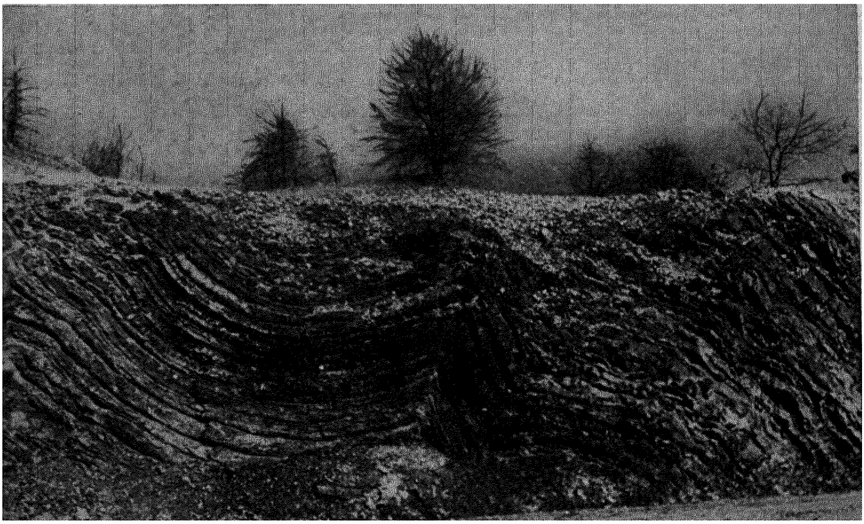


Photo by [illegible]

FIG. 16-1.—Outcroppings of rocks on the surface tell their story to the prospector for minerals. Petroleum, coal, and metallic minerals are eagerly sought.

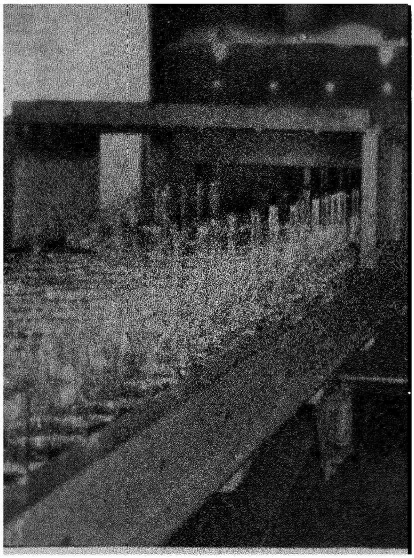
If in ages past an arm of the sea became enclosed by land and water evaporated from it faster than water came in, a salt deposit was formed. The Great Salt Lake in Utah is slowly drying up and forming a solid mass of salt. Such deposits formed in ancient time may be far below the surface, as are the famous Stassfurt mines in Alsace.

Again, in this country, several dried-up lakes, such as Searles Lake in Trona, California, yield not only salt but borax ($Na_2B_4O_7$), soda (Na_2CO_3), and potassium compounds as well.

When sea water is warmed and evaporated slightly, a deposit of calcium sulfate falls out of solution. From this experiment it is a simple matter to see how deposits of gypsum ($CaSO_4 \cdot 2H_2O$) might be formed.

Rocks with Special Uses. Stones for buildings or monuments should resist the weather well. An observation of the stones in an old cemetery will show which are durable. Here we find that sandstone (SiO_2) slabs tend to peel off layers as the natural cementing material weathers away. Limestone, or marble ($CaCO_3$), crumbles and powders away in time, especially if it is near a manufacturing city. Granite (feldspar, mica, and silica) weathers much more slowly than the other two sorts of rocks.

Large sheets of mica (isinglass) are used as electrical insulators that withstand heat. Limestone and marble are popular building stones. The less attractive pieces are used to make lime and to serve as a flux in furnaces. Powdered limestone is used to "sweeten" acid soils. Gypsum is used to make wallboard, building blocks, and plaster of Paris [$2(CaSO_4)\cdot 1H_2O$]. Road stone is secured from any local supply of hard rock. Magnesite ($MgCO_3$) and dolomite ($MgCO_3\cdot CaCO_3$) are both used for furnace linings.



Courtesy of Corning Glass Works

FIG. 16-2.—Borosilicate glass is made from sand, borax, and other materials. The first two important ingredients are found as natural minerals, silica and kernite. The glassware shown here is passing into an electric annealing oven.

Minerals with Special Uses. One of the most curious rocks is asbestos. Although it is a hard mineral, it can be shredded into fibers readily. These fibers can be spun into a thread, and from the threads cloth can be woven. Such cloth is fireproof and a good insulator. It finds many uses with which we are all familiar.

Some minerals have a definite color and are used for pigments—coloring matter in paints. Titanium dioxide (TiO_2) is white, and iron oxide (Fe_2O_3) is found in a variety of brown and red shades.

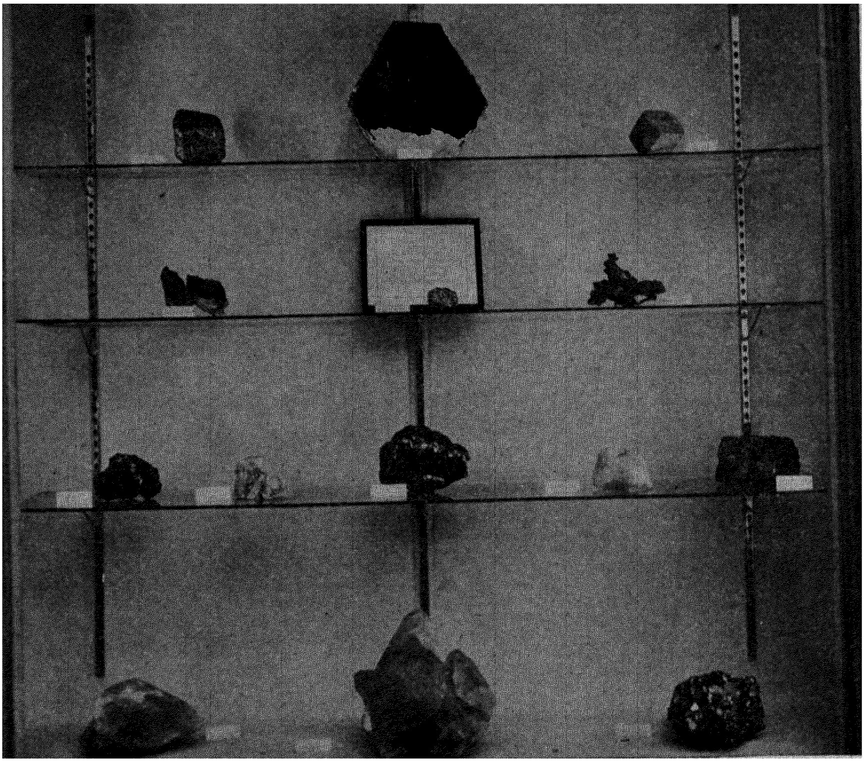
A few minerals are used for cleansing. These have a range from coarse to fine and from hard to soft. Sand, powdered pumice, powdered mica, and ground seismotite are all popular scouring minerals in household and industrial cleansers. (See Fig. 16-3.)

Ores. From a chemical standpoint, the chief useful ores are native elements, oxides, sulfides, and carbonates. Other ores are silicates, phosphates, chlorides, and sulfates.

Native elements, found free or uncombined but mixed with other substances, include gold, copper, sulfur, and many others in smaller amounts.

Useful oxides include those of iron (hematite, Fe_2O_3, and magnetite, Fe_3O_4), copper (cuprite, Cu_2O), tin (cassiterite, SnO_2), and aluminum (bauxite, $Al_2O_3\cdot 2H_2O$).

Many sulfides are useful ores. Copper sulfide (chalcocite, Cu_2S, and chalcopyrite, $CuFeS_2$), lead sulfide (galena, PbS), zinc sulfide (sphalerite, ZnS), and mercury sulfide (cinnabar, HgS) are important ores of their respective metals.



Courtesy of Buffalo Museum of Science

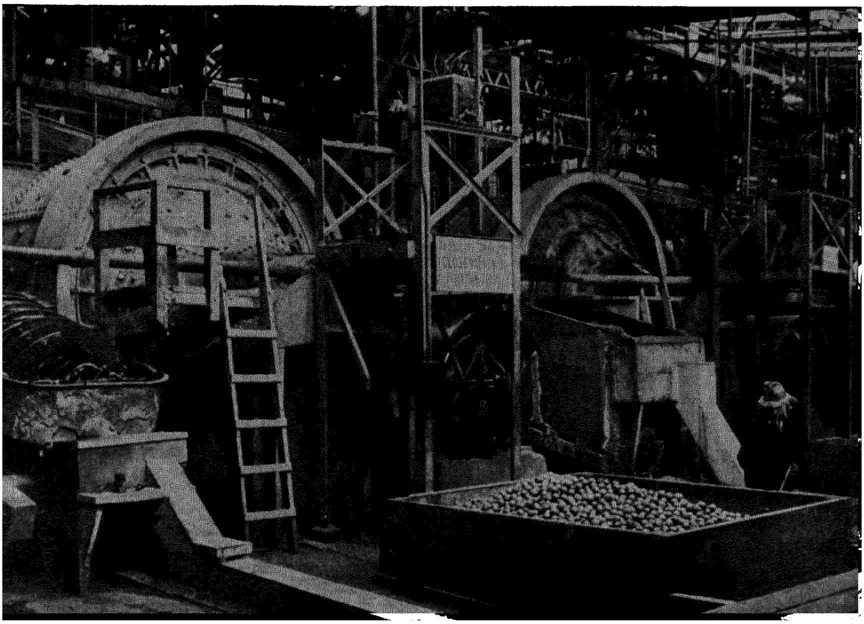
FIG. 16-3.—Exhibit of useful minerals, from top to bottom shelf:

graphite		mica		garnet
silver		turquoise		copper
sphalerite	asbestos	hematite	sulfur	galena
halite		calcite		pyrite

The important ores of iron in addition to hematite and magnetite are limonite ($Fe_2O_3 \cdot H_2O$) and siderite ($FeCO_3$). Thus we see that some metals are derived from several ores.

We shall now consider how the ores are "dressed," or concentrated for the removal of the valuable metal. We shall also investigate the chemical and physical principles that are employed in separating the metals from their ores.

Concentration of Ores. Ores are usually blasted from their location in rock layers by the use of an explosive. Some of the rock fragments loosened by the blast are useful, and some are worthless. The worthless rock is called ***gangue.*** The problem of the ore dresser now is to separate ore from gangue, or to ***concentrate*** the ore. Concentration may be done in many ways, depending upon conditions.



Courtesy of Anaconda Copper Mining Company

FIG. 16-4.—Minerals may be ground in a ball mill. These Hardinge ball mills are used in the preparation of copper ore for the smelter.

1. Hand Sorting. Hand sorting is expensive, but sometimes it is the only effective way to pick out good ore. Only the promising-looking chunks of radium ores are transported by air from the Far North to the refinery (see page 639). In some mines pieces of slate are removed from coal by hand. Many other ores pass under the eyes of experienced workers, who cull out unprofitable chunks of gangue from conveyer belts loaded with ore.

2. Gravity Separation. Air to be used in an automobile engine may be cleaned by whirling it. The denser particles of dirt go to the outside, and the engine draws cleaned air from the center of the air cleaner. If a mixture of sandlike material is placed on a slightly sloping board that jigs back and forth, the denser particles tend to go to one side and the lighter to the other. Other ore-concentration processes use the same principles of gravity separation illustrated in the examples given.

In addition to such dry methods, the ores may be suspended in moving water, the densest particles being least buoyed up by the stream. The classifying machine effectively combines the use of moving water, a sloping trough, and mechanical raking to concentrate large amounts of ore cheaply. Coal is separated from slate by floating the coal on a dense calcium chloride solution. The slate sinks.

A sluice in placer gold mining is a simple example of gravity separation by the wet method. Cleats are firmly nailed across the bottom of the sloping trough, which is called the sluice. A stream of water is directed through the sluice and gold-bearing sand shoveled in hopefully. The gold if any, settles against the cleats while the lighter rock particles wash over them. (See Fig. 16-5.)

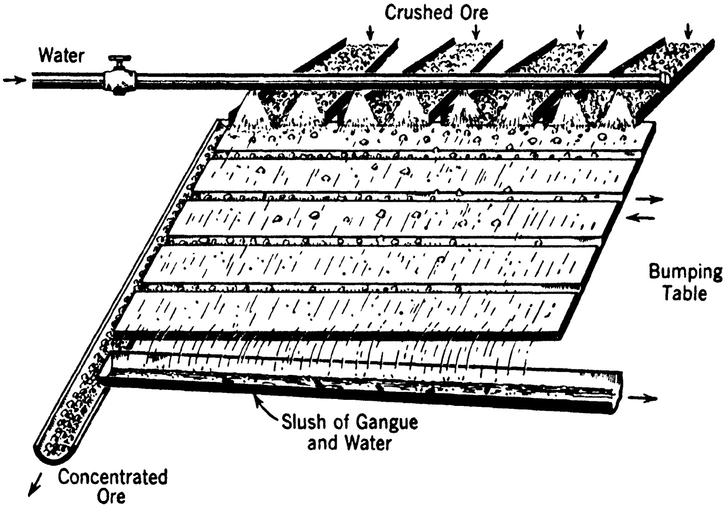


FIG. 16-5.—The slanting table shakes north-south and east-west at the same time, a double motion, while a stream of crushed ore and water flows onto the upper part and then over its surface. A separation of light from dense particles is accomplished.

*3. **Surface-tension Separation.*** Cheap oil and acid are churned into a froth. When ground sulfide ores are stirred into this suds, the particles of ore stick to the foam. The gangue sinks. Skimming off the foam brings about a neat separation of a sulfide ore from useless rock. This unique method of ***froth flotation*** has been developed to apply satisfactorily to many sorts of ores. New flotation reagents have extended the applications of this method.

*4. **Leaching.*** In order that the useful part of an ore can be made soluble, crushed rock is sometimes soaked in a solvent to leach out the valuable mineral. Gold is soluble in sodium cyanide (NaCN) solution in the presence of air. Leaching rocks that were once tailings from previous extraction processes has proved profitable when new extraction methods are applied.

Roasting. Many ores must be heated as another distinct step in their preparation. They are spread out on open trays and put into a furnace, where they are either burned or heated strongly. Carbonates change to oxides in this process, and many sulfide ores are roasted (burned) to remove part or all of their sulfur. This treatment produces an oxide, which is then readily reduced with carbon. Zinc ores illustrate well the effect of roasting. If the ore is zinc blende, or sphalerite (ZnS), both elements in the compound burn in the supply of hot oxygen (air) available in a roasting furnace.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The sulfur dioxide may be captured and made into sulfuric acid as a by-product. The calcined or roasted zinc ore is a brown powder, for it contains substances other than zinc oxide, which is white when pure. The impure zinc oxide is now ready to be reduced to the metal.

If the ore is smithsonite ($ZnCO_3$), roasting drives out carbon dioxide. This sort of action is general for carbonate ores when they are heated.

$$ZnCO_3 \rightarrow ZnO + CO_2\uparrow$$

Fluxing. In roasting an ore, a flux is sometimes used. A flux is almost always used in the final step of reducing the ore to the metal.

The word ***flux*** means "flows" and refers to fluid treatment. From one viewpoint the process is similar to laundering, or washing, the impurities out of an ore in a furnace at a high temperature. The liquid most suitable for this purpose is a glass (see page 409). Such a mixture of silicates flows around the hot rock as a pasty, sticky fluid, acts chemically on some materials, and gathers in the rest of the gangue. The glass is not added to the furnace as such; rather, it is formed in the furnace by the addition of a flux. Usually the gangue is a mixture of silicate rocks or silica. Limestone is a suitable flux to remove impurities of this sort.

$$\underset{\text{flux}}{CaCO_3} + \underset{\substack{\text{silica or}\\ \text{silicates in gangue}}}{SiO_2} \rightarrow \underset{\text{glassy slag}}{CaSiO_3} + CO_2\uparrow$$

The resulting slag is a very dirty glass indeed, not transparent. When it is cool it is hard, brittle, full of holes due to gas bubbles, and seldom of much use.

Reduction. After all the preliminary steps of purification are performed, we are ready for the "big show." This step is the actual smelting, or obtaining the metal from its ore.

If the metal is a very active one, the reduction must be carried on by electrolysis of molten salts, in the absence of water, or in a few cases by heating with a more active metal. These processes are expensive, but are necessary for aluminum, magnesuim, sodium, and a few other metals.

Examples are

$$\underset{\text{fused}}{2NaOH} \rightarrow \underset{\text{at cathode}}{2Na} + O_2\uparrow + H_2\uparrow \qquad \text{(electrolysis)}$$

$$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3 \qquad \text{(replacement)}$$

Usually coke, coal, or carbon monoxide are used as the reducing agents. The oxide is heated strongly, with carbon present in excess. A transfer of oxygen takes place, freeing the metal in its elementary state. For example,

$$\underset{\text{Metal oxide}}{ZnO} \underset{}{+} \underset{\text{carbon}}{C} \rightarrow \underset{\text{free metal}}{Zn} + \underset{\text{carbon monoxide}}{CO\uparrow}$$

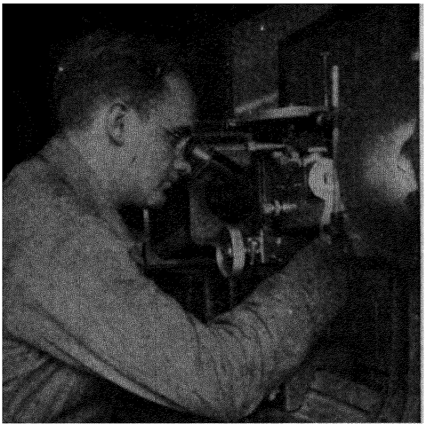
In general,

$$2e^- + Zn^{++} \rightarrow Zn^0$$

Refining. If the metal as prepared is not pure enough for some of its commercial uses, it must be refined. Zinc (b.p. 907°C) and mercury (b.p. 356.9°C) are refined by simply heating them and condensing the vapors. Copper, zinc, and several other metals are refined by electrolysis (see page 247). The impure metal is made the anode in an electrolytic cell, and the pure metal plates out on the cathode.

Example of Ore Treatment. Let us assume that a large deposit of a sulfide ore has been discovered by a prospector. It is located close enough to a road and a railroad to make its mining an attractive venture.

A sample of the ore is sent to the assayer's laboratory, and the report received shows that it contains 15 per cent of the valuable mineral compound of which 10 per cent, or two-thirds, is the metallic part. By concentration of the ore at the mine, enough material is rejected to bring the concentration up to 48 per cent ore, or 32 per cent metal. The ore is shipped and treated at the smelter. Roasting changes sulfides to oxides and consequently reduces the formula weight 16 units (S = 32; O = 16; 32 − 16 = 16). The ore now weighs less and has increased slightly in percentage purity, but no gangue (unless volatile) is removed by roasting alone.



Courtesy of American Iron and Steel Institute

FIG. 16-6.—A highly polished small section of steel is being examined at high magnification. The metallurgist gains much information concerning the quality of steel by this method.

It is advisable to remove gangue at this stage if the temperature of roasting is hot enough to melt a flux. Let us assume in this case that a flux was added and that a slag was formed.

$$\text{Flux} + \text{gangue} \rightarrow \text{slag}$$

Many of the impurities are taken into the slag. Therefore, the material ready for the final reduction is 75 per cent metallic oxide or 50 per cent available metal.

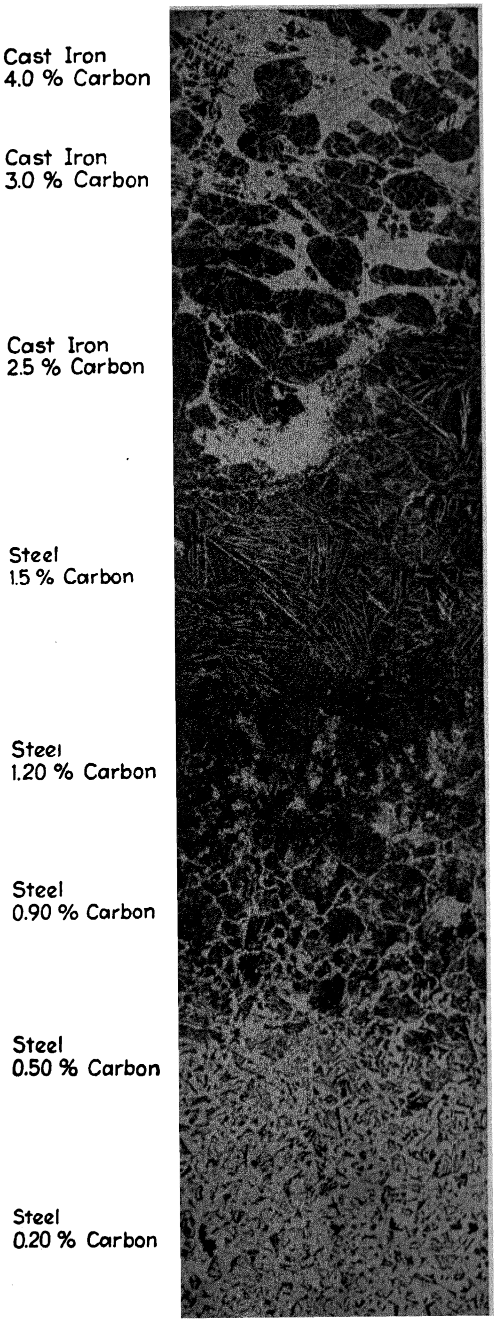
The oxide is now reduced by mixing it with the cheapest form of carbon available for the purpose and heating. Again a slag is used to gather in the impurities. The reducing furnace produces two streams of fluids, one the molten metal, the other the slag floating on top of the metal.

The metal is now 95 per cent pure. The remaining 5 per cent consists of other metals that were chiefly present in the original ore, carbon, or slag inclusions. In most cases the metal is refined by heat or electricity. A metal of purity 99.5 per cent or better results. All figures given in this example are not actual but are included to help visualize the effect of each treatment of an ore.

Metallurgy. The study of extracting a metal from its ore is a part of ***metallurgy.*** Metallurgy includes another equally important part, namely, the relationship of metals, their treatment and composition, to their properties.

IMPORTANT SOURCES OF METAL ORES

Aluminum	United States, Germany, Russia
Antimony	China, Mexico
Beryllium	Germany, France, United States
Bismuth	Peru, Bolivia, Mexico, Canada
Cadmium	United States, Mexico, Canada
Calcium	Germany, United States, Sweden
Chromium	Russia, Rhodesia, Turkey
Cobalt	Belgian Congo, Canada
Copper	United States, Chile, Africa
Gold	Transvaal, Russia, United States, Canada
Iron	United States, Germany, Russia
Lead	United States, Mexico, Australia, Canada
Magnesium	Germany, United States, France
Manganese	Russia, Africa, India
Mercury	Spain, Italy, United States
Molybdenum	United States
Nickel	Canada, New Caledonia
Platinum metals	Russia, Canada, Colombia
Silver	Mexico, United States, Peru
Tin	Malaya, Bolivia
Tungsten	Burma, China, Malaya
Vanadium	Peru, Africa, United States
Zinc	United States, Belgium, Canada, Germany



Courtesy of General Motors Corporation

FIG. 16-7.—A series of photomicrographs shows the effect of the percentage of carbon on the grain structure of steel and iron.

Metallurgists carry out tests for tensile strength, hardness, elasticity, and other properties of metals. They also examine the microstructure of metals. A carefully polished sample of metal or alloy is etched with acid and viewed under the microscope. From a study of the size and arrangement of the crystals a real insight is gained into the cause of its strength or weakness. A photomicrograph such as is used by a metallurgist is shown here. (See Fig. 16-7.)

SUMMARY

Rocks are solid, stony matter of the earth; they are usually mixtures of minerals. Minerals are substances of definite chemical composition found in the earth. A mineral from which a metal may be extracted with profit is called an ore.

Most ores consist of native elements, oxides, sulfides, or carbonates. Ore dressing, or concentration of ore from gangue, is accomplished by hand sorting; gravity methods of separation, wet or dry; froth flotation; and leaching.

In the preparation of a metal from an ore, active metals are prepared by electrolysis of fused salts or by replacement by a more active metal. Sulfide or carbonate ores are roasted, forming oxides. Fluxing may be used with this process as well as with the reduction process. In general, a flux plus gangue forms a slag.

Reduction with hot carbon is the most common method of smelting metals of moderate activity. Some metals are refined by electrolysis or by distillation.

Metallurgy studies the obtaining of the metals from their ores, the properties of the metals, and their alloys. In this branch of applied science photomicrographs of etched metals are used extensively.

QUESTIONS

1. Define *stone; rock; mineral; ore.*

2. Which of the above four terms may be used in describing anthracite coal?

3. Some memorials consist of a bronze tablet bolted to a quartz boulder. How lasting is such a memorial, provided that it is not disturbed?

4. What minerals are used for (*a*) insulating steam pipes; (*b*) insulating electrical wires; (*c*) coloring cosmetics; (*d*) coloring house paint; (*e*) making plaster of Paris; (*f*) making lime; (*g*) lining furnaces; (*h*) sweetening sour soil; (*i*) making scouring powder; (*j*) adsorbing colors from liquids?

5. In what forms are most of our useful ores found in nature?

6. Define *concentration; gangue; flux; slag.*

7. What is accomplished by roasting (*a*) a sulfide ore; (*b*) a carbonate ore? Illustrate each process with an equation.

8. What flux should be used for an ore that contains limestone as a gangue?

9. What useful substance does slag resemble in its chemical composition?

10. Each of the following equations represents the preparation of a metal by the reduction of its oxide with powdered aluminum. Balance each of the following (*do not write in this book*):

$$Fe_3O_4 + Al \rightarrow Al_2O_3 + Fe$$
$$Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$$
$$Mn_3O_4 + Al \rightarrow Al_2O_3 + Mn$$
$$Cr_2O_3 + Al \rightarrow Al_2O_3 + Cr$$
$$WO_3 + Al \rightarrow Al_2O_3 + W$$

11. Complete and balance the following equations (*do not write in this book*):

$$B_2O_3 + Al \rightarrow$$
$$Co_3O_4 + Al \rightarrow$$

12. Which ore contains the higher percentage of iron, Fe_2O_3 or Fe_3O_4?

13. As between zinc carbonate, 85 per cent gangue, and zinc oxide, 90 per cent gangue, which ore is richer in zinc?

14. Find the percentage of titanium in TiO_2.

15. Trace the flow of electrons from the electric generator through a cell in which molten magnesium chloride is being electrolyzed; a cast-steel pot serves as the cathode, and graphite bars serve as anodes.

UNIT FOUR - - - - - - - - - - - - CHAPTER XVII

THE EARTH AND ITS SOIL

The earth under our feet consists of sand, clay, decayed organic matter (called ***humus***), more or less moisture, and living organisms. The first two items are formed by the weathering of rocks. Chemically, sand is silica (SiO_2), and clay is a complex aluminum silicate with more or less water. Clay is formed by the weathering of feldspar.

$$\underset{\text{feldspar}}{2KAlSi_3O_8} + 2H_2O + CO_2 \rightarrow \underset{\text{clay}}{H_4Al_2Si_2O_9} + 4SiO_2 + K_2CO_3$$

Clay adsorbs many other substances, notably water and iron oxide. Mixed throughout are the oxidized fragments of former plant and animal life, or humus.

Living plants, seeds, roots, bacteria, spores, insects, worms, and other creatures are found in the soil.

Soil Horizons. Layers, or horizons, of the soil, designated *A*, *B*, and *C* from the top downward, make up the soil profile. The *A* horizon is the upper, or surface, soil, where life is most abundant and organic matter is plentiful. This is the region commonly plowed. The *B* horizon has a deeper color than the *A*, and a heavier texture in humid regions. It might be called "reserve" soil, but ordinarily it is too low in organic matter to be used successfully for crops without treatment. The *C* horizon consists of weathered, unconsolidated material below the *B* horizon. It is called the parent material.

The structure of the horizons determines the ease with which the roots of plants can penetrate the soil. A granular or crumblike structure is the most favorable for the growth of crops.

Movement of soil water is influenced by gravity, evaporation, and capillary action (rise of water in small tubes or pores). In regions of high rainfall, minerals are carried downward from the *A* horizon. In dry regions where subsurface water rises in the soil, dissolved minerals are carried upward by capillary action and deposited in the *A* horizon when the water evaporates.

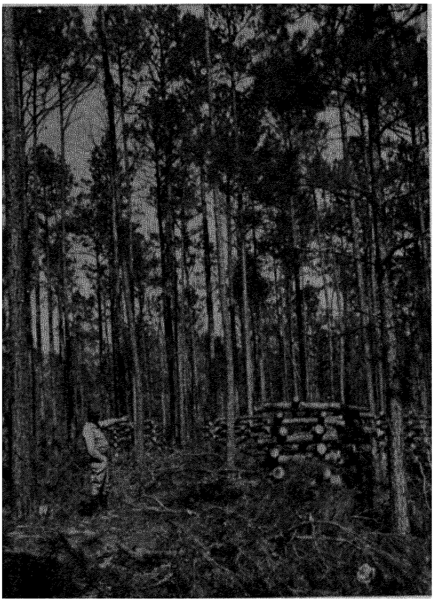
New Terms

caliche
sour soil
hydroponics
soil horizons
fertility
nodules

Our Use of the Soil. Almost all our food comes from the soil, directly or indirectly. No more striking evidence of the importance of the soil could be given.

The productivity of the soil is so important that in former years people estimated the limit of population of a country on the basis of the ability of the soil to produce crops. In arriving at their figure they failed to foresee two important developments. These are (1) modern agricultural machinery and (2) chemical fertilizers.

In former years it was necessary to allow land to lie fallow or idle every second or third year in order to restore its fertility. It is no longer necessary to do this, for chemical fertilizers can be added to the soil. In fact, it is possible in very sunny regions to produce more than one crop per year of quick-growing produce. Today a man with a tractor can plow or cultivate many times the acres that a man with a horse could till a generation ago.



Courtesy of U.S. Forest Service

FIG. 17-1.—Every tree is a chemical factory with a complicated plumbing system. Not only do trees manufacture wood fibers and lignin, but some trees also produce valuable gums and resins. This mixed stand of short leaf and loblolly pine in Arkansas is about 50 years old. The wood will be used for making paper.

Plant Food. Plants take carbon dioxide from the air through their leaves and stems. Moisture with some mineral matter is brought up from the ground through the roots. The carbon dioxide and the water combine to make starch in the presence of sunshine. This change is brought about by chlorophyll, the green coloring matter in leaves, and the process is called ***photosynthesis.***

$$6CO_2 + 5H_2O \rightarrow \underset{\text{starch}}{(C_6H_{10}O_5)_x} + 6O_2$$

This is the most important of all chemical reactions.

Plants in sunlight remove carbon dioxide from the air, supplying oxygen to the air and building organic matter. We should notice that this process is essentially the opposite of burning, decay, or oxidation. It is a reduction process, taking in light energy, and by this means energy is stored.

The process of photosynthesis, however, is not as simple as the equation above would indicate. Obviously, plants are not all starch; they must build other tissues in order to carry out the whole of their life cycle. Plants need an abundant supply of compounds of nitrogen, for they build proteins into their tissues. Proteins are complex compounds containing carbon, hydrogen, oxygen, and nitrogen and sometimes sulfur, phosphorus, and other elements.

Plants must take the nitrogen compounds for building proteins in through their roots. These compounds of nitrogen, soluble nitrates and ammonium compounds, must be present in the soil. Nitrites apparently are poisonous to more complex plants, but fortunately bacteria change soil nitrites into nitrates quite promptly. (See Fig. 17-2.)

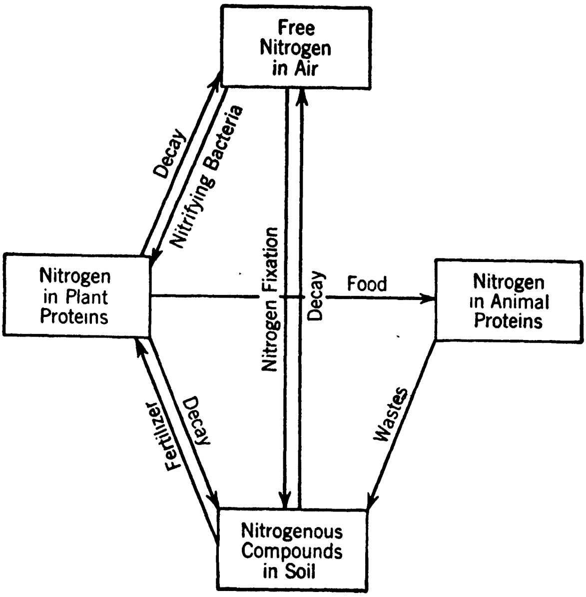


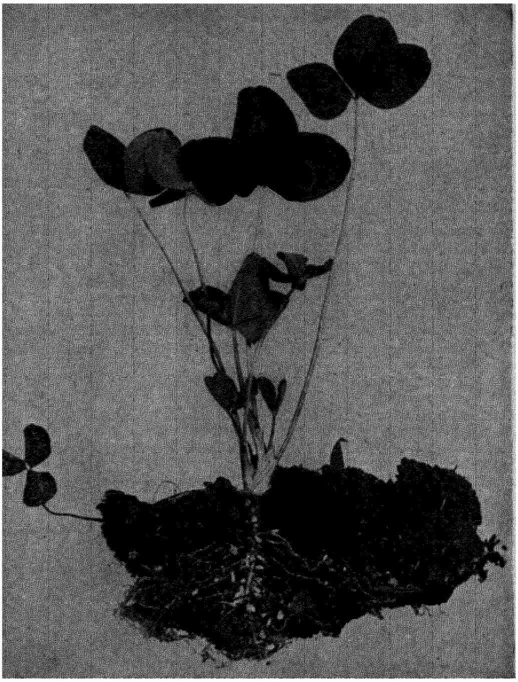
FIG. 17-2.—The nitrogen cycle in nature. Notice the missing link.

Important minerals that are easily exhausted from the soil are potassium compounds, phosphates, and sulfates, especially the phosphate and sulfate of calcium.

The three primary plant needs are compounds of nitrogen, potassium, and phosphorus. The chief secondary needs are compounds of calcium, sulfur, and magnesium. Other elements that may be needed include boron, copper, manganese, zinc, and iron in trace amounts. In some regions, plants sometimes cannot obtain enough of one or more of the common elements from the soil. It is known, for example, that chlorophyll contains magnesium and that without magnesium a plant cannot grow normally. Iron is usually abundant in soils, and certain plants, spinach, for example, require iron. When any of these elements is completely lacking, plants develop abnormalities or even wither and die.

When a crop grows, these essential elements are removed to some extent from the soil. Unless they are resupplied or an adequate amount remains in the earth, the soil becomes worthless for crops the following year. Some idea of the amount of material taken from the soil can be gained from the fact that the average variety of sugar cane removes 824 lb of potash, 235 lb of lime, and 124 lb of phosphoric acid per acre for the parts of the plant above the earth.

Nature's Fertilization Program. Certain plants of the ***legume*** family—including peas, beans, alfalfa, clover, vetch, and peanuts—are host to species of bacteria that live attached to their roots. These bacteria have the remarkable ability to take free, elementary nitrogen from the air and make it into nitrates. This chemical change is notable because no chemical laboratory can duplicate it at the low temperature used by the bacteria. The nitrates produced by the bacteria are left with the plant in small pockets on the roots, resembling miniature potatoes. These



Courtesy of Bureau of Plant Industry, Soils, and Agricultural Engineering, U.S. Department of Agriculture

FIG. 17-3.—The nodules on clover roots resemble little potatoes. They contain bacteria that can take free nitrogen gas from the air and form compounds of nitrogen useful for fertilizer. Mankind has not yet found a way to carry on this change at a low temperature.

nodules (see Fig. 17-3) are scattered throughout the soil when the plant is plowed under or decays, enriching the soil. Nitrogen-producing crops that are grown to be plowed under are called ***green manure***. The nitrates in the nodules can furnish fertilizer to the host plants as well as to following crops. In return for the nitrates, the bacteria take some starch and mineral matter from the host plants. The good effect of planting legumes was noticed by early Roman farmers, but the real cause of the benefit was not discovered until 1886. Anyone who takes the trouble to dig up a clover plant carefully can see the nodules on the roots.

QUESTIONS

1. What is the general composition of soil?

2. From what source does the soil obtain (*a*) sand; (*b*) clay; (*c*) humus?

3. What horizon of the soil "profile" is commonly reached in plowing?

4. Do all soils have all three horizons well developed and in distinct layers?

5. Name five useful substances, other than chlorophyll, that plants (including trees) produce.

6. Define *photosynthesis*.

7. Certain plants, for example mushrooms, have no green coloring matter in them. Do they produce starch? Do they carry on photosynthesis?

8. Give three examples of important bacterial actions within the soil.

9. List the three primary mineral requirements of most plants.

10. Of what value is a cover crop of clover, sown in the fall and plowed under in the spring?

Lightning. Nitrogen is also carried into the soil in the form of nitrates as a result of thundershowers. The U.S. Weather Bureau estimates a yearly average of 12 lb of fixed nitrogen per acre from lightning, or 770 million tons for the entire earth. In the lightning flash some of the energy of the electric discharge causes oxygen and nitrogen to unite.

$$\begin{aligned} N_2 + O_2 &\rightarrow 2NO \\ 2NO + O_2 &\rightarrow 2NO_2 \\ 3NO_2 + H_2O &\rightarrow 2HNO_3 + NO \end{aligned}$$

The nitric oxide formed is oxidized easily to nitrogen dioxide, dissolved in the rain, and carried to the earth in the form of a bath of dilute nitric acid. Limestone or other basic substances in the soil act quickly, on the nitric acid to convert it into calcium nitrate, a readily soluble plant food.

$$\underset{\text{limestone}}{CaCO_3} + \underset{\text{nitric acid}}{2HNO_3} \rightarrow \underset{\substack{\text{calcium}\\\text{nitrate}}}{Ca(NO_3)_2} + H_2O + CO_2\uparrow$$

Physical Condition of the Soil. Several facts about a good soil are evident on close observation. (1) The soil particles should be of the right size. If they are too large, they permit moisture to leave too rapidly. If they are too fine, they may pack and form a rocklike layer into which roots can hardly penetrate. (2) The soil should contain the right amount of moisture. Dry regions must be irrigated and swampy soils drained. (3) The moisture in the soil should be well distributed over the growing season. Most crops require about 20 in. of rainfall per year or an equivalent amount of water from irrigation. (4) A soil too sandy will not keep moisture or grow most crops well. A soil too rich in clay is hard to cultivate, slimy in wet weather, and hard-baked in dry. A soil rich in loam is inclined to become acid, a condition unfavorable to some crops. Obviously, a proper mixture of sand, clay, and humus is desirable. The most desirable set of conditions depends, of course, upon the crop to be raised.

Good soil should contain enough clay to make it jellylike when moist. In such a condition the soluble plant food will not wash away readily in the rainfall. Moreover, the soil should contain enough organic matter to retain moisture in the soil where the plants can obtain it. The moisture-retaining property is one of the most valuable qualities of barnyard fertilizers and peat moss.

Sources of Nitrogen Compounds. In addition to those nitrogen compounds which nature supplies, our principal sources of nitrogen include the following:

1. Chile Saltpeter (**$NaNO_3$**). This compound is imported from Chile, where it is found as a rocky deposit called *caliche*. The crude material is refined to 95 to 98 per cent purity by crystallization. It is equivalent to 15.6 to 16 per cent of nitrogen, readily soluble in water, and is used to force the growing of crops.

Synthetic sodium nitrate, or saltpeter, is now available. It is formed by running nitric acid onto soda ash.

$$2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + H_2O + CO_2\uparrow$$

2. Ammonium Salts. Ammonia, a by-product of the destructive distillation of soft coal (see page 386), is run into acid. The resulting compound, depending upon the acid used, may be ammonium sulfate [$(NH_4)_2SO_4$], ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), or diammonium hydrogen phosphate [$(NH_4)_2HPO_4$]. The equation for the reaction in the last case is

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$$

Today, great supplies of ammonium compounds are manufactured by synthetic processes.

3. ***Calcium Cyanamide*** **($CaCN_2$).** This compound is made by passing nitrogen over calcium carbide heated in an electric furnace (see page 252). It may be used directly as a fertilizer in limited amounts.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

4. ***Urea*** **[$CO(NH_2)_2$].** This compound is found in the urine of mammals and undoubtedly accounts for some of the fertilizing value of barnyard manures. Today, urea is produced synthetically in large quantities. It is soluble in water, and the commercial product contains about 46 per cent nitrogen. A small amount of synthetic urea is added to stock food.

5. ***Organic Nitrogen-containing Materials.*** (The figures in parentheses are the percentages of available nitrogen.) These include the meal from cottonseed, linseed, and castor beans after the oil has been extracted; scraps and tankage of many sorts including dried blood (12), fish scrap (8), garbage tankage (3), sewage sludge (2.5), and slaughterhouse tankage (10).

Fertilizer containing ammonium compounds should not be added to freshly limed soil since a reaction may take place that will result in a loss of nitrogen.

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O + 2NH_3\uparrow$$

Sources of Phosphates for Fertilizers. The chief source of phosphates is from natural rock phosphate, crude calcium phosphate [$Ca_3(PO_4)_2$]. This is treated to make phosphoric acid (H_3PO_4) (see page 368), or "superphosphate," although sometimes it is finely ground and applied to the soil without treatment.

1. ***Superphosphate.*** Ground rock phosphate is treated with about an equal weight of dilute sulfuric acid. The resulting mixture is composed of a calcium dihydrogen phosphate and calcium sulfate dihydrate. Both compounds are more soluble than calcium phosphate, but only moderately soluble, a desirable condition.

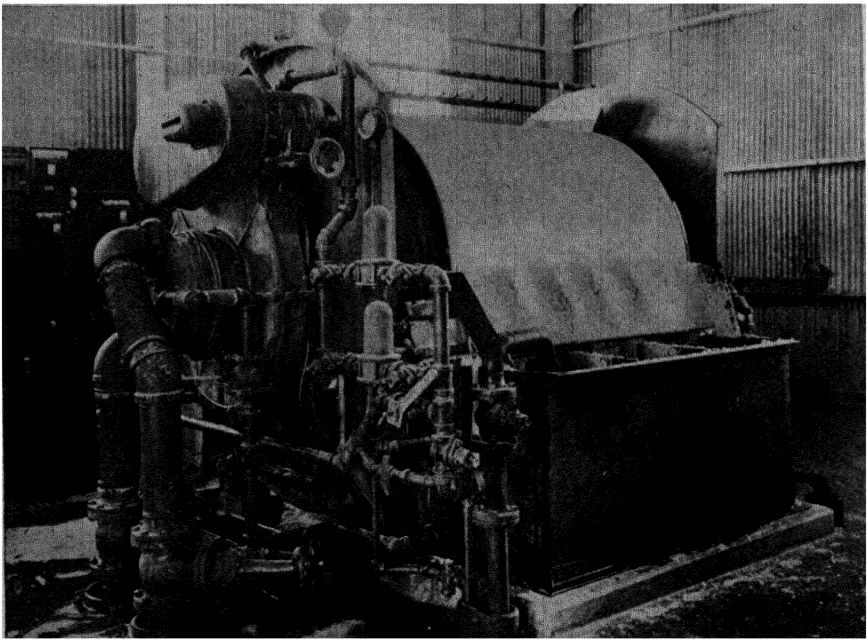
$$\underset{\text{tricalcium phosphate}}{Ca_3(PO_4)_2} + 2H_2SO_4 + 5H_2O \rightarrow \underbrace{\underset{\text{calcium dihydrogen phosphate}}{Ca(H_2PO_4)_2 \cdot H_2O} + \underset{\text{gypsum}}{2CaSO_4 \cdot 2H_2O}}_{\text{"superphosphate" of lime}}$$

Triple superphosphate, which contains 40 to 48 per cent available P_2O_5 against 16 to 20 per cent for the ordinary superphosphate, is made by using phosphoric acid instead of sulfuric acid. Calcium dihydrogen phosphate soon becomes converted to insoluble tricalcium phosphate in alkaline soil, making it unavailable to plants. This difficulty is overcome by applying it in rows parallel to the crops, where it does not become so thoroughly mixed with the alkaline soil.

2. ***Bones.*** Bones may be ground and used directly as a fertilizer. Their action is slow but lasting. They contain 20 to 25 per cent available

P_2O_5 and also about 3.5 per cent nitrogen. Their action may be hastened by treatment with sulfuric acid. In this case they become similar to superphosphate.

3. ***Slag.*** This waste product from the making of steel contains phosphorus, an undesired impurity in the steel. Experiments show that ground slag has beneficial effects on certain types of soil. This slag is a mixture of tricalcium phosphate and calcium silicate.



Courtesy of Oliver United Filters, Inc.

FIG. 17-4.—This continuous vacuum filter is handling potash at Trona, California. Potash is used extensively in fertilizers. The operating principle of such a filter is relatively simple. Can you explain it?

Sources of Potassium Compounds for Fertilizers. *1.* ***Mineral Deposits.*** The famous Stassfurt deposits of kainite ($MgSO_4 \cdot MgCl_2 \cdot K_2SO_4 \cdot 6H_2O$) and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) furnish enormous quantities of potash salts. Other European deposits also provide large amounts of potash. Deposits of potash minerals in the United States are found at Searles Lake in California (see Fig. 17-4) and in the Permian bed, which lies beneath portions of Texas and New Mexico.

2. ***Miscellaneous Sources.*** Flue dust, from cement kilns or blast furnaces, and wood ashes are rich in potash. These are saved and used for fertilizer. Wastes from sugar beet and molasses contain usable potash, as do seaweeds and tobacco by-products. By using all the miscellaneous sources and exploiting the natural resources within the country, the supply within the United States has been found adequate to meet the demand without depending upon European potash.

For the Land's Sake. Analyzed mixed fertilizers with certain percentages of plant food are available. Three figures, such as 4-16-4, are plainly shown to the purchaser. In most states the first figure means the percentage of available nitrogen calculated as N, the second the percentage of phosphorus calculated as P_2O_5, and the third the percentage of potash calculated as K_2O. Many states require that commercial fertilizer mixtures contain a certain minimum figure for *total* plant food, such as 16, 14, or 12.

The correct fertilizer for a farm depends upon (1) the crop to be grown, (2) the plant food already available in the soil, (3) the degree of acidity (pH) of the soil, (4) the moisture content of the soil, and (5) the state of maturity of the crop.

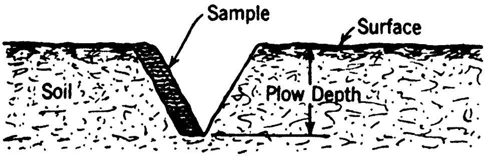


FIG. 17-5.—A proper method of sampling soil. A soil sample should not be taken from the surface only.

While the higher analysis mixed fertilizers cost more per ton, the increased percentage of available plant food often makes them really less expensive in the long run. In fact, usually fertilizers that contain less than 16 per cent total plant food, such as 3-8-3, are not economical, although they are very easily spread.

Soils should be analyzed to determine their fertility. Farmers are finding that a yearly analysis of the soil, not only for nitrogen, phosphorus, and potash, but also for trace elements, leads to better yields and better quality crops. Experiment stations in many state universities and elsewhere will analyze samples of soil submitted to them. The instructor may obtain a pamphlet[1] that summarizes the methods used, so that the student can analyze soils himself. Soil-testing kits are available from farm-supply companies.

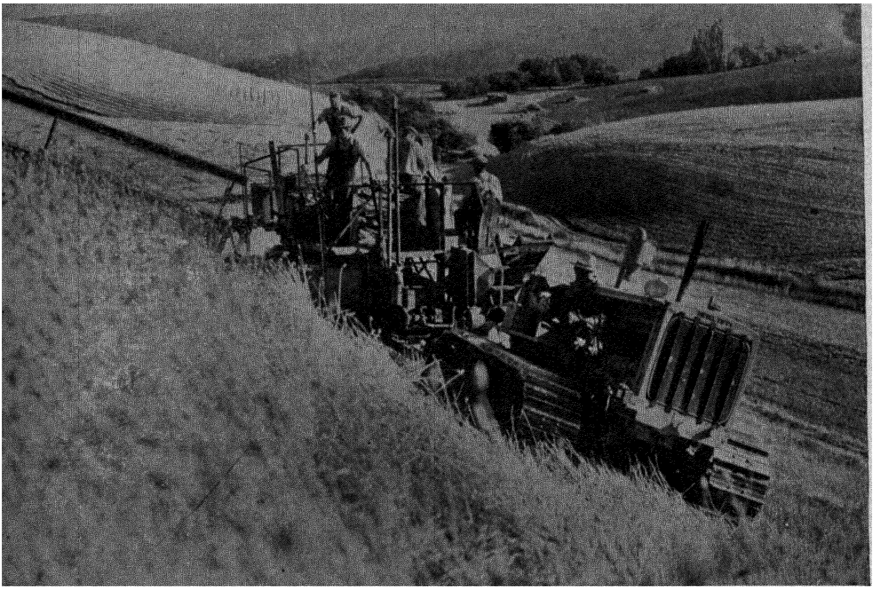
Sour Soil. When plants and rocks decay, the remains in the soil are acid. Unless the soil contains an abundance of carbonates, such as limestone ($CaCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$), in finely divided condition,

---

[1] MORGAN, M. F., Chemical Soil Analysis by the Universal Soil Testing System, *Bulletin* 450 (October, 1941), Connecticut Agricultural Experiment Station, New Haven, Conn.

the acid will remain. Most plants do not grow well unless the soil is neutral or slightly alkaline.

The cheapest and most effective way to sweeten sour soil is to "lime" it. Slaked lime [$Ca(OH)_2$] or quarry dust from marble or limestone ($CaCO_3$) deposits is an effective neutralizer of soil acids. In addition, lime improves the physical condition of the soil and makes plant foods generally more available. When the soil is too alkaline, ammonium sulfate [$(NH_4)_2SO_4$] is spread over it to neutralize the excess lime and to add nitrogen.



esy of Caterpillar Tractor Company

FIG. 17-6.—Contour farming on a slope saves soil. This is a wide-gauge diesel-engine-powered tractor pulling a combine near Walla Walla, Washington.

Hydroponics. Many experiments have recently been carried out on the growing of plants without soil. The seeds are planted in a tank containing a solution of mineral salts, adjusted to the ideal condition for the growth of a plant. The plant stalk and roots are supported by wires and excelsior. The results show that extra-large vegetables and fruit can be produced when a plant is grown under these ideal conditions. For many, hydroponics has become an interesting hobby as well as a business. Growing plants without soil, however, only emphasizes the importance of good soil.

Keeping the Soil. With modern farm machinery many more acres can be plowed and harrowed than was possible by the use of horse-drawn implements. Using chemical fertilizers and rotating crops instead of waiting for soils to revive after use have decreased the amount of idle land on a farm. The net result is that more acres per farmer are cultivated than formerly. Many acres lie open, prepared for a crop or awaiting a growing crop. Such land has very few binding roots to hold the soil in place. When strong winds or rain comes, this soil is easily moved, resulting in a loss to the farmer.

Soil has always been movable and is constantly on the move. New soil is constantly being formed. Under some conditions at present, however, the rate of loss far exceeds the rate of recovery of the soil. Intelligence must be used to conserve the valuable part of a farm, the soil. (See Fig. 17-6.)

SUMMARY

Soil consists of sand, clay, humus, and moisture. Humus comes from decayed organic matter. Clay and sand come from weathered rocks.

Soil may be classified in layers or horizons. The *A* horizon represents topsoil, rich in humus. The *B* horizon represents reserve soil, lacking humus. The *C* horizon represents parent material.

Plant food consists of minerals and moisture from soil and carbon dioxide from the air. Compound building by plants is a reduction process, the opposite of the oxidation processes carried on by most of man's activities; it is accomplished by chlorophyll in the presence of sunlight. Nitrogen, potassium, and phosphorus compounds are most readily exhausted from the soil by plant growth. Many other elements are essential to plant growth.

Natural fertilization is supplied in three ways:

1. Legumes supply nitrates through bacterial action.
2. Lightning storms add nitrates.
3. Soil water may bring minerals up from lower depths or from adjacent lands.

For continued farming, minerals must be supplied by fertilizer.

Important aspects of the physical condition of the soil are

1. Size of soil particles
2. Amount of moisture and its distribution throughout the growing season
3. Acid or alkaline conditions of the soil
4. Amount and distribution of humus

Sources of nitrogen for fertilizing soils include nitrogen compounds obtained from Chile saltpeter, nitrates from fixation of atmospheric nitrogen, ammonium compounds, calcium cyanamide, urea, manures, and refuse material.

Sources of phosphates for fertilizing include rock phosphate, or superphosphate; bones; and some slags.

Sources of potash for fertilizing include mineral potash deposits in ancient lake beds, ashes, and wastes.

Fertilizers are rated by a three-number system: The first number is the percentage of available nitrogen. The second number is the percentage of phosphorus, calculated as P_2O_5. The third number is the percentage of potassium, calculated as K_2O.

Alkaline soils can be treated with decayed vegetation or ammonium sulfate if more acidity is required. Sour soils may be treated with limestone, dolomite, or hydrated lime.

Erosion is an important soil problem. Successful farming uses methods of binding the soil to the farm to prevent loss of topsoil by wind and rain erosion.

QUESTIONS

11. Tropical vegetation grows in lush abundance in regions of many thunderstorms. Give three conditions that favor plant growth in these regions.

12. Would adding carbon dioxide to the air in a greenhouse be of value?

13. What treatment is recommended for changing the following into good farming land: a desert; a swamp; sour soil; hard-packed clay; a boulder-strewn field; land covered with stumps of trees?

14. During World War II a certain brand of fertilizer changed from 6-8-6 rating to 2-8-6. Account for the change.

15. For what purpose would (*a*) sodium nitrate be more desirable to use on crops than organic nitrogen compounds; (*b*) organic nitrogen compounds rather than sodium nitrate?

16. List the sources of synthetic nitrogen compounds.

17. Compare the availability to plants of the mineral matter in (1) dog-buried bones, (2) bone meal, (3) bone meal treated with sulfuric acid.

18. Is mineral fertilizer alone, used year after year, sufficient to grow successful crops, or is the addition of barnyard manure desirable?

19. Point out an advantage of ground dolomite over ground limestone for sweetening the soil.

20. Hillsides are sometimes cultivated in strips, by leaving grasslands between cultivated areas and plowing along contour lines. Point out the advantages of this practice.

21. What is the percentage of nitrogen in (*a*) sodium nitrate; (*b*) urea; (*c*) calcium nitrate?

22. What is the percentage of phosphorus in tricalcium phosphate? In "superphosphate"?

23. What is the percentage of P_2O_5 available from calcium phosphate?

24. What is the percentage of K_2O in potash (K_2CO_3)?

25. Account for the odor of ammonia near a manure pile. Tell why such a condition should be avoided.

26. What is "compost"? State one advantage and one disadvantage in adding compost to soil.

27. Has kitchen garbage any value as fertilizer?

UNIT FOUR .... CHAPTER XVIII

CHEMISTRY OF THE SEA— THE HALOGEN SALTS

The general conditions of life in the sea are not vastly different from those on land; plants must live and grow by the process of photosynthesis, absorbing at the same time nutrient substances, such as phosphate and nitrate, from their surroundings; the smaller animals "graze" upon the plants and are in turn consumed by the larger animals. And when they finally die, large and small, all decay and are decomposed by the ever-present bacteria, and their substance is thrown back into solution again in the form of carbon dioxide, nitrate, phosphate, and the like. One of the chemist's principal contributions has been the study of this cycle, particularly the role played by nitrate and phosphate in the fertility of the sea. For different parts of the sea are as vastly different as are different parts of the land. The sea has its barren deserts, where little life goes on, as well as its areas of abundant growth.

A nitrogen cycle exists in the sea as on land. The ammonia resulting from protein decay is oxidized successively to nitrite and nitrate, and it is likely that under certain conditions this process may also be reversed. These changes are brought about by means of bacteria similar to, if not identical with, those which bring about the same changes on land. These organisms inhabit the water, but apparently occur in very much larger numbers in the bottom mud of shallow seas, where most of this oxidation probably takes place. The conditions of the deep-sea bottom are largely known. Although nitrogen-fixing bacteria, capable of utilizing atmospheric nitrogen, have been isolated from the sea, it is rather unlikely that they play an important part in the marine nitrogen cycle.[1]

Composition of the Sea. The most impressive fact about the sea is its tremendous extent. We all know that the sea covers 70.73 per cent of the earth's surface and that most of the uninhabited portion of this globe lies under water. Only recently have chemists made the sea a source of raw materials.

New Terms

halogens
fluorine
chlorine
bromine
iodine
sublime

---

[1] Rakestraw, Norris W., "The Chemistry of Sea Water," *Report, New England Association of Chemistry Teachers*, vol. 35, No. 1, 1933.

One liter of sea water weighs about 1030 g. A liter of pure water weighs 1000 g. We say that the specific gravity of sea water is 1.03.

Water makes up about 993.7 g of the 1030 g, or 96.4 per cent of the weight of sea water. Ordinary salt ($NaCl$) accounts for 27.87 g, or 2.79 per cent. Other constituents are magnesium chloride ($MgCl_2$) 3.78 g; Epsom salts ($MgSO_4$) 2.37 g; calcium sulfate ($CaSO_4$) 1.45 g; potassium chloride (KCl) 0.79 g; calcium carbonate ($CaCO_3$) 0.03 g; and magnesium bromide ($MgBr_2$) 0.03 g.

> Let us take 1 cubic mile of sea water out of the 331 million cubic miles of whole ocean. This 1 cubic mile will contain 128 million tons of sodium chloride ($NaCl$), 18 million tons of magnesium chloride ($MgCl_2$), 358,000 tons of magnesium bromide ($MgBr_2$), 1400 tons of fluorine, and so on, in solution. The deposits of the bottom contain the insoluble excesses as precipitates, probably in quantity even greater than that which is dissolved and in solution.[1]

In the sea water these salts are dissolved and are of course present only in the form of ions rather than being associated into definite compounds. They are given as compounds to show the relative amounts. As such, the principal metal ions in the sea are sodium (Na^+), magnesium (Mg^{++}), calcium (Ca^{++}), and potassium (K^+). The chief nonmetal ions are chloride (Cl^-), sulfate (SO_4^{--}), and bromide (Br^-).

Gold from the Sea. The total amount of gold in the sea is more than has ever been mined on land. This fact comes as a result of simple arithmetic. A tiny trace multiplied enough times will give an amazingly large figure.

Many attempts have been organized to extract gold from sea water, and many clever chemical methods have been proposed to accomplish this. Some of these proposals are the result of overenthusiasm or possibly fraud, as we shall see presently.

After Fritz Haber of Germany had worked so hard and with so great a measure of success during World War I to solve his country's nitrogen-fixation problem (see page 387), with the coming of peace he turned his attention to a possible solution of her economic troubles—the securing of gold from sea or river water. With remarkable diligence he perfected a method of analysis for gold in sea water that was reliable to an extent never before approached. The results of his analysis were most disappointing to his hopes, however. He found, a result recently confirmed by William E. Caldwell of Oregon State College, that the value of the gold in a metric ton of sea water was about one one-hundredth of a cent ($0.0001).

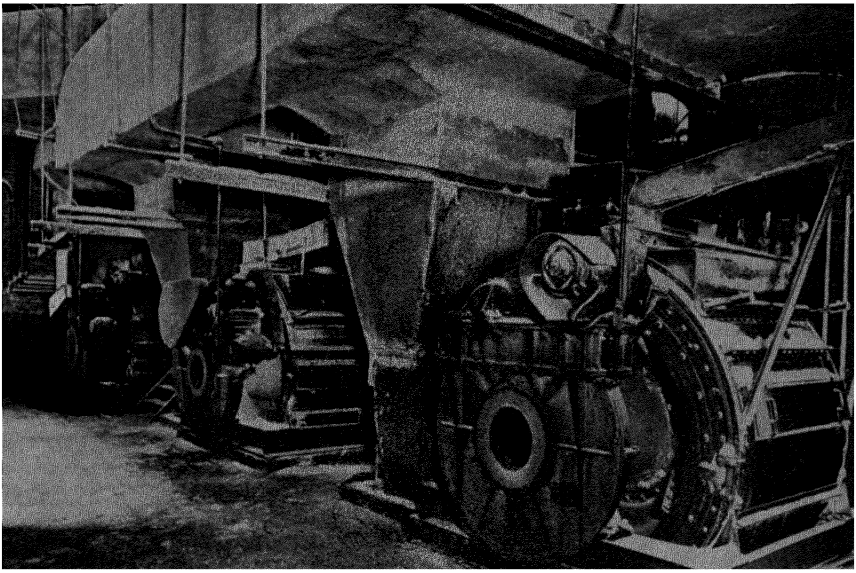
It now becomes evident that, if gold is to be obtained from sea water,

---

[1] TAYLOR, HARDEN F., "Chemical Resources of the Ocean," *The Chemist*, vol. 19, No. 4, 1942.

most of it will be obtained by the sale of other substances obtained from the sea. Small samples of gold, however, have been prepared from sea water. Their cost at present far exceeds their value as metal.

Sea Salt. The salt we use today is either from the sea directly or from arms of the sea that have long since dried up, leaving the dissolved salt as crystals. Enormous deposits of such salt beds are known, one of them under the city of Detroit, Michigan. Vast quantities of salt are found in the United States in New York, California, Kansas, Utah, and Louisiana. Mines that have been worked for hundreds of years are famous in continental Europe. While salt deposits only 8 ft thick are worked in some places, a Texas salt dome is known to be 3000 ft thick. The Stassfurt salt deposit that underlies the potash deposit is several thousand feet deep.



Courtesy of Oliver United Filters, Inc.

FIG. 18-1.—Salt from an ancient sea is mined and filtered in Ohio. The picture shows rotary filters in operation.

Some of the salt is harvested as solid mineral from ancient deposits as high as 99.4 per cent pure, as at Avery Island, Louisiana. Sometimes it is brought out of the earth as brine and used without purification after evaporation of the water. In the Great Salt Lake area and around San Francisco Bay the salt water is evaporated by the heat of the sun. Salt is concentrated by freezing out the water in northern Russia.

Common salt cakes, or sticks together, in moist weather. This effect is caused by the presence of small amounts of magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) in the salt. These impurities absorb moisture from the air. Their effect can be counteracted by adding about 1 per cent of calcium carbonate ($CaCO_3$) or tricalcium phosphate [$Ca_3(PO_4)_2$] to the salt. Starch will also produce a similar result.

Salt is a necessity for life. Human beings and animals crave salt if it is not supplied in sufficient quantities in the diet. Salt licks in dairy barns are a familiar sight. Because of the common human need for salt, this compound has sometimes served for money among primitive peoples. Salt is a well-known symbol of friendship. Many stories and traditions have arisen dealing with this substance.

The Ancient Use of Salt. In the Bible we read, "Ye are the salt of the earth: but if the salt have lost his savour, wherewith shall it be salted? It is thenceforth good for nothing, but to be cast out, and to be trodden under foot of men."[1]

The Palestinian housewife used sea salt for cooking, but it was often dirty from mud gathered with the salt. She therefore tied the salt and dirt together in a little cloth bag and used the salt bag to season her cooking in a manner similar to the use of tea bags today. When the flavor of the salt was gone, the contents were worthless.

Uses of Salt. In addition to its obvious use for flavoring, great amounts of salt are employed for preserving meats and fish, glazing pottery, printing textiles, making soap, and making brines for refrigerating.

Salt is the starting substance from which are made all chlorides and compounds of sodium as well as the elements sodium and chlorine themselves. This includes the manufacture of such needed substances as lye ($NaOH$), baking soda ($NaHCO_3$), washing soda (Na_2CO_3), hydrochloric acid (HCl), sodium sulfate (Na_2SO_4), and trisodium phosphate (Na_3PO_4).

Sodium fluoride, sodium bromide, and sodium iodide as well as bromine and iodine can be made from sea water, directly or indirectly. These elements are found together in group VIIb of the periodic table (page 329).

The Halogens. The family name, halogen, of the four elements fluorine, chlorine, bromine, and iodine, means "salt producer." They all have similar properties, for each element has an ionic charge and a combining number of 1. Each has seven electrons in its outermost orbit and a pronounced tendency to fill the one remaining space. As the atomic weight of the elements increases from F 19 to I 127, the chemical reactivity decreases from fluorine, most active, to iodine, least active. The compounds are graded similarly in stability from hydrogen fluoride (H_2F_2), most stable, to hydrogen iodide (HI), least stable.

Fluorine. This element is so active that for 75 years it challenged the ingenuity of chemists to isolate it. Although it was thought that it could

---

[1] Matthew 5: 13.

be produced by the strong reducing action of an electric current, it always reacted with the apparatus as soon as it was liberated. Finally, Henri Moissan made a platinum apparatus in which, in 1886, he electrolyzed potassium fluoride (KF) in liquid hydrogen fluoride (H_2F_2). He was successful in obtaining a pale yellow gas, which he kept in a bottle carved from transparent mineral fluorite (CaF_2). Copper vessels are now used.

Fluorine is the most active of all chemical elements. It acts violently with water, and because of its fierce untamable activity it is not used frequently in the free state. Recently, however, it has found some use in chemical syntheses.

Fluorides. Traces of fluorides are found in the enamel of the teeth. Fluorite (CaF_2) and cryolite, a complex fluoride of sodium and aluminum (Na_3AlF_6), are useful compounds of fluorine found in nature.

In some regions traces of fluorides are found in the drinking water. People living in these regions are much less subject to dental caries (tooth decay) than those in other regions. Since excess fluorides cause mottled teeth and even serious poisoning, it is not safe for a person to add this element to his drinking water.

Some insect poisons contain sodium fluoride (NaF). The dust from fluorides is poisonous, and should not be breathed. Some of the new harmless, nonflammable refrigerants contain fluorine, difluoro-dichloromethane (CF_2Cl_2), for example.

Hydrogen Fluoride. Hydrogen fluoride can be made by the action of sulfuric acid on powdered fluorite. The materials are mixed in a lead dish

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2\uparrow$$

At room temperature hydrogen fluoride is a gas that dissolves in water, forming hydrofluoric acid, a weak acid. The most remarkable property of this acid is its attack on glass, or sand.

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4\uparrow + 2H_2O$$

Sand, or silica (SiO_2), can be considered the most inactive portion of common glass, so the equation above describes the action of the acid on glass, simplified. The silicon tetrafluoride (SiF_4) escapes as a gas, and the reaction tends to go to completion.

Hydrofluoric acid is used for marking or etching glassware and light bulbs. The portions of the glass that are to be shielded from its corrosive action are covered with paraffin. Of course, we cannot keep this acid in glass bottles. Bottles made of Bakelite or ceresin, a mineral waxlike paraffin, are suitable for this purpose. A paste containing ammonium fluoride (NH_4F) is also used for etching glass.

Chlorine. Like fluorine and the other members of the halogen family, chlorine is too active to be found free in nature. It is found in chlorides, chiefly common salt (sodium chloride).

Chlorine can be freed from sodium chloride by electrolysis of its solution in water. We shall again consider this change in connection with the making of sodium hydroxide. (See page 374.) Chlorine can also be freed from salt by first changing it into hydrogen chloride and then oxidizing the hydrogen chloride. (See Fig. 18-2.) The two actions are

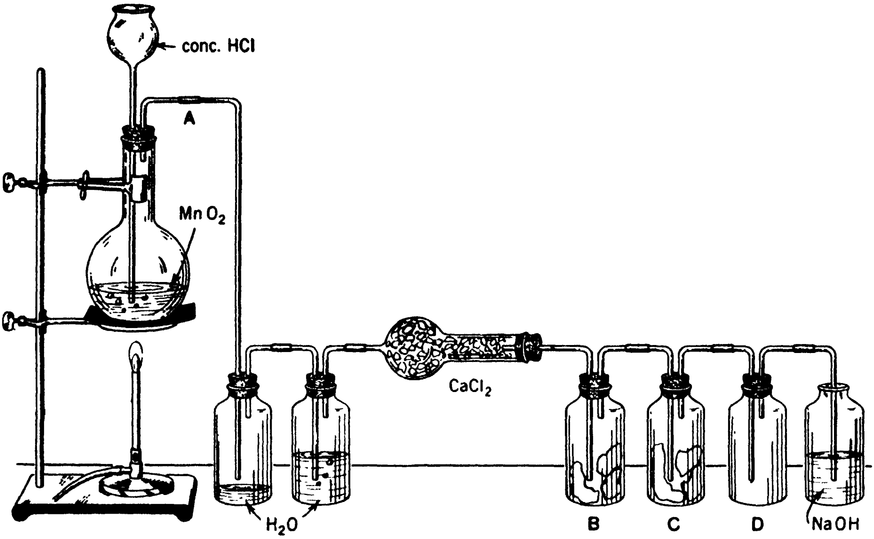


FIG. 18-2.—Chlorine may be prepared and its properties demonstrated by use of this apparatus. Chlorine has little effect on the pieces of dry cloth in *B*, but it bleaches the moist cloth in *C*. Bottle *D* may be replaced when it is filled with chlorine.

$$NaCl + H_2SO_4 \rightarrow HCl\uparrow + NaHSO_4$$
$$4HCl + MnO_2 \rightarrow 2H_2O + MnCl_2 + Cl_2\uparrow$$

QUESTIONS

1. Point out three similarities and one difference between life in the ocean and life on land.

2. If after treatment $\begin{cases}80\\90\end{cases}$ per cent of the bromine is removed from some sea water, how many tons of magnesium bromide remain in a cubic mile of the water?

3. List the seven most abundant ions in sea water.

4. Review the reasoning which leads to the conclusion that obtaining gold from sea water is likely to be unprofitable.

5. What compounds other than sodium chloride are obtained by evaporation of sea water?

6. List 10 uses for common salt.

7. List the halogens in order of increasing chemical activity.

8. Write formula equations for (*a*) the explosive reaction of fluorine on water; (*b*) action of concentrated sulfuric acid on calcium fluoride; (*c*) action of hydrofluoric acid on sand; (*d*) action of ammonium fluoride on sand.

9. Point out two ways to obtain elementary chlorine from common salt.

10. Write formula equations for (*a*) electrolysis of common salt in water; (*b*) reaction of salt with concentrated sulfuric acid; (*c*) reaction of salt solution with silver nitrate solution; (*d*) electrolysis of melted salt.

What Is Chlorine Like? Chlorine is a pale-green gas at room temperature. Its color can be observed easily when a piece of white paper is held behind a bottle or test tube containing the gas. This gas was first observed by Scheele, of Sweden, in 1774 and was later proved to be an element by Sir Humphry Davy. The gas is about 2½ times as dense as air and dissolves moderately well in water.

When breathed, chlorine irritates the throat and lungs. Large amounts may be fatal, but in very small concentrations the gas has been tried as a cure for colds. The results were not favorable.

Chlorine burns quietly in hydrogen, but a mixture of the two gases will explode if ignited or even brought into strong light.

$$H_2 + Cl_2 \rightarrow 2HCl$$

So ready is this element to combine with hydrogen that chlorine will take hydrogen out of compounds. Warmed turpentine, a compound of hydrogen and carbon, or a wax candle, also of the same two elements, burn in a jar of chlorine with a yellow, sooty flame, forming carbon.

$$C_xH_y + \frac{y}{2}Cl_2 \rightarrow xC + yHCl$$

In the equation, x stands for the number of carbon atoms and y for the number of both hydrogen and chlorine atoms.

Metals will glow or burn in chlorine. A warmed sheet of thin copper becomes red-hot in the gas while copper chloride is formed. Sodium's action on the gas is so violent that it may be observed safely only from behind a suitable protecting barrier. Pieces of arsenic or antimony rubbed together over a bottle of chlorine drop off chips that burn spontaneously in the gas, forming a white smoke. The equations are

$$\begin{gathered} Cu + Cl_2 \rightarrow CuCl_2 \\ 2Na + Cl_2 \rightarrow 2NaCl \\ 2As + 3Cl_2 \rightarrow 2AsCl_3 \\ 2Sb + 3Cl_2 \rightarrow 2SbCl_3 \end{gathered}$$

We should expect phosphorus, a nonmetal, also to combine with chlorine. This occurs readily, forming the higher-valence compound of phosphorus, phosphorus pentachloride.

$$2P + 5Cl_2 \rightarrow 2PCl_5$$

Chlorine acts slowly on water in which it has dissolved. The eventual product of the action is oxygen.

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

Evidence shows that this action is one that proceeds in interesting stages. In the first step the action is

$$HOH + ClCl \rightarrow \underset{\text{hydrochloric acid}}{HCl} + \underset{\text{hypochlorous acid}}{HClO}$$

The hypochlorous acid is quite unstable, ready to part with its oxygen for the second step.

$$HClO \rightarrow HCl + [O]$$

At the moment of its liberation the oxygen is very active because of the energy of the chemical action. This freshly made element is said to be in the *nascent* condition. It will oxidize germs in drinking water or sewage or will bleach oxidizable dyes.

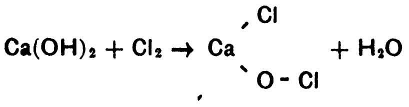
When chlorine is passed into dilute lye solution, sodium hypochlorite is formed.

$$2NaOH + ClCl \rightarrow NaCl + NaClO + H_2O$$

This solution, with a stabilizer to prevent its too rapid decomposition, is sold under various trade names as a household bleach. In hospitals a 0.5 per cent solution of sodium hypochlorite with sodium hydrogen carbonate ($NaHCO_3$) is used to irrigate infected wounds. It is called Dakin's solution. The product of its decomposition is merely salt water of such a concentration that it will not smart in an open wound.

$$NaClO \rightarrow NaCl + [O]$$

How Chlorine Is Sent to Market. Chlorine is sent to the local grocer's in two forms. (1) Household bleach (NaOCl) has already been mentioned. (2) Chlorinated lime (incorrectly "chloride of lime"), used for bleaching purposes, is a convenient substance from which chlorine can be liberated by the action of any acid, even carbonic acid from the air. It is made by passing chlorine gas over moist slaked lime.



$$Ca(OH)_2 + Cl_2 \rightarrow Ca\begin{matrix} Cl \\ \\ O-Cl \end{matrix} + H_2O$$

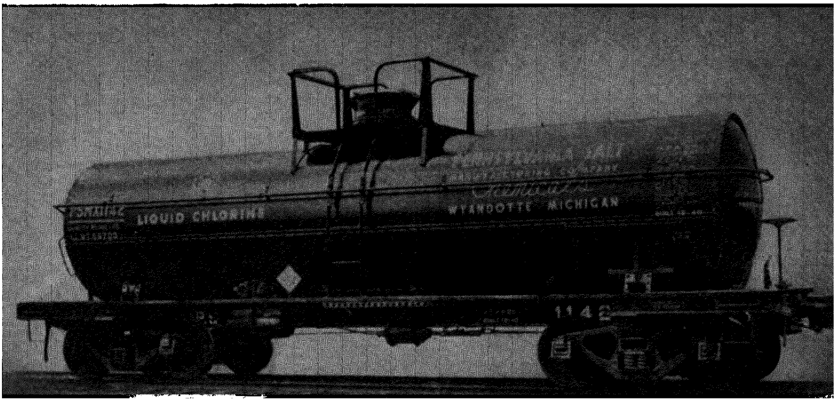
Common bleaching powder is a mixed compound, part calcium chloride and part calcium hypochlorite ($CaOCl_2$).

Recently a method of making true calcium hypochlorite [$Ca(OCl)_2$]

has been developed. This is marketed under the trade names H.T.H. (high-test hypochlorite) and Perchloron, among others. Because of its increased strength it is more effective for killing germs than the older bleaching powder. Solutions of calcium hypochlorite are used in wading pools to prevent the spread of foot-borne infection at public baths.

Chlorine also is sold in strong steel tanks. Compressed under moderate pressure, the gas turns to a liquid. Many cities buy tanks of liquid chlorine for purifying water supplies. (See Fig. 18-3.)

Uses for Chlorine. The uses of chlorine for bleaching, for purifying water, and for making chlorides have been mentioned. Most of our paper is bleached with chlorine, and some textiles, cotton for example, are similarly whitened. Many useful substances are made from chlorine—chlorates, bromine, and chlorinated compounds of all sorts. The production of this gas in the United States alone is about 2000 tons per day, more in wartime.



Courtesy of Pennsylvania Salt Manufacturing Company

FIG. 18-3.—Chlorine is shipped in strong steel tanks. The tanks contain liquified gas (no water). Commercial chlorine is made from salt by the electrolysis of brine.

QUESTIONS

11. Write the formula equation for the action of chlorine with (*a*) hydrogen; (*b*) zinc; (*c*) aluminum; (*d*) water; (*e*) methane (CH_4). Assume complete chlorination.

12. Why should chlorine water for bleaching be freshly prepared?

13. Distinguish these three compounds in respect to composition: calcium chloride; bleaching powder; calcium hypochlorite.

14. Soldiers are sometimes supplied with hypochlorite tablets. For what purpose may they be used?

15. A strong steel tank is being filled with compressed chlorine. How will the operator know when the tank is full?

16. What percentage of common salt is chlorine?

17. From the formula Cl_2, find the density of chlorine gas at STP.

18. What two conditions are helpful for changing gaseous chlorine into a liquid?

19. In what form is chlorine purchased to disinfect small swimming pools?

20. Suggest a reason why book paper in wartime has a grayish cast rather than its customary white appearance.

Bromine. Sea water contains about 0.0064 per cent bromine. This is less than 70 parts in a million. Nevertheless, patient research and experimenting have shown that this valuable element can be obtained profitably from the sea. This achievement is a masterpiece of technical skill.

A bromine plant is located at the mouth of the Cape Fear River, North Carolina, and another at Freeport, Texas. Sea water is pumped into the plant, acidified, and treated with chlorine. The bromine, which is present as bromide ions, is replaced by the more active chlorine.

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2 \qquad \text{(ionic equation)}$$

The freed bromine, 15,000 pounds a day, is blown by air into an absorbing agent and then made into ethylene dibromide ($C_2H_4Br_2$), which is chiefly used as a part of the Ethyl fluid in gasoline.

It is interesting to note that most of both the bromine and the sodium prepared in the United States goes into the manufacture of leaded gasoline.

Bromine is also obtained from salt brine residues in Michigan, Ohio, West Virginia, Stassfurt (Germany), and Tunis (North Africa).

In the laboratory we prepare bromine by mixing a bromide with an oxidizing agent and moistening the mixture with concentrated sulfuric acid. Manganese dioxide is a convenient oxidizing agent, although sodium chlorate is used commercially.

$$2NaBr + MnO_2 + 2H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Br_2\uparrow$$

The bromine is separated as a gas when the mixture is heated. When cooled to 63°C, it forms a brown-red liquid, which vaporizes easily.

Bromine can also be made by electrolysis. A solution of sodium bromide is used. The element collects at the anode. The process is similar to the electrolysis of sodium chloride solution (see page 374).

Bromine is unpleasant and very irritating to breathe. Its name comes from a Greek word meaning "stench." Liquid bromine, if spilled on the hands, destroys the tissue and causes sores that are very painful and slow to heal.

Bromine joins with active metals, zinc or magnesium, and will also add to phosphorus.

$$Mg + Br_2 \rightarrow MgBr_2$$
$$2P + 3Br_2 \rightarrow 2PBr_3$$

It is less active than chlorine, and it will not replace chlorine from chlorides. It does, however, replace iodine from iodides.

$$2NaI + Br_2 \rightarrow 2NaBr + I_2$$

Uses of Bromine. Bromine is used in many chemical syntheses, especially those in organic chemistry. It is also used in the preparation of some dyes. Some of its compounds are used as "tear gas" by law-enforcement officers. Silver bromide is the most important compound in photographic films. By far the largest use of bromine is in the preparation of compounds that go into "leaded gasoline."

Iodine. "Iodine" when placed on a cut stings and smarts. This "iodine" is a tincture or alcohol solution of iodine prepared by the druggist. It contains potassium iodide as well. We may use "iodized salt" at home, that is, ordinary salt to which a small amount of potassium iodide has been added. The use of iodized salt helps prevent simple goiter, a disease of the thyroid gland in the neck, sometimes caused by lack of sufficient iodine in the body.

Iodine comes from two sources: (1) An impurity in Chile saltpeter, sodium iodate ($NaIO_3$), is separated from the main deposit of sodium nitrate ($NaNO_3$) by crystallization. Iodine is prepared easily from the iodate. (2) The water found under certain oil wells contains small quantities of iodides. These wells are in California, Texas, Russia, and Italy. The iodine is prepared in a fashion similar to that of making bromine (see page 306).

A laboratory method of preparing iodine is to mix sodium iodide with an oxidizing agent and concentrated sulfuric acid. When warmed, vapors of iodine arise from this mixture and condense as a solid on a cooled surface above. When manganese dioxide is used for the oxidizing agent, the equation is

$$MnO_2 + 2NaI + 2H_2SO_4 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$

The disagreeable odor of hydrogen sulfide is noticeable when this mixture is prepared. Some hydrogen iodide forms and reduces the sulfuric acid.

$$H_2SO_4 + 8HI \rightarrow 4I_2\uparrow + H_2S + 4H_2O$$

Both reactions produce iodine.

Iodine can also be made from the ashes of some seaweeds or kelps. These ashes are also a source of potassium compounds.

What Is Iodine Like? Iodine forms glistening, dark crystals, which make a brown mark on paper. The crystals dissolve in benzene (C_6H_6), carbon tetrachloride (CCl_4), and several other solvents, forming a purple solution. They dissolve in water containing potassium iodide (KI) or in alcohol, forming a brown solution. When iodine is heated, a purple vapor forms, which crystallizes as steel-gray needles on a cold surface. Apparently iodine can change from a solid to a vapor, and vice versa, without forming a liquid. Solids like iodine and solid carbon dioxide (Dry Ice) that omit the liquid state when they evaporate at atmospheric pressure are said to ***sublime.*** When the pressure is higher, both these substances exist as liquids.

Tincture of iodine is an effective antiseptic; in fact, iodine is used extensively in medicine. It is also used to make some dyes and as a catalyst. Silver iodide is used in photography. Methylene iodide (CH_2I_2), specific gravity 3.325, is one of the densest liquids at room temperature. It is used in mineral separation experiments.

Tests for Halogens. As has been previously stated fluorides act with concentrated sulfuric acid to produce a gas that when dissolved in water produces an acid that will eat into glass. This experiment serves as a convenient test to recognize a fluoride.

A soluble chloride forms a curdy white precipitate when silver nitrate solution is added. The precipitate is soluble in ammonium hydroxide and insoluble in nitric acid.

To the solution to be tested for bromide or iodide ion, we add fresh chlorine water. We then obtain the free element bromine or iodine, shown by a darkening of the solution. Next we add carbon tetrachloride (CCl_4) to the mixture and shake well. The carbon tetrachloride, which is not soluble in water, dissolves the halogen and forms, if bromine, a red-brown layer; if iodine, a violet-purple layer.

Free elementary iodine colors starch blue. When this test is applied to foods, it is better to boil the food before making the test. The steam formed ruptures the woody wall that surrounds the starch grains. An iodide or, better, iodide ions will not give this test with starch.

Replacement of Negative Ions. Chlorine will replace bromine from a solution of a bromide or iodine from a solution of an iodide.

$$Cl_2 + MgBr_2 \rightarrow MgCl_2 + Br_2$$
$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

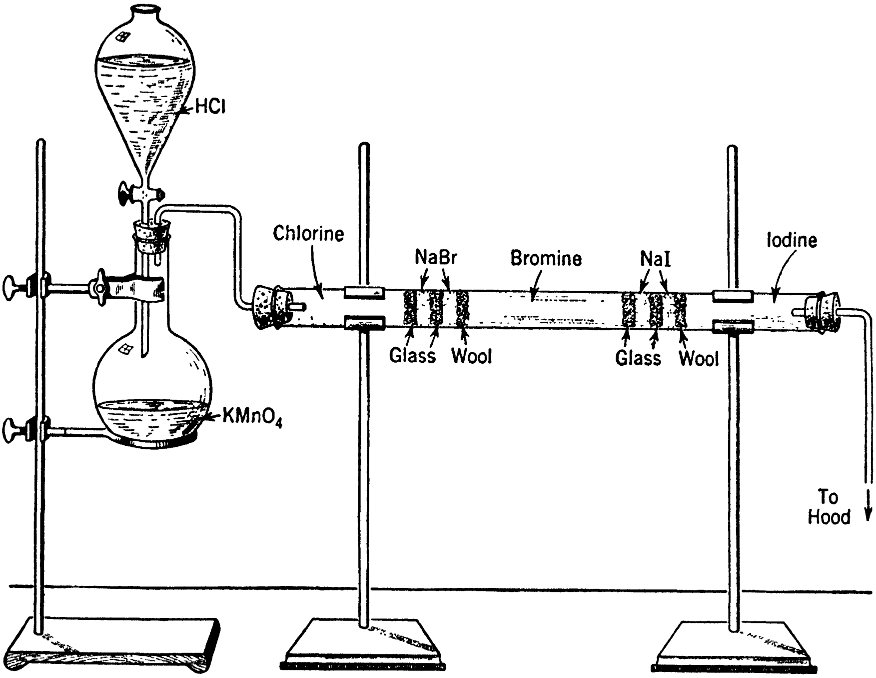
Bromine will replace iodine from an iodide solution, but bromine does not act on the solution of a chloride.

$$Br_2 + 2NaI \rightarrow 2NaBr + I_2$$

Iodine will not act on a chloride or a bromide. Hence it has the least replacing ability.

F
Cl
Br
I

From such experiments as these we can make an activity list of the halogens. Obviously, the very active fluorine comes first, followed by chlorine, bromine, and iodine in that order. We are not surprised to find that this order is identical with that given in the periodic table (see page 329).



Courtesy of Journal of Chemical Education

FIG. 18-4.—This apparatus can be used to show successive replacement of the halogens. Reading from left to right, chlorine is generated, replaces bromine, which in turn displaces iodine.

This sort of replacement is similar to the replacement of hydrogen by zinc, except that it is replacement of negative ions.

$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$ (formula equation)

$2Na^+ + 2Br^- + Cl_2 \rightarrow 2Na^+ + 2Cl^- + Br_2$ (complete ionic equation)

$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$ (ionic equation)

That is, each chlorine atom takes an electron from a less active bromide ion. The chlorine atom becomes a chloride ion, and the bromide ion changes into the free element.

Comparison of the Halogens. The following table shows a regular gradation in the properties of the four halogens.

	Atomic weight (approx.)	Color	Boiling point, °C	Density	Heat of formation of hydrogen halide, cal
Fluorine	19	Pale yellow	−187	1.108 (liquid)	63,991
Chlorine	35.5	Yellow-green	− 33.7	1.567 (liquid)	22,030
Bromine	80	Red-brown	58.78	3.19 (liquid)	8,650
Iodine	127	Black; vapor violet	183	4.93 (solid)	−5,926

SUMMARY

The sea and the land both have a nitrogen cycle; both depend upon bacterial action to maintain balanced life cycles. The sea is a source of enormous quantities of raw materials for chemical manufacturing. Common salt occurs abundantly in sea water and in salt deposits in many places. Impurities of $CaCl_2$ and $MgCl_2$ in common salt cause it to absorb moisture from the air. Common salt is used for seasoning, preserving, soapmaking, and chemical manufacturing.

The halogen family is in group VIIb of the periodic table. The family includes fluorine, chlorine, bromine, and iodine. Fluorine is very active, it is prepared by electrolysis of KF in liquid H_2F_2 in absence of water. Important fluorides include cryolite (Na_3AlF_6), used in the preparation of aluminum, and fluorite (CaF_2), the source of hydrofluoric acid. Fluorides are used in some insect powders.

Hydrogen fluoride is prepared by action of concentrated sulfuric acid on calcium fluoride. A solution of the gas, called hydrofluoric acid, is used to etch glass.

Chlorine is prepared: (1) By the electrolysis of brine

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2\uparrow + H_2\uparrow$$

(2) By the oxidation of hydrochloric acid by manganese dioxide or other strong oxidizing agents.

The physical properties of chlorine are that it (1) is a pale-green gas at room conditions, (2) has a density of 3.2 g per liter, (3) is easily liquefied, and (4) is moderately soluble in water.

The chemical properties of chlorine are that it (1) is an active element; (2) burns or explodes with elementary hydrogen; (3) combines with hydrogen in compounds; (4) unites with metals to form metal chlorides; (5) unites with some nonmetals, such as phosphorus, to form chlorides; (6) decomposes water slowly, forming hydrochloric and hypochlorous acids; and (7) acts on a solution of lye, forming common salt and sodium hypochlorite.

Elements at the time of liberation from a compound (nascent condition) have extra energy and are extra active chemically. Uses of chlorine are as a bleach, for purifying water, as a disinfectant, and for the preparation of chlorides and of bromine.

Bromine is now obtained from bromides in sea water. Bromine is prepared by (1) oxidation of sodium bromide in the presence of manganese dioxide and concentrated sulfuric acid, (2) replacement from a bromide by chlorine, and (3) electrolysis of sodium bromide solution.

The physical properties of bromine are that it (1) is a red-brown liquid, (2) vaporizes readily at room temperature, (3) is very irritating to breathe, (4) forms a red-brown solution in carbon tetrachloride.

The chemical properties of bromine are similar to those of chlorine, but bromine is less active.

Bromine is used to make Ethyl fluid for gasoline and in the manufacture of drugs and photographic compounds.

Iodine is found as an impurity in Chile saltpeter and in water in some oil wells.

The preparation of iodine is by methods similar to those for preparing bromine.

The physical properties of iodine are that it (1) has metallic gray crystals; (2) makes a brown mark on paper or on the hand; (3) is soluble in alcohol, carbon tetrachloride (purple solution), and potassium iodide solution; and (4) sublimes when heated, forming purple vapor.

Iodine is an important antiseptic. It is used to make medicines and photographic compounds. Also, iodine is important to the health of the body.

QUESTIONS

21. What percentage of sodium bromide is bromine?

22. In what respect is the modern source of bromine significant?

23. Write formula equations for (*a*) preparation of bromine from fused sodium bromide; (*b*) preparation of bromine by electrolysis of sodium bromide solution; (*c*) preparation of bromine from sodium bromide by oxidation; (*d*) replacement of bromine from potassium bromide solution by chlorine; (*e*) action of bromine on zinc.

24. Name two nonmetallic elements that bromine will not replace from their compounds and one that can be replaced by bromine.

25. Describe in detail a chemical test by which sodium chloride can be distinguished from sodium bromide.

26. From what two sources is iodine obtained commercially?

27. A certain sample of Chile saltpeter weighing $\left\{\begin{matrix}5\\8\end{matrix}\right.$ pounds contains 1 per cent sodium iodate. What weight of elementary iodine could be secured from it, assuming $\left\{\begin{matrix}50\\70\end{matrix}\right.$ per cent recovery?

28. Write formula equations for the following reactions: (*a*) chlorine and sodium iodide solution; (*b*) bromine and potassium iodide solution; (*c*) manganese dioxide, sodium bromide, and concentrated sulfuric acid; (*d*) hydriodic and hypochlorous acids; (*e*) hydriodic acid and hydrogen peroxide.

29. Graphite and iodine are both dark metallic crystalline substances. Tell how to distinguish them from each other.

30. A certain white crystalline compound colors a Bunsen flame yellow. When it is mixed with potassium dichromate ($K_2Cr_2O_7$), a strong oxidizing agent, and a few drops of concentrated sulfuric acid and heated, a purple vapor arises. What are the probable name and formula of this compound?

MORE CHALLENGING QUESTIONS

31. To make potassium iodide from elementary iodide, the element is added to caustic potash solution. Write the equation for the reaction that takes place. Assume that the action is similar to that of chlorine on sodium hydroxide solution.

32. What is the purpose of using chlorine solution in the test for iodide ion?

33. Which has the higher percentage of iodine, sodium iodate or sodium iodide?

34. What is the density of Freon gas (CF_2Cl_2)?

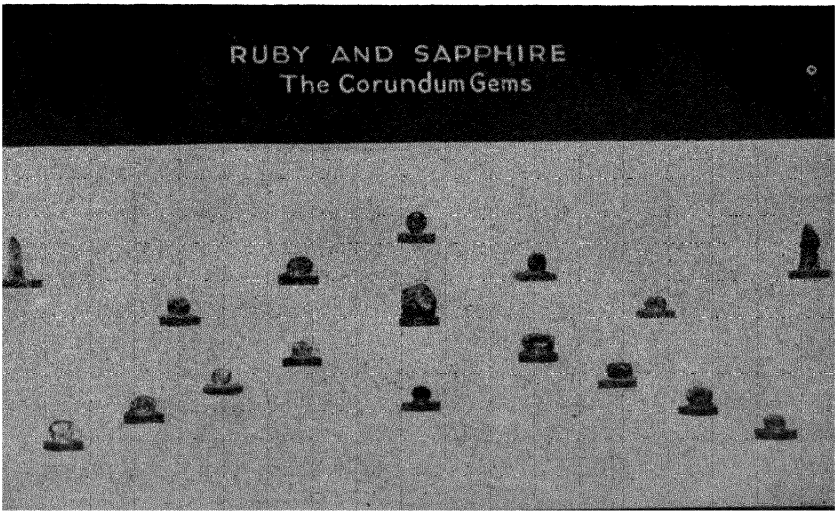
35. Dichloro-ethane contains 14.1 per cent carbon, 2.4 per cent hydrogen, and 83.5 per cent chlorine. One liter of the gas weighs 3.83 grams. Find its molecular formula.

36. If a factory is designed to make $\left\{\begin{matrix}10\\15\end{matrix}\right.$ tons of chlorine per day, what weight of common salt must be supplied daily?

37. Investigate the properties of iodine in detail, using as a reference an advanced chemistry book. Find out why iodine dissolves better in potassium iodide solution than in pure water.

CRYSTALS OF COMMERCE

Among the most interesting crystals used commercially are those we commonly call gem stones or jewels. In this chapter we shall consider, among other jewels, ***diamonds*** (see page 318), which are made of pure crystalline carbon and are used as sparkling gems in jewelry and as cutting stones in shops and in oil fields. Their commercial use depends upon their extreme hardness.



Courtesy of American Museum of Natural History

FIG. 19-1.—The ruby and sapphire are chiefly aluminum oxide. These gem stones were removed from display when the military emergency arose.

Rubies, usually deep red in color, ***sapphires,*** often pale blue, and ***emeralds,*** dark green, are also gem stones of high hardness and attractive appearance. Rubies and sapphires are crystalline aluminum oxide (Al_2O_3) with a slight amount of impurity. Rubies are found in India, Ceylon, and Siam. Emeralds are also definite green crystals; chemically they are

---

New Terms

alum	**mordant**	**lake**

beryl [beryllium aluminum silicate ($Be_3Al_2Si_6O_{18}$)]. They are found in Colombia, South America, and in the Ural Mountains, U.S.S.R. (See Fig. 19-1.)

Watches may contain between 7 and 23 jewels. Watch jewels are drilled and used as hard bearing sockets for the axles of the watch gear wheels. (See Fig. 19-2.) Jewels for watches and meters may be rubies, sapphires, garnets, synthetic sapphires, or even glass. Contrary to the common belief, these small gems are not necessarily expensive. They cost from a few cents to approximately $1 each.

In addition to the natural supply, synthetic rubies and sapphires are made by fusing aluminum oxide in a high-temperature flame. These synthetic stones are practically identical with those found naturally, and it is almost impossible for an expert to distinguish them.

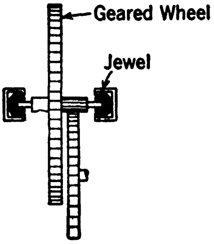


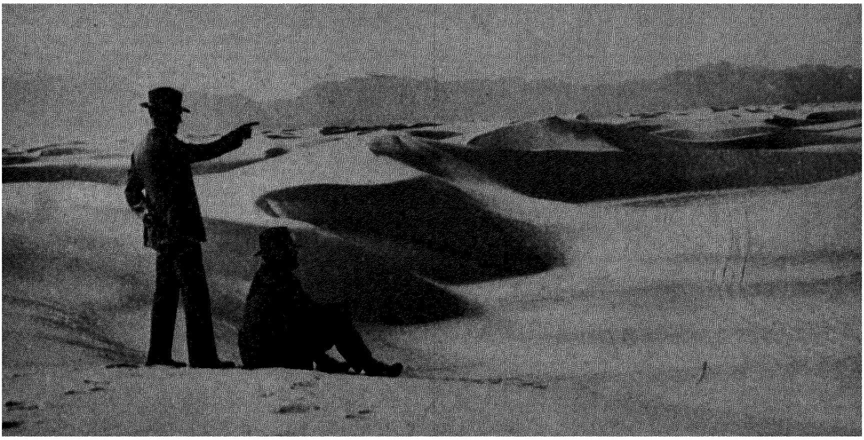
FIG. 19-2.—Drilled jewels are used for bearings in watches.

Emery. Natural aluminum oxide, colored black by impurities, is called ***emery.*** Crushed and sorted for size, this material is familiar to all as an abrasive, a hard scratching substance. Emery cloth is more abrasive than sandpaper or garnet paper. All are used similarly. In making them a high electric voltage is applied to the grains as they rest on the cloth or paper backing. Under the influence of the electric charge, the sharpest cutting edges point outward, and the grains space themselves evenly.

Fused Aluminum Oxide Abrasives. Natural ***corundum*** (Al_2O_3) may be dark or light. In fact, sapphires, rubies, and emery are all examples of corundum. This mineral is extremely hard and is therefore used for grinding wheels and whetstones.

Experience shows that white grinding wheels run cooler than black ones—hence the demand for light-colored abrasives. When aluminum oxide is made by fusing bauxite (hydrated aluminum oxide) in an electric furnace, the product is usually light brown to white. The product has several trade names, and many tons are used each year for grinding metals and for lining furnaces. Perfectly white, fused, and crystallized aluminum oxide can also be made in an electric furnace, but in this case purer aluminum oxide is used as a starting material.

Borax. We usually associate ***borax*** with Death Valley, California. From this famous valley the mineral from which borax was obtained was once hauled by 20-mule teams. Our sources of this material at present are the brines of Searles Lake, California, and a mineral called rasorite ($Na_2Ba_4O_7{\cdot}4H_2O$) found in Kern County of the same state. This mineral is merely dissolved, filtered, and recrystallized as the borax of commerce ($Na_2B_4O_7 \cdot 10H_2O$). It is used as a softener for water, as an aid to cleaning, and as a flux in brazing. Large amounts of borax are used in making Pyrex and other borosilicate glass (see page 412).



Underwood and Underwood

FIG. 19-3.—Crystals used in industry are found sometimes in desert regions. This picture shows the heart of a valuable gypsum deposit, 270 miles long, in New Mexico.

Boric Acid. When borax solution is treated with sulfuric acid, boric acid precipitates.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow 4H_3BO_3\downarrow + Na_2SO_4$$

As a powder or as shiny, thin, slippery crystals, boric acid is well known to us, for it is used in solution as an eyewash. A saturated solution is mildly antiseptic; also, it is impossible to dissolve enough boric acid in slightly warm water to injure normal eyes, for at 20°C only 4.8 g of boric acid dissolves in 100 g of water. Not all authorities agree on the value of boric acid as an eyewash.

The test for borates used by both prospector and laboratory workers is to burn alcohol (either grain or wood) to which the powdered borate has been added. The addition of a little sulfuric acid aids the test. A flame fringed with deep green results if a borate is present.

Alums. Among the most beautiful and perfectly formed crystals of commerce is a class of compounds called ***alums.*** These are double sulfates that crystallize from solutions containing singly charged metal ions such as Na^+, K^+, Ag^+, or NH_4^+, triply charged ions such as Al^{+++}, Cr^{+++}, Fe^{+++}, and so on, and the sulfate ion (SO_4^{--}) or its equivalent. They are represented by the following names and formulas: potassium aluminum sulfate {common alum [$KAl(SO_4)_2 \cdot 12H_2O$]}, ferric ammonium sulfate [$NH_4Fe(SO_4)_2 \cdot 12H_2O$], potassium chromium sulfate {chrome alum [$KCr(SO_4)_2 \cdot 12H_2O$]}. Formulas double the above were once given for these alums, but the simpler formulas are now considered to be the correct ones.

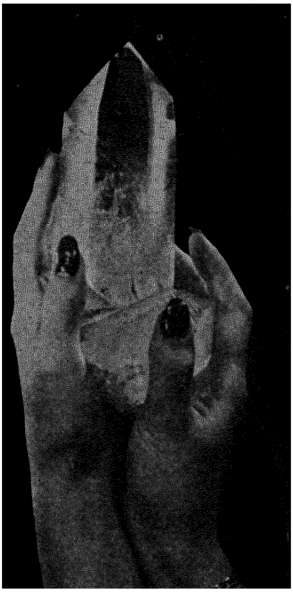
Chrome alum forms deep purple crystals, perfect octahedra. These are easy to grow, and they may be made the basis of fascinating experiments. One single, well-formed crystal is reported to have been grown from a saturated solution to weigh over 80 lb.[1]

In solutions the ions of alums are not combined, but each gives its usual reactions without interference. Common alum, for example, acts like a mixture of K^+ ions, Al^{+++} ions, and SO_4^{--} ions. The solution is acid owing to hydrolysis (page 233) just as is aluminum sulfate solution. For this reason, sodium aluminum alum is used in baking powders and common alum in foam fire extinguishers.

Common alum is a cheap and convenient source of soluble aluminum ions. When it is added to an alkali, a colloidal, gelatinous, sticky precipitate of aluminum hydroxide forms.

$$Al^{+++} + 3OH^- \rightarrow Al(OH)_3\downarrow$$

This sticky precipitate collects particles as it settles through muddy water, leaving a clear liquid above. It is used to clarify water on a large scale. Also, dyes cling to aluminum hydroxide when it is precipitated on cotton fibers. When used in dyeing it serves as a ***mordant,*** a fastening agent between fiber and dyestuff. The resulting colored precipitate is called a ***lake.*** Cotton, rayon, and linen can be dyed fast to washing by using a mordant.



Courtesy of American Museum of Natural History

FIG. 19-4.—This quartz crystal was not cut. It was found in nature just this way. All crystals grow in definite patterns. This one grew in Hot Springs, Arkansas.

Salt Cake. Salt cake is not a bakery delicacy but the commercial name for sodium sulfate (Na_2SO_4). Some salt cake is mined from natural deposits, but larger amounts are made from sodium hydrogen sulfate ($NaHSO_4$), the by-product from making either hydrochloric or nitric acid with sulfuric acid (see pages 358 and 361). The sodium hydrogen sulfate is mixed with the proper amount of salt and heated. Hydrogen chloride

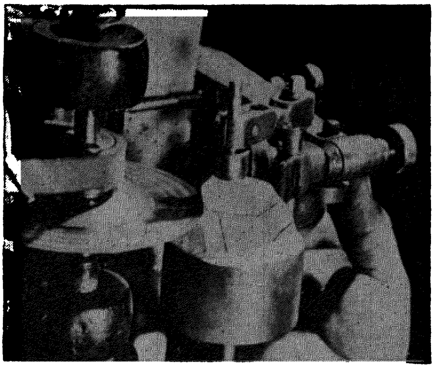
---

[1] FLIEDNER, L. J., "A Crystal Grows Up," *Journal of Chemical Education*, vol. 18, No. 1, January, 1941.

is formed, and salt cake is a valuable by-product.

$$\underset{\text{salt}}{NaHSO_4 + NaCl} \rightarrow \underset{\text{salt cake}}{Na_2SO_4} + HCl\uparrow$$

The salt cake in the anhydrous condition is used to make kraft paper, glass, and sodium sulfide. When it is dissolved in water and crystallized, Glauber's salt forms ($Na_2SO_4 \cdot 10H_2O$). The Glauber's salt crystals are beautiful, long, colorless needles. They lose water readily in air (efflorescence) (see page 114) and form a white, anhydrous powder. Glauber's salt is used chiefly in the dye industry to cause the dye to precipitate onto the fabric.



World Wide Photo

FIG. 19-5.—Cutting the "ice" is a slow process. The high-speed revolving disk impregnated with diamond dust cuts through a one-carat diamond in eight hours. The cutting of the Jonker diamond, shown here, was undertaken after a year of study, for a cut on a wrong plane would shatter the gem and destroy millions of dollars of value.

Diamonds. The interest of chemistry pupils in diamonds is not altogether chemical. Every year the freshman class in a certain college is called into the chemistry laboratory. A diamond, which has previously been on exhibition, is burned by the chemistry instructor in pure oxygen in a suitable apparatus as a lecture demonstration. The gas formed by burning the diamond is collected and run through limewater. A white precipitate forms. The chemical actions are described by the equations:

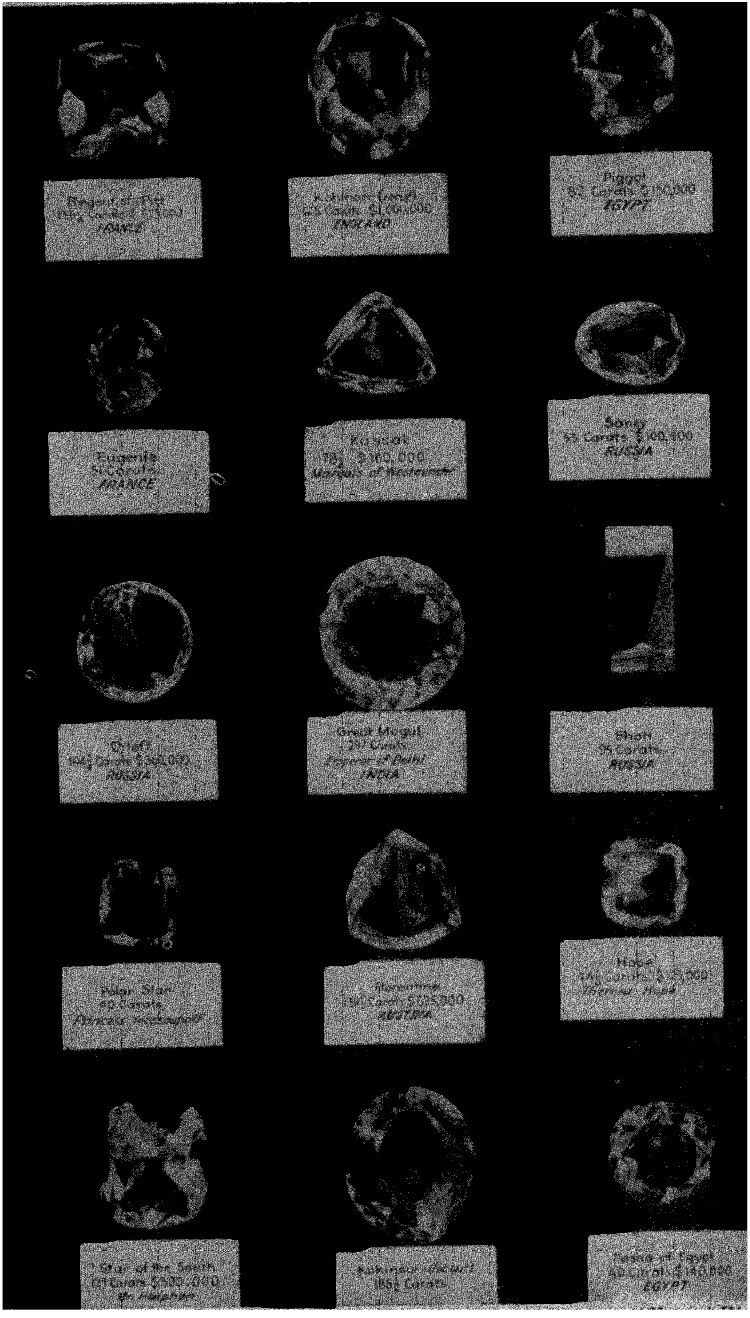
$$C + O_2 \rightarrow CO_2$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2H_2O$$

This is a convincing, but expensive, proof that a diamond is carbon. The experiment was first performed by Lavoisier.

Hardness. When two different substances are rubbed together each is worn away, but the harder substance makes a far deeper scratch on the softer one. An arrangement of minerals in order of hardness is given in the accompanying table. Diamond, last in the list; is the hardest substance; it will scratch everything else. The list, however, is not even-

HARDNESS SCALE

1. Talc
2. Rock salt
3. Calcite
4. Fluorite
5. Apatite
6. Feldspar
7. Quartz
8. Topaz
9. Corundum
10. Diamond



Courtesy of American Museum of Natural History

FIG. 19-6.—Regent of Pitt (136¼); Kohinoor—recut (125); Piggot (82); Eugenie (51); Kassak (78⅝); Saney (53); Orloff (194¾); Great Mogul (297); Shah (95); Polar Star (40); Florentine (139½); Hope (44⅛); Star of the South (125); Kohinoor—first cut (186½); Pasha of Egypt (40). Weights are in carats.

spaced. The interval between 1 and 2 is much smaller than that between 9 and 10. Silicon carbide (see page 251) and boron carbide are synthetic abrasives that fall between 9 and 10. More satisfactory hardness tests than scratching are made by the Brinell or Rockwell methods.

The uses of diamonds for dressing grinding wheels and drilling into the earth and for dies through which wire is drawn into a smaller size all depend on the extreme hardness of this beautiful crystalline form of carbon.

SUMMARY

Rubies and sapphires are natural crystalline aluminum oxide, colored with slight impurities. They are used for ornamental gems and also for bearings in precision instruments. They can be produced synthetically. Emery, an impure aluminum oxide, is used as an abrasive. Borax ($Na_2B_4O_7 \cdot 10H_2O$) is mined from salt deposits of ancient lakes. It is used to make glass, to soften water, and as a flux. Boric acid, made from borax, is used as a mild antiseptic.

Alums are double sulfates, hydrated. Potassium aluminum alum is used to clarify muddy water and in dyeing. Sodium aluminum alum is used in baking powder.

Sodium sulfate (Na_2SO_4) is called salt cake. $Na_2SO_4 \cdot 10H_2O$ is Glauber's salt, which is used in the dye industry.

Diamond (crystallized carbon), extremely hard, is used for gems and in cutting tools. The relative hardness of metals is determined roughly by scratching and more accurately by the Rockwell test and other methods.

QUESTIONS

1. List four gem stones, and with each give the chemical composition and the usual color.

2. State a reason for using jewels for bearings in watches.

3. What important properties of aluminum oxide make different forms of it useful for (*a*) gems; (*b*) abrasives; (*c*) furnace lining?

4. List three uses for borax.

5. Write formula equations for the following reactions: (*a*) calcium borate and sodium carbonate solutions; (*b*) sulfuric acid, borax, and water; (*c*) boric acid heated.

6. Flame tests for barium, copper, and borax all involve a green-colored flame. What distinguishes the borax test from the others?

7. Write the formula for (*a*) common alum; (*b*) ammonium iron alum; (*c*) ammonium aluminum alum; (*d*) burnt (dehydrated) alum.

8. List three uses for common alum.

9. When Glauber's salt is dehydrated to form salt cake, what is the percentage loss of weight?

10. Beryllium is obtained from crystalline beryl. What is the percentage of the element in the crystal?

SPECIAL REPORTS

1. Make a report on the six main classes of crystals. Illustrate each by a cardboard model of an ideal crystal and a model of the axes. Place each with a sample of a representative chemical compound.

2. Report on the history of borax mining in Death Valley, California.

3. Become a local expert on gems, both precious and semiprecious. A collection of gems can be obtained without too great expense if small samples are used to start.

4. For what purposes do machinists use diamonds? Well drillers? Make a report on the Kimberley (South Africa) diamond mines; the cutting of diamonds; the grading and valuation of diamonds; famous diamonds.

5. Make a report on new synthetic abrasives and cutting-tool tips, including boron carbide and tungsten carbide, and show their importance in the modern machine-tool industries.

THE GREAT CLASSIFICATION

"Spy work! We must get to the bottom of this and find out who is the sender of this secret code message," agreed the Soviet officials.

A letter had been mailed by a New York college student to his sister in the U.S.S.R. The letter, along with other information, contained a chart quite similar to the table on page 324. This table, in 1931, was refused admission to the very country where it originated over 60 years before. The sender and receiver of the letter were both suspected of being spies because the chart was thought to be the key to a secret code.

FIG. 20-1.—The U.S.S.R. honored Mendeleyev in 1934 by issuing commemorative postage stamps. Both the 5 and 10 kopek values shown here have the periodic table in the background.

The chart is the periodic table of the elements, one of the truly great generalizations of chemistry. It is found in some form in almost every book on elementary chemistry. It contains no secrets. While it might be used as a code, we have no evidence that the suspicions of the U.S.S.R. officials were correct.

Three years later, some compensation was made for this serious blunder. Other officials of the U.S.S.R. saw fit to commemorate the one hundredth anniversary of the birth of Dmitri Ivanovich Mendeleyev (1834–1907) of Tobolsk, Siberia. A special set of postage stamps (see

---

New Terms

periodic law
atomic number
atomic weight
periodic table
phosphorus

Fig. 20-1) was issued in his honor. On one stamp a portrait of the distinguished scientist appears in the foreground, surrounded by a laurel wreath. In the background we find the periodic chart of the elements, which he was largely instrumental in developing.

In addition to learning about the work of this famous Russian, we are also to follow the lengthening shadow of John Dalton and his thinking (page 141), until we arrive at modern cyclotrons (atom smashers) and induced radioactivity.

Similarities Among Elements. We have already noted how similar oxygen is to sulfur in many respects. Oxides resemble sulfides in a chemical way (see page 61). Again, if a chemist runs short of a sodium compound he may often substitute a potassium compound with entirely satisfactory results, provided that he adjusts the amount to be used and disregards the difference in cost. In like manner, a bromide or an iodide may often serve if a chloride is not available. There are many such cases of similar elements, substances that are more or less like each other.

Early Classifications of the Elements. If we consider the three elements, lithium (atomic weight 7), sodium (23), and potassium (39), which are surprisingly alike, we find that the atomic weight of the middle one, 23, is about the average of the weights of the other two:

$$\frac{7 + 39}{2} = 23.$$

Chlorine (35.5), bromine (80), and iodine (127) show a similar relationship, as does the group calcium (40), strontium (87.6), and barium (137). These groups of three similar elements, along with some others that are less impressive and some that are inaccurate, were pointed out by a German professor of chemistry, Johann Wolfgang Döbereiner (1780–1849), as early as 1839.

After several other workers had noticed more comparisons and the accuracy of finding atomic weights had improved, John Newlands (1838–1898), in England, set down the following list of the then known elements in order of their increasing atomic weights, starting with lithium.

NEWLANDS' LIST OF ELEMENTS AND THEIR ATOMIC WEIGHTS (1866)

Li 7	Be 9	B 11	C 12	N 14	O 16	F 19
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5
K 39	Ca 40					

If we start with lithium and count until we reach an element very similar to lithium, sodium, it will be the eighth element in the list. If we count further, the eighth element beyond sodium is potassium, which is similar to both lithium and sodium in its properties. Likewise, from oxygen to sulfur, or from fluorine to chlorine, or from one to the other of any pair of similar elements the interval is eight. Prof. Newlands in 1866 reported this to the English Chemical Society and pointed out the similarity to the octave of the musical scale, with its interval of eight notes. "The similar properties come back every eighth element," he said, in effect.

This was a long step forward in organizing chemistry into a systematic science and was also a great help to all learners of the subject. Nevertheless, Newlands' thanks were at first jeers and laughter. One fellow chemist even asked what he could learn by arranging the elements alphabetically. We are glad to find that jeers eventually changed to praise; 20 years later he was awarded a medal in honor of his discovery.

A Famous Russian Prophet. After Newlands, Julius Lothar Meyer (1830–1895), in Germany, and the famous chemist Mendeleyev, in Russia, continued this study on the similarity of elements. Mendeleyev also organized the elements by their atomic weights into a table (see page 324). While his arrangement was quite similar to that of Newlands, he made the following important advances: (1) He left spaces for elements that might some day be discovered. (2) After comparing the properties of certain elements with those of other elements, he boldly placed them where he thought they belonged in the table on the basis of their properties, disregarding atomic weights when necessary. He assumed that the atomic weights as then known might be somewhat in error. (3) He saw the necessity for subgroups within the groups or families (vertical columns). For example, in Group I, lithium, sodium, potassium, rubidium, and cesium are placed to the left-hand side in one family, for these elements are alike. Copper, silver, and gold are quite similar to each other; they are in the same group, but on the right-hand side.

Mendeleyev was a distinguished teacher, author, and chemist. He had the vision to call this regularity of nature, which he observed from the study of his table, the periodic law (page 326). For a better understanding, let us examine the table as Mendeleyev built it with the addition of some elements discovered since his time. (See page 324).

The natural elements are arranged according to increasing atomic weights, the lowest, hydrogen, first and the highest, uranium (240, now 238), last. There are eight columns, or groups, and 10 rows, or periods. Hydrogen is separately classified, the only element in the first period. Like Newlands, Mendeleyev started with lithium and arranged the elements with seven in a row. When he reached iron (56), he had to make an eighth column, with the three elements iron, cobalt, and nickel in it. Much later, to accommodate the newly discovered inert elements of the

PERIODIC TABLE, OLDER FORM

Period	Group 0	Group I		Group II		Group III		Group IV		Group V		Group VI		Group VII		Group VIII		
		a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*			
1	Inert Gases	1 H 1.0080																
2	2 He 4.003	3 Li 6.940		4 Be 9.02		5 B 10.82		6 C 12.010		7 N 14.008		8 O 16.0000		9 F 19.00				
3	10 Ne 20.183	11 Na 22.997		12 Mg 24.32		13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.06		17 Cl 35.457				
4	18 A 39.944	19 K 39.096	29 Cu 63.57	20 Ca 40.08	30 Zn 65.38	21 Sc 45.10	31 Ga 69.72	22 Ti 47.90	32 Ge 72.60	23 V 50.95	33 As 74.91	24 Cr 52.01	34 Se 78.96	25 Mn 54.93	35 Br 79.916	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
5	36 Kr 83.7	37 Rb 85.48	47 Ag 107.880	38 Sr 87.63	48 Cd 112.41	39 Y 88.92	49 In 114.76	40 Zr 91.22	50 Sn 118.70	41 Cb 92.91	51 Sb 121.76	42 Mo 95.95	52 Te 127.61	43 Ma —	53 I 126.92	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
6	54 Xe 131.3	55 Cs 132.91	79 Au 197.2	56 Ba 137.36	80 Hg 200.61	57 to 71 Rare Earths	81 Tl 204.39	72 Hf 178.6	82 Pb 207.21	73 Ta 180.88	83 Bi 209.00	74 W 183.92	84 Po* (210)	75 Re 186.31	85 —	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
7	86 Rn* (222)	87 —		88 Ra* 226.05		89 Ac* (227)		90 Th* 232.12		91 Pa* (231)		92 U* 238.07						

* Radioactive.

FIG. 20-2.—The periodic table, older form, was organized by Mendeleyev.

air it was found necessary to add another group, Group O, containing helium, neon, argon, krypton, and xenon (and later radon) to the left-hand side of the table.

Elements of atomic number 93, 94, 95, and 96, not found in nature, have been synthesized in connection with work on atomic bombs. Their position in the periodic table has not yet been established.

What Mendeleyev's Table Did for Chemistry. To chemists, Mendeleyev's periodic table became a card catalogue, filing system, reference chart, and comparison table all rolled into one. Roughly speaking, instead of learning 92 different chemistries, 1 for each element, 8 chemistries suffice.

There are three important contributions of the periodic grouping:

1. It has classified and systematized our chemistry; therefore, this discovery is called the great unifying force within the science.

2. It has suggested new elements. In fact, not only were they suggested, but hints were given as to where they could be found and what they would be like. Mendeleyev ventured to predict three of these elements, all of which were discovered within his lifetime. He stated, "When in 1871 I wrote a paper on the application of the periodic law to the determination of the properties of as yet undiscovered elements, I did not think that I should live to see the verification of this consequence of the law, but such was to be the case."

How fine a piece of work he did in predicting can be judged from the following chart.

MENDELEYEV'S PREDICTION FULFILLED

	Prediction of properties for an element like silicon—1871	Properties found later for this element, named germanium—1886
Atomic weight	72.0	72.3
Specific gravity	5.5	5.47
Specific gravity of oxide	4.7	4.7
Boiling point of chloride	100°C or less	86°C
Boiling point of ethyl compound	160°C	160°C
Formula of oxide	XO_2	GeO_2
Formula of chloride	XCl_4	$GeCl_4$

3. Atomic weights were checked critically, and instances of possible errors were located. Many errors in atomic weights were corrected. For example the atomic weight of indium was shown to be 114, not 76 as originally suggested. We may be sure that much work has been expended on the atomic weights of iodine and tellurium, cobalt and nickel, and

later the pair argon and potassium, for they were out of order in the table and still are. From a chemical standpoint, however, tellurium is like sulfur and selenium, and iodine obviously belongs in the family with chlorine and bromine. Also, argon, an inert gas, goes with neon, not with sodium.

Difficulties Presented by Mendeleyev's Periodic Table. A few difficulties are easily observed when we examine the periodic table of Mendeleyev: (1) The "rare earths," a group of 15 similar elements, have to be crowded into one place in the table. (2) Group VIII with its three sets of three elements is out of place, for these metals are located where the nonmetals belong. (3) The system of families within the groups is a makeshift and is on the whole unsatisfactory. (4) As has already been pointed out, certain elements are not in order of their atomic weights. To explain this, two possibilities suggest themselves: (*a*) Perhaps the arrangement of the table according to Mendeleyev's method is not the most satisfactory method. (*b*) Perhaps the atomic weight is not the fundamental property of atoms on which to base a table.

The Periodic Law. In spite of these difficulties, the genius of Mendeleyev glistens. In spite of the imperfections of the arrangement, in spite of all complications, the outstanding truth he discovered shone out clearly. He called this truth the ***periodic law,*** namely: ***The chemical properties of the elements are a periodic function of their atomic weights.***

The different phases of the moon—new moon, first quarter, and so on—are a periodic function of the moon's revolution. These moon phases occur again after a definite time, or period—after 28 days. Just so, as we proceed from element to element, the similar properties repeat themselves after a definite interval. Among the lighter elements in the periodic table (omitting the inert gases) this interval is found to be the octave as discovered by Newlands, and a repetition of properties occurs on simply counting eight elements ahead.

Later Progress in Periodic Grouping. A young Englishman, H. J. Moseley (1887–1915), who died fighting for his country in World War I, made another step forward in the study of atoms and periodic grouping. He was, of course, using the work of many other experimenters as a foundation and building on into the unknown in his own brilliant fashion. In his experiments he used an X-ray tube (see Fig. 20-3), a glass bulb from which the air had been removed and provided with suitable electrodes. When a high electric pressure or voltage is applied to such a tube, the cathode (−) shoots out streams of electrons, tiny bits of electricity (page 179). The cathode is curved so that these electrons strike upon a target as if they were focused. Just as a stone striking the surface of a

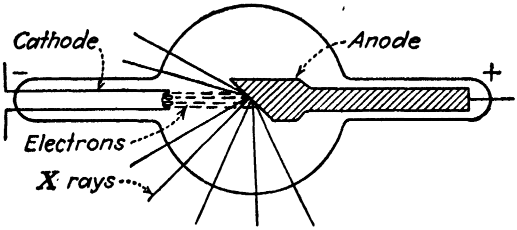


FIG. 20-3.—A simple X-ray tube is a device in which cathode rays (a stream of electrons) hit a target. The excited target sends out penetrating X rays.

pond sets up water waves caused by the disturbance, so the electrons hitting the target set up X rays from the target.

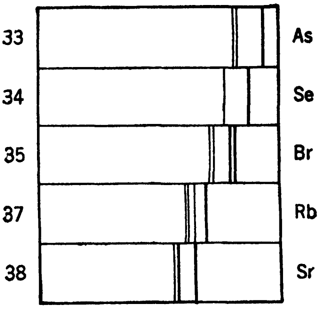


FIG. 20-4.—The principal lines in the X-ray spectra of the elements are shown here. The atomic numbers assigned by Moseley are at the left. Notice that as the atomic number increases, the lines shift to the left in a fairly regular fashion.

When the electron stream strikes the target, the material of the target becomes energized, or excited. It becomes a source of energy radiating X rays. X rays are quite like visible light, except that their wave lengths are very short, too short for our eyes to observe.

Moseley arranged his X-ray tubes so that different elements could be brought into position as targets and determined the wave lengths of the X rays. He analyzed them by means of a spectroscope (page 48), using a crystal to reflect and focus the rays upon a photographic plate. (See Fig. 20-3.) Although our eyes are not sensitive to X rays, everyone is familiar with the fact that X rays affect a photographic plate.

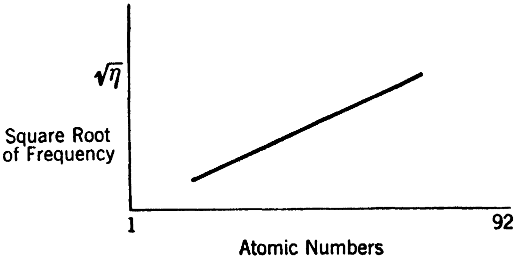
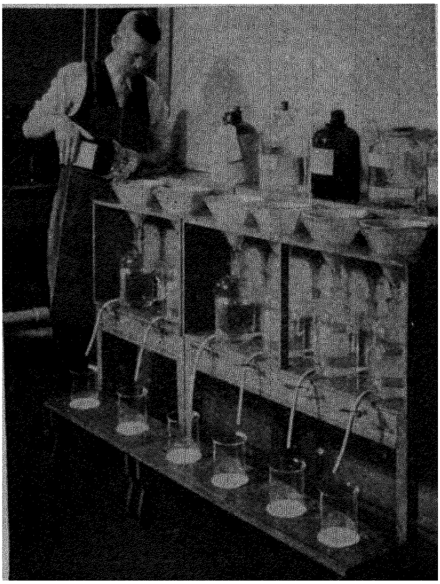


FIG. 20-5.—Moseley's results show that the atomic numbers of the elements are directly related to the square root of the frequency of their X rays.

The result of these experiments was a series of pairs of lines on the plate. (See Fig. 20-4.) With elements of successively increasing atomic weight he found that the positions of the line pairs on the plate were different. These line pairs were regularly spaced, one space apart for each element of the next higher atomic weight. Further, when he made a chart on graph paper of the results of calculations based on his experiments (see Fig. 20-5), he found a perfectly regular straight-line conclusion. All the elements had lined up! He numbered the positions of the elements on the chart and called these consecutive numbers ***atomic numbers.*** Spaces were left for missing elements.

Now comes the startling advance. Moseley's chart showed this straight-line regularity only when he used ***atomic numbers,*** instead of ***atomic weights.*** Apparently, then, the atomic number is a more fundamental fact about an atom than its atomic weight. If so, then we can restate the ***periodic law*** in more modern form: ***The chemical properties cf the elements are a periodic function of their atomic numbers.***



Courtesy of The Travelers Insurance Company

FIG. 20-6 —We should not forget that generalizing in chemistry and all theories are based on *facts*. The great source of facts is the laboratory. This chemist is carrying on the laboratory operation called filtering.

A Modern Periodic Table. A preferred classification of the elements is given on page 329. This arrangement consists of 18 vertical columns and seven rows. The first row contains hydrogen and helium only; the second and third rows contain eight elements each. In these two rows are included most of the elements important in elementary chemistry. The elements in Group O are the inert gases; these resemble each other, as do all elements in the same column or group.

All the elements in Groups Ia and VIIb have a combining number of 1. Salts are readily formed between the members of these two groups, as, for example, lithium and fluorine, potassium and chlorine, and sodium and iodine. Salts are formed when active metals combine with active nonmetals.

Combining numbers may be listed as follows:

Group	Combining numbers	Group	Combining numbers
Ia	1	VIIb	1
IIa	2	VIb	2
IIIa	3	Vb	3

PERIODIC CLASSIFICATION OF THE ELEMENTS

The atomic numbers are placed above the symbols of the elements; the atomic weights below the symbols

Group	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII			Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	O
Type	R_2O RH	RO RH_2	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4			R_2O	RO	R_2O_3	RO_2 H_4R	R_2O_5 H_3R	RO_3 H_2R	R_2O_7 HR	Inert Gases
Period 1 2 elements	1 H 1.0080																	2 2 He 4.003
Period 2 8 elements	3 Li 6.940	4 Be 9.02											5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.0000	9 F 19.00	10 2 8 Ne 20.183
Period 3 8 elements	11 Na 22.997	12 Mg 24.32			Transitional Elements								13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 2 8 8 A 39.944
Period 4 18 elements	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 2 8 18 8 Kr 83.7
Period 5 18 elements	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Ma	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 2 8 18 18 8 Xe 131.3
Period 6 32 elements	55 Cs 132.91	56 Ba 137.36	57 *58–71 La 138.92	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po (210)	85	86 2 8 18 32 18 8 Rn (222)
Period 7	87	88 Ra 226.05	89 Ac	90 Th 232.12	91 Pa 231.	92 U 238.07	93 Np (237)	94 Pu (239)	95 Am	96 Cm								

*Rare Earth Elements Group IIIa	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il	62 Sa 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.94	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

FIG. 20-7.—Periodic classification of the elements.

In the modern table the light metals are located at the left in Groups Ia, IIa, and IIIb, in the upper periods (omitting hydrogen). Here we look for metals suitable for airplane construction.

The nonmetals are generally in the upper right-hand corner (omitting Group O) and extend by a diagonal line roughly from carbon (diamond) through phosphorus, sulfur, selenium, and iodine to radon.

The low-melting heavy metals extend from atomic numbers 80 to 83 and directly above; the high-melting heavy metals extend from 22 to 29 and below. The strongly active metals are in Groups Ia to IIIa, and the strongly active nonmetals are in Groups VIIb to Vb.

Advantages of the Modern Table. The basis of the arrangement of the modern table is atomic numbers and atomic structure (page 187). Hence many of the difficulties found in older tables are avoided.

Four sorts of elements are evident in this classification. They are

1. Normal elements (Groups Ia, IIa, Ib to VIIb)
2. Transitional elements (Groups IIIa to VIII)
3. Inert gases (Group O)
4. Rare-earth elements (in Group IIIa, No. 58 to 71)

We find from this table that there are nine sorts of normal elements. The metals are in general on the left of the table, the nonmetals on the right. The inert gases are separated in a group by themselves.

The so-called "transitional" elements are alike in that all have more than one combining number. Furthermore, the use of the modern table has great advantages over the older one in the study of atomic structure. We can predict the properties of an element from its position in this table more clearly than with Mendeleyev's earlier table.

The location of elements Th(90), Pa(91), and U(92), which occur naturally and elements Np(93), Pu(94), Am (95), and Cm (96), which were synthesized in connection with the atomic-bomb project during World War II, is not established. It is believed, however, that all these seven elements will be assigned to Group IIIa, in which they will constitute a group similar to the rare-earth elements.

From Periodic Table to Production. A striking example of applying the periodic table as a very useful tool in research work is pointed out by the late Thomas Midgley, Jr., director of a research project for finding a nonflammable, nontoxic refrigerant.

> . . . the elements on the right-hand side are the only ones sufficiently volatile . . . for the purpose in hand. In fact, only a certain number need be considered. Volatile compounds of boron, silicon, phosphorus, arsenic, antimony, bismuth, selenium, tellurium, and iodine are all too unstable and toxic to consider. The inert gases are too low in boiling point. Now look over the remaining elements. (See Fig. 20-8.) Every refrigerant used has been made from combinations of these elements. Flammability decreases from left to right. Toxicity

(in general) decreases from the heavy elements at the bottom to the lighter elements on top. These two *desiderata*[1] focus on fluorine. It was an exciting deduction. Seemingly, no one previously had considered it possible that fluorine might be nontoxic in some of its compounds. This possibility had certainly been disregarded by the refrigeration engineers. If the problem before us was solvable by the use of a single compound, then that compound would certainly contain fluorine.

TABLE USED TO FIND A REFRIGERANT

IVb	Vb	VIb	VIIb
C	N	O	F
		S	Cl
			Br

FIG. 20-8.—This is the part of the periodic table that was used by Thomas Midgley, Jr., to find a refrigerant.

The final result of this search was the discovery of Freon (CF_2Cl_2) as a refrigerant.

A similar story is told about the search for Ethyl fluid, which is used with gasoline.

> We abandoned the Edisonian method[2] in favor of a correlational procedure based on the periodic table. What had seemed at times a hopeless quest, covering many years and costing a considerable amount of money, rapidly turned into a "fox hunt." Predictions began fulfilling themselves instead of fizzling. . . . We thereupon predicted that tetraethyl lead would solve the problem. The record of the past decade has borne out that prediction.

In fact, Ethyl fluid containing tetraethyl lead is used in over 70 per cent of the nation's cars, and it has flown with Admiral Byrd over both poles.

QUESTIONS

1. List the names of three investigators who contributed to the periodic classification of the elements. Tell briefly the contribution of each.

2. What was the amount of error in Mendeleyev's prediction of the atomic weight of germanium? What was the percentage of error?

3. What reasons are given for placing argon in Group O instead of Group Ia in place of potassium?

4. Explain the term *periodic function*, using the seasons of the year as an example.

5. Point out the difference between the periodic law stated by Mendeleyev and that stated by Moseley.

6. Does the fact that the original wording of the periodic law was improved show that it was entirely wrong at first? Valueless at first? Is it possible that the law may be further restated?

---

[1] Latin—things desired.

[2] Enlightened trial and error.

7. In the modern periodic table, which are the longest groups? The shortest? How many periods are there? Judging by the position of hydrogen and of oxygen, which part of the table do we discuss most in elementary chemistry?

8. Name two elements similar to each of the following: sodium; sulfur; bromine; aluminum; neon.

Applying the Table. Let us investigate the elements in Group Vb, studying them together. They are nitrogen, phosphorus, arsenic, antimony, and bismuth. They all have a combining number of 3 and sometimes of 5. With oxygen they have a combining number of 5 as in N_2O_5 (nitrogen pentoxide) and P_2O_5 (phosphorus pentoxide). With hydrogen the combining number is 3 as in NH_3 (ammonia), PH_3 (phosphine), AsH_3 (arsine), SbH_3 (stibine), and the unstable BiH_3.

This group shows a gradual change of properties. If we start with nitrogen, a typical nonmetal, and go down the list, the metallic properties become stronger at the expense of the nonmetallic properties. Finally we arrive at bismuth, which is really a metal. Arsenic is intermediate. It has a metallic luster and forms alloys, but its oxide (As_2O_5) forms an acid, arsenic acid (H_3AsO_4).

Nitrogen. The first member of the family, nitrogen, differs considerably from the others in its chemical properties. This inactive gas has already been discussed (see page 44). Later we shall consider its two very important compounds, nitric acid (HNO_3) and ammonia (NH_3).

GROUP Vb

Element	M.P., °C	B.P., °C	Density, g/ml	Formulas of oxides	
7 (at. no.) **N** 14 (at. wt.)	−195.8	−209.9	0.00125 gas at 0°C	N_2O_3	N_2O_5
15 **P** 30.9	44	280	Y 1.82 R 2.2	P_2O_3	P_2O_5
33 **As** 74.9	Sublimes	615	5.73	As_2O_3	As_2O_5
51 **Sb** 121.7	630	1635	6.68	Sb_2O_3	Sb_2O_5
83 **Bi** 209	271	1450	9.78	Bi_2O_3	Bi_2O_5 (unstable)

A comparison of the elements in this group may be had from the table on page 332. We should not be surprised to find a few exceptions to a regular gradation of properties. The surprising thing is that the elements and compounds change so regularly when they are compared in tabular form.

Phosphorus. When a popular brand of breakfast food is advertised as a source of "phosphorus and iron," this means that these two elements are present in the grains from which the breakfast food was made, in the form of compounds. Phosphorus compounds are indeed necessary for our bodies. We need calcium phosphate [$Ca_3(PO_4)_2$] in our bones and lecithin, a complex protein compound containing phosphorus, in our nerve tissues and brain. We get phosphorus from compounds in our food, especially wheat, nuts, the white of eggs, fish, and milk.

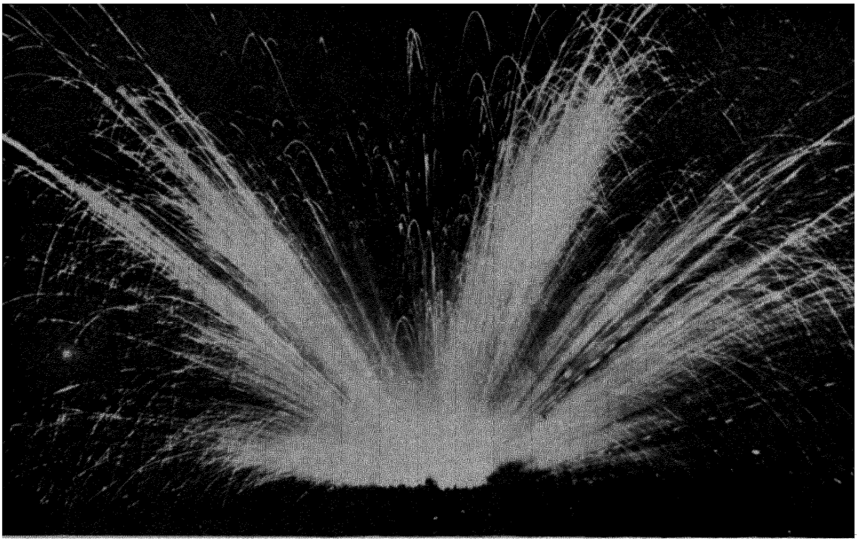
Natural deposits of calcium phosphate, called mineral phosphate, are extensive. Great quantities are quarried in northern Africa and in the United States, especially in Florida, Tennessee, and South Carolina. This compound is by far the most important phosphorus mineral. Most of it is used in making fertilizers. Phosphorus is never found in nature as a free element for it undergoes spontaneous ignition when left exposed to air.

Let our imagination go back to 1669 in Bavaria, Germany, where we shall see an alchemist named Brand (or Brandt) performing a curious experiment over a charcoal fire. He is evaporating human urine and from this is obtaining a solid material, microcosmic salt ($NaNH_4HPO_4 \cdot 4H_2O$), a phosphorus-containing compound. To this witches' brew he now adds sand and charcoal, places the mixture within a retort having a long neck, and heats it once more to redness. While he works, darkness falls, but he labors on into the night. From the mouth of the retort a white smoke is seen to arise. He places an earthen dinner plate above the white smoke and catches some of the smoke as a deposit on the plate. He then carries the plate into a dark part of the laboratory, where it glows by itself for quite a while. Here surely is something wonderful! He scrapes a quantity of the material off the plate, and it catches fire spontaneously.

In those days of powerful superstitions, Brand's achievement seemed magical. He was invited to the royal courts all over Europe to demonstrate his experiment. Anyone could see that he was but a step away from the true elixir of eternal life!

The modern method of making phosphorus from ores is similar to that of the alchemist except that heat is applied in an electric furnace (see page 252). A mixture of rock phosphate, sand, and coke is supplied to the furnace. The phosphorus issues from the furnace in the form of a vapor. This may be run directly into a waiting tank car and condensed under water, or it may be sealed in air-free cans.

White or Yellow Phosphorus. Except for military purposes, white phosphorus is of interest chiefly in the chemical laboratory. In this form the element is waxy and white if pure and often slightly yellow if impure. It dissolves well in carbon disulfide, but not in water. Because it ignites in air spontaneously, it is usually kept under water. (See Fig. 20-9.) If exposed to air, it reaches its kindling temperature by its own oxidation (see page 55). White phosphorus can be easily cut with a knife if it is held under warm water while the operation is performed. But care must be used not to allow it to touch the fingers, for it causes burns that are painful and slow to heal. It is a poison to the body both externally and internally, although small amounts are sometimes used in certain medicines.



Courtesy of Chemical Warfare Service, U.S. Army Photograph

FIG. 20-9.—The burst of a projector shell filled with white phosphorus. The burning element provides enough light to take its own picture at night.

Purple or Red Phosphorus. When heated in an airtight retort, yellow phosphorus changes into a purple form, composed of very fine, mealy, garnet-red crystals. This form is not nearly so poisonous as the white, does not dissolve in carbon disulfide, and does not spontaneously ignite in air. Such forms of the same element, differing probably in the number of atoms per molecule, are called ***allotropic*** forms.

With an ample air supply, both forms of phosphorus and other allotropic forms of the element that are less well known burn to form phosphorus pentoxide. The burning may be summarized by the equation

$$\underset{\text{Phosphorus vapor}}{P_4} + \underset{\text{oxygen from air}}{5O_2} \rightarrow \underset{\text{phosphorus pentoxide}}{2P_2O_5}$$

This common oxide of phosphorus is a soft, white powder. It combines readily with water, and can be used for drying gases, but not those with which it reacts chemically. When the oxide joins with water, its outstanding action, it finally becomes phosphoric acid solution:

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

Matches. One of the most interesting uses of phosphorus is in making matches, although its compounds are used also in making fertilizers, baking powder, cleaners, and water softeners.

White phosphorus alone is no longer used in the manufacture of matches; instead, a compound of unpleasant odor, phosphorus sesquisulfide (P_4S_3), is substituted. This is because the workers in match factories where white phosphorus was once used suffered from a horrible disease that attacked the bones of the face. A prohibitive tax on matches made with white phosphorus now protects workers.

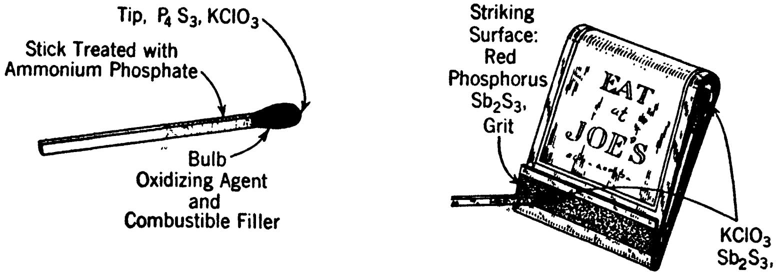


FIG. 20-10.—Matches must be heated in order to start a fire. Striking a match changes friction (motion) energy into heat energy. The heat energy starts a chemical change on the head of the match.

A match consists of (1) a low-kindling material, such as P_4S_3; (2) some substance that burns readily, such as a mixture of rosin and potassium nitrate (KNO_3); and (3) potassium chlorate, with other oxidizing agents. These are held together by glue and mixed with grit, which increases friction. Matches so made will "strike anywhere."

In safety matches, the low-kindling material is on the box, separate from the match head, which contains potassium chlorate and antimony trisulfide (Sb_2S_3). Let us strike a safety match in the dark. We notice that the dark, rough material (the low-kindling material) on the booklet or box burns first. It consists of a thin layer of red phosphorus, antimony trisulfide, and powdered glass mixed with glue. The whole lighting surface does not take fire because the kindling temperature of phosphorus in contact with potassium chlorate is lower than that of phosphorus and air alone. The diagrams illustrate the composition of typical matches. (See Fig. 20-10.)

QUESTIONS

9. In which group of the periodic table are the elements of the nitrogen family?

10. Tabulate the elements of the nitrogen family, their atomic weights, atomic numbers, and combining numbers.

11. What is the chief use of the most important compound of phosphorus?

12. Why is phosphorus never found free in nature?

13. Why should phosphorus be kept under water?

14. Water containing a lump of white phosphorus is boiled. What observation may be made?

15. Tongs are used when phosphorus is handled. Phosphorus is cut while it is in water. Give reasons for these ways of handling the element.

16. Some phosphorus is placed in a dish that is floating on water in a container. Both dish and container are then covered with a large inverted jar. Soon the air within the jar (*a*) decreases in volume, (*b*) becomes filled with a dense white smoke that (*c*) later disappears. Explain each event.

17. Define *allotropic* forms; give an example.

18. Name one use of phosphorus pentoxide.

19. Write equations for (*a*) burning phosphorus; (*b*) dissolving the product of burning phosphorus in water; (*c*) burning phosphorus sesquisulfide (P_4S_3)—SO_2 is one product.

20. Compare the use on the head of matches of phosphorus sesquisulfide with that of white phosphorus.

21. Give a military use for phosphorus.

Arsenic: "Poison, Beware." "These trees have been sprayed with arsenate of lead," is a familiar sign. Calcium arsenate is also a well-known insect poison. Arsenic poisons sprayed on cotton plants kill the boll weevil; this is often done from an airplane.

The outstanding uses of arsenic depend on its poisonous nature. White arsenic, or arsenic trioxide (As_2O_3), is the substance usually meant when a person mentions arsenic. Some mountaineers, however, are said to eat tiny doses of this powder to increase their endurance. By gradually increasing the amount they build up a tolerance until they can take many times the normal fatal dose. Surely it would be better to put arsenic oxide to its regular uses of making certain kinds of glass, of preserving skins of animals, and of making Paris green, copper aceto-arsenite [$3Cu(AsO_2)_2 \cdot 1Cu(C_2H_3O_2)_2$], which is used as an insecticide.

One case is known in which a woman became seriously sick from eating apples that had been sprayed with arsenic insecticides—from her own trees, too. Careful washing, especially in dilute hydrochloric acid, is good treatment for arsenic-sprayed fruit. Egg white is a ready antidote for arsenic poisoning.

Arsenic has been known since ancient times. The element is silvery bright when newly made but in time becomes dull gray, hard, and porous. It burns easily when a fresh chip is dropped into a jar of chlorine. It also will burn in air. One-half to 1 per cent of arsenic, alloyed with lead, makes lead shot harder and helps in the manufacture of the shot.

Antimony. The symbol for antimony is Sb; it comes from the Latin word *stibnium*. This element also was known to ancient people. Black antimony sulfide (stibnite) was used as a cosmetic for coloring the eyebrows in Egypt perhaps as early as 5000 years ago.

Elementary antimony is sometimes found free, but the sulfide is the chief ore. Red-rubber hot-water bottles, laboratory tubing, and other such goods are prepared with antimony sulfide (Sb_2S_3) as a filler, the same compound that is used in safety matches.

The element has extensive use in alloys, often with lead. This metal makes possible the linotype machine, the mechanical type-casting device, which in turn makes possible the modern newspaper. Antimony in the type metal causes the latter to expand slightly as it solidifies and to take a clear impression of the mold into which it was cast or poured. Other uses for antimony alloys include storage-battery plate grids, bearings, and the coverings of telephone cables (see the next table).

Bismuth. In the Gay Nineties practical joking is said to have reached the heights of a fine art. For example, a guest at dinner might be supplied with a spoon that looked like the rest of the tableware but that was really made of low-melting alloy. A very hot cup of tea would then be served. Imagine the surprise of the guest to find his spoon melt away as he stirred the tea, leaving just the upper part of the spoon handle in his hand. In the bottom of his teacup would remain a silvery liquid, resembling mercury.

Wood's metal alloy [Bi (4 parts), Pb (2), Sn (1), Cd (1)] melts easily in hot water. This substance is called a ***fusible*** alloy. We see it or similar alloys in fire-protection equipment, used as a solder to hold together the parts of a sprinkler head. (See Fig. 20-11.) When a fire starts, the fusible part melts and the parts which are

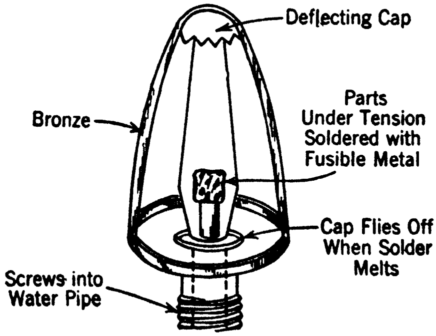


FIG. 20-11.—Heat from a fire melts the Wood's metal solder of the sprinkler head. The parts then fly away from the head, allowing water to rush forth and douse the flame.

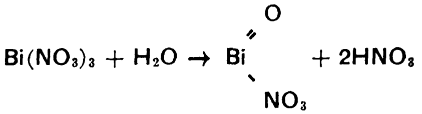
under tension spring out, allowing water to flow from the pipe to which the sprinkler head is attached, dousing whatever is below. We can notice these sprinkler heads in stores, theaters, schools, warehouses, and shops, awaiting a temperature rise to put them into action. Many fire-protection devices depend on a fusible alloy that melts and flows away when the temperature rises, thus allowing doors to close, curtains to drop, or the electric current to stop. A widely used fusible alloy melts at 155°F (68.3°C).

ALLOYS CONTAINING ANTIMONY OR BISMUTH

Name	Percentage composition	Uses
Babbitt metal....	Sn 90, Sb 7, Cu 3	Antifriction bearings
Britannia metal...	Sn 90, Sb 10	Tableware
Battery plate.....	Pb 94, Sb 6	In storage batteries
White metal......	Sn 82, Sb 12, Cu 6	Bearing metal
Type metal..... ..	Pb 82, Sb 15, Sn 3	Printing type
Pewter...........	Sn 85, Cu 6.8, Bi 6, Sb 1.7	Dishes
Wood's metal.....	Bi 50, Pb 25, Sn 12.5, Cd 12.5	Low-melting alloy, 60°C
Rose metal.......	Bi 50, Pb 27.1, Sn 22.9	Low-melting alloy, 93.75°C
Lipowitz alloy....	Bi 50, Pb 27, Sn 13, Cd 10	Low-melting alloy, 70–74°C

The bismuth for this alloy may come from Bolivia, where it is found both free and combined in oxides and sulfides. The metal has a noticeable pink tint, although it is in general silvery. It is brittle and by far the densest of the members of this group of elements. Some bismuth is obtained in the United States as a by-product of the electrolytic refining of lead.

When we shake bismuth nitrate with water, we find that a clear solution is not produced. The compound acts on water to produce a white substance.



$$Bi(NO_3)_3 + H_2O \rightarrow \underset{NO_3}{\overset{O}{Bi}} + 2HNO_3$$

This bismuth compound, bismuth oxynitrate, along with others that may form at the same time, is called bismuth subnitrate, a well-known medicinal. The same material has been used in face powders for hundreds of years. It has been discovered that the compound acts with perspiration to make nitric acid. Nitric acid turns the flesh yellow and is irritating. The desirability of using this compound in cosmetics is at least questionable.

SUMMARY

Early history of classification of elements: Döbereiner arranged groups of three similar elements and showed that the atomic weight of the middle element of a group was approximately that of the average of the other two. Newlands arranged elements according to atomic weights and discovered a repetition of properties in octaves. Meyer and Mendeleyev, especially, constructed a periodic table. Mendeleyev first stated the periodic law, pointing out the periodic relationship of the properties of the elements, as follows: ***The chemical properties of the elements are a periodic function of their atomic weights.***

The usefulness of Mendeleyev's table lay in the fact that it

1. Classified the elements
2. Aided in the discovery of new elements
3. Provided a check on the accuracy of atomic weights

The work of Moseley, who used the X-ray spectrograph, led to a new statement of the periodic law, as follows: ***The properties of the elements are a periodic function of their atomic numbers.***

A modern periodic classification of elements has advantages over the old because the altered form is (1) superior in a study of atomic structure and (2) a more useful tool in chemical investigations.

The nitrogen family, Group Vb: phosphorus is never free in nature. Its chief compound is calcium phosphate, which is found in rock phosphate and in bones. Some organic proteins contain phosphorus.

Elementary phosphorus is prepared by heating rock phosphate with coke and sand in an electric furnace without air. Phosphorus vaporizes and is condensed under water in the white form. White phosphorus is a waxy solid, soluble in carbon disulfide and insoluble in water. White phosphorus ignites spontaneously and is poisonous. The red form of phosphorus is not soluble in carbon disulfide, it has a higher kindling temperature than the white, and it is not so poisonous. Both allotropic forms burn, forming phosphorus pentoxide, a powerful dehydrating agent.

Matches are classified as "strike anywhere" and safety. Strike-anywhere match heads contain phosphorus sesquisulfide, rosin, potassium chlorate, glue, and grit. Safety match heads contain antimony sulfide, potassium chlorate, glue, and grit; there is red phosphorus on the box. The sticks are treated to prevent afterglow.

Arsenic compounds are poisonous and are used extensively as insecticides. Elementary arsenic is used to harden lead shot.

Antimony is found free in nature or as a sulfide. Its chief use is in the preparation of alloys, especially type and bearing metals.

Bismuth is found free in nature. It is an ingredient of certain fusible (low-melting) alloys. Compounds of bismuth are used to some exent in medicines.

QUESTIONS

22. Name an important use for each of the following: white arsenic; antimony sulfide; bismuth oxynitrate; lead arsenate.

23. Name one alloy containing each of the following elements: (*a*) arsenic; (*b*) antimony; (*c*) bismuth. Tell the other elements in each alloy.

24. Explain the means of protecting a theater audience from a fire within the projection booth. (See Fig. 20-12.)

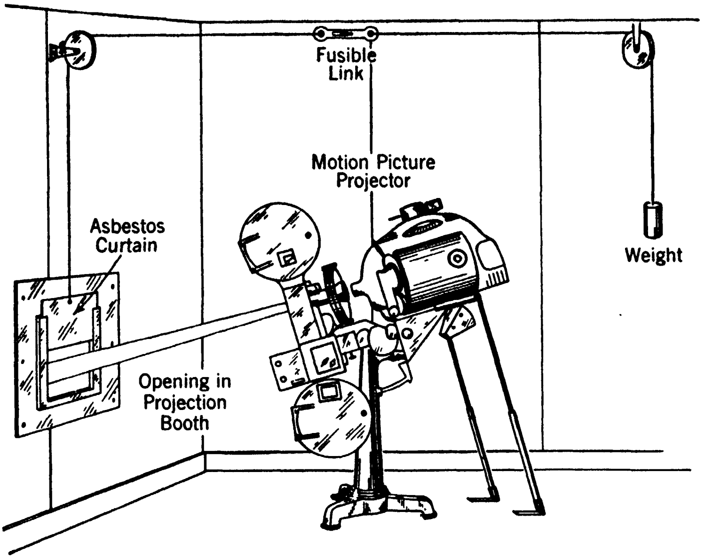


FIG. 20-12.—Flammable film is a fire hazard in theaters. Fusible alloys protect both audience and operator.

MORE CHALLENGING QUESTIONS

25. What is the percentage of copper in Paris green?

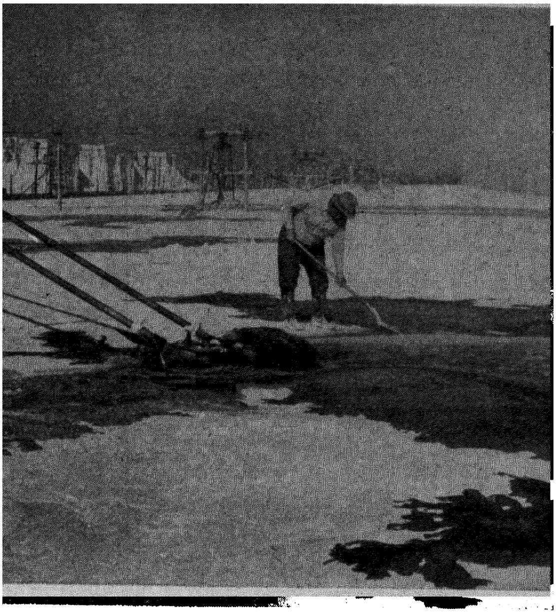
26. Which contains the higher percentage of arsenic, calcium arsenate [$Ca_3(AsO_4)_2$] or lead arsenate [$Pb_3(AsO_4)_2$]?

27. White phosphorus may be copperplated by placing a stick of it in copper sulfate solution. A deposit of metallic copper coats the stick, making it easier to handle. Balance the following equation:

$$P + CuSO_4 + H_2O \rightarrow Cu + H_2SO_4 + H_3PO_4$$

This reaction illustrates the use of copper sulfate solution as a remedy for phosphorus burns.

UNIT FIVE



Courtesy of Texas Gulf Sulphur Company

CHEMICAL INDUSTRIES

In 1865 a group of geologists drilled a hole in the earth in Louisiana in the hope of finding oil beneath the surface. No oil was found, but at a depth of about 500 ft sulfur was discovered. Attempts to mine this sulfur resulted in disaster; for the shaft had sunk through quicksand and poisonous hydrogen sulfide fumes overcame the miners.

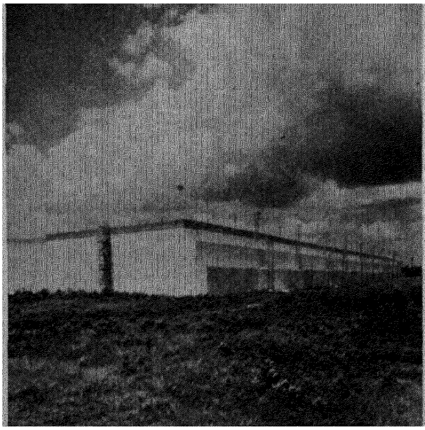
Then a young chemist, Herman Frasch (1852–1914), solved the problem by studying the properties of sulfur. The melting point of sulfur is 112.8°C, a little above the boiling point of water, 100°C. Frasch had the idea of melting the sulfur in the earth by using water heated under pressure. Then the molten sulfur could be raised to the surface by pumping it through pipes. Here is the story of the critical trial in his own words:

When everything was ready to make the first trial . . . , we raised steam in the boilers and sent the superheated water into the ground without a hitch.

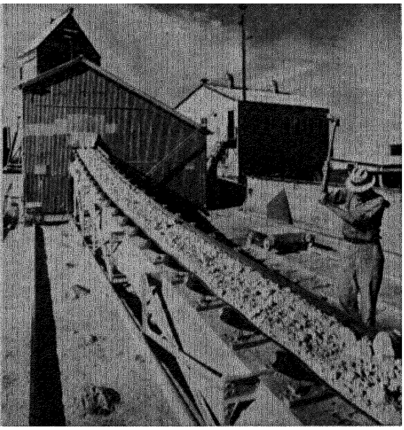
After permitting the melting fluid to go into the ground for 24 hours, I decided that sufficient material must have been melted to produce some sulfur. The pumping engine was started on the sulfur line, and the increasing strain against the engine showed that work was being done. . . . More steam was supplied, until the man at the throttle sang out at the top of his voice, "She's pumping." A liquid appeared on the polished rod, and when I wiped it off I found my finger covered with sulfur. Within five minutes the receptacles under pressure were opened, and a beautiful stream of the golden fluid shot into the barrels we had ready to receive the product. After pumping for about 15 minutes the 40 barrels we had supplied were seen to be inadequate. Quickly we threw up embankments and lined them with boards to receive the sulfur that was gushing forth; and since that day no further attempt has been made to provide a vessel or a mold into which to put the sulfur.

When the sun went down we stopped the pump to hold the liquid sulfur below until we could prepare to receive more in the morning. The material on the ground had to be removed, and willing hands helped to make a clear slate for the next day. When everything had been finished, the sulfur all piled up in one heap, and the men had departed, I enjoyed all by myself this demonstration of success. I mounted the sulfur pile and seated myself on the very top. It pleased me to hear the slight noise caused by the contraction of the warm sulfur, which was like a greeting from below—proof that my object had been accomplished. . . .

This was especially gratifying as the criticisms I had received from technical papers and people who had heard what I was attempting to do had been very adverse. . . . A fair illustration is the remark of the mail boy who drove me to the railroad the morning after our first pumping. He said: "Well, you pumped sulfur sure, but nobody believed it but the old carpenter, and they say he's half crazy!"



This solid lump of sulfur covers about six acres and is five stories high.



Courtesy of Texas Gulf Sulphur Company

The load of sulfur on this conveyer belt is automatically weighed as it passes the shed.

UNIT FIVE . . . . CHAPTER XXI

THE ACID HEAVY CHEMICALS

We are now ready to discuss the big business of chemistry. The acid heavy chemicals—sulfuric, nitric, hydrochloric, and phosphoric acids—are important in a big way. Demands for these substances are for carload lots, not test tubes full. Chemists control the manufacture of these acids; chemical engineers design the apparatus and containers for them; and chemists with their specially designed apparatus take samples and check on their purity. In a recent year about 8 million tons of (dilute) sulfuric acid valued at about $8 per ton were used in the United States alone. Although these acids are not spectacular, they are the necessary background for the more flashy products of the chemist's art. They are the lifeblood of our industrial organism.

At a modern plant for producing sulfuric acid, a truck drives up with some sulfur and dumps it into a bin. No other sign of activity is noted. The attendant checks the meter readings and makes certain routine tests. The operation is practically automatic. Yet many tons of sulfuric acid are being produced by this plant daily. It is shipped out through pipes or in tank cars or tank trucks that have acid-resisting linings.

These acids are needed for the making of fertilizers, rayon, explosives, motion-picture films, and paper, for refining petroleum, and for hundreds of other purposes.

The Source of Sulfuric Acid—Sulfur. Some of the sulfur used for making sulfuric acid is found in compounds: hydrogen sulfide (H_2S), metal sulfides such as iron pyrites [fool's gold (FeS_2)], and zinc blende (ZnS). A large amount of the sulfuric acid of commerce today, however, is made directly from sulfur. (See Fig. 21-1.)

Free sulfur is found around volcanic regions in Sicily, Japan, Greece, and Mexico; there are deposits below the surface of the earth in Texas and Louisiana. Sulfides of many metals are commonly found—lead, iron, copper, zinc, and arsenic. Gypsum ($CaSO_4 \cdot 2H_2O$), Epsom salts

---

New Terms

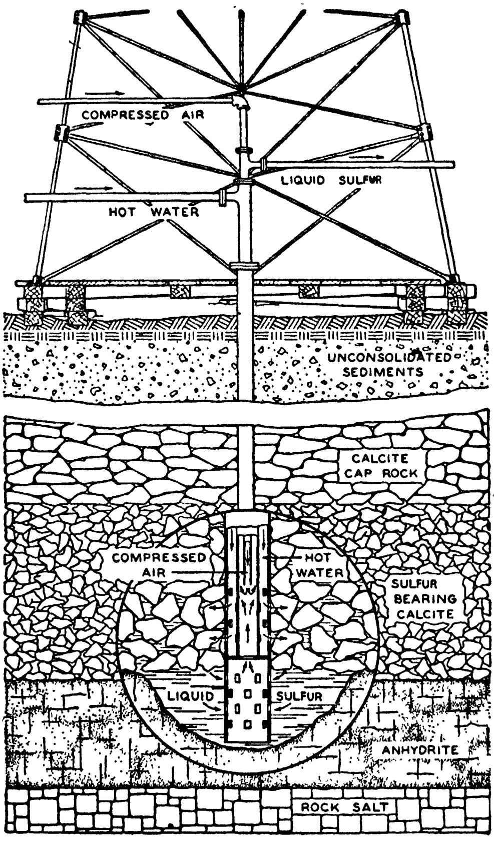
rhombic
monclinic
desiccator

oleum
aqua fortis

polymer
polymerization

($MgSO_4 \cdot 7H_2O$), and barite ($BaSO_4$) are among the sulfates found in nature. Also, certain proteins contain sulfur; compounds found in eggs and in any other food that turns a silver spoon black have sulfur combined in them.

Sulfur is a yellow substance, hard and brittle if in the cylindrical, or roll, sulfur form or a soft yellow powder if in the form called flowers of sulfur. It is about twice as dense as water, insoluble in water, soluble in carbon disulfide (CS_2), a nonconductor of electricity, and without marked odor.



Courtesy of Texas Gulf Sulphur Company

FIG. 21-1.—This is the Frasch method of mining sulfur—notice the three concentric pipes. The break in the diagram represents 700 ft of rock. In order to get the water (outermost pipe) hot enough to melt sulfur, a high pressure is used.

Let us put some sulfur into a test tube and heat it very slowly so that the heat has time to enter the poorly conducting sulfur. When the sulfur reaches 112.8°C, it forms a clear, straw-colored liquid, which rapidly darkens to amber color and thickens when the temperature is raised. At about 160°C the test tube can be inverted without loss of the sulfur, for it is now like thick, dark tar. (See Fig. 21-2.) More heating makes it flow again while still dark, and finally it boils at 444.6°C. The vapor of sulfur formed in such an experiment is cloudy, with some condensed sulfur in it. When the sulfur is boiling, some of the vapor condenses in the form of a yellow powder (flowers of sulfur) on the cooler walls of the test tube. The hot sulfur vapor burns when it reaches the air. A blue flame shows this, and a colorless gas that has a sharp and choking odor is formed (sulfur dioxide).

If this molten sulfur is quickly chilled by pouring it into cold water, a dark, sticky mass is formed that resembles smoked rubber in appearance. This plastic form of sulfur can be molded into any desired form while warm, but it cools quickly and hardens into a shapeless, dark mass, which gradually becomes yellow again.

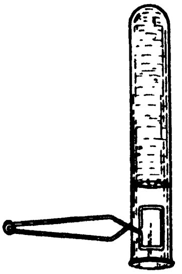


FIG. 21-2.—Plastic sulfur flows like tar at 160°C. When cooled, it resembles well-chewed chewing gum for a while. Finally it hardens to the stable rhombic form.

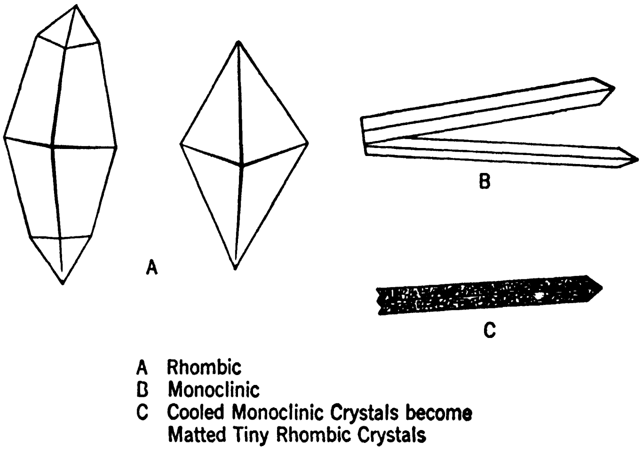


FIG. 21-3.—*A*, stable crystals of sulfur are diamondlike rhombs. *B*, above 115°C, sulfur crystallizes in the monoclinic form. *C*, after monoclinic crystals have cooled, the rhombic form is present although the general outline remains the same.

The ordinary crystalline form of sulfur is called ***rhombic*** sulfur, and it consists of a matted group of crystals. Separate crystals are obtained by making a solution of sulfur in carbon disulfide (CS_2) and evaporating the solvent slowly. (See Fig. 21-3*A*.) A second crystalline form can be made by pouring sulfur that has been heated above 115°C into a paper cone held in a funnel. The crystals this time are needlelike in shape, and they start to form on the cooler top and at the sides first. (See Fig. 21-3*B*.) As soon as the top has formed a crust, it is pierced with a matchstick and the excess molten sulfur poured off. Then the paper is broken open, and a bristling miniature forest of ***monoclinic*** sulfur crystals is discovered. (See

Fig. 21-3*C*.) These crystals are stable as long as the temperature remains above 95.5°C. When they are cooled below this temperature, they slowly change into the ordinary rhombic form, although retaining the same outward needlelike form.

Sulfur burns readily, $S + O_2 \rightarrow SO_2$, and joins directly with many other elements. Zinc dust mixed with powdered sulfur and heated burns rapidly. $Zn + S \rightarrow ZnS$. Copper will join sulfur easily. $2Cu + S \rightarrow Cu_2S$.

Courtesy of Koppers Company, Inc.

FIG. 21-4.—The sulfur candle as a means of fumigation has a limited use. Thoroughly scrubbing a room with soap and water while admitting sunlight and fresh air is considered a satisfactory disinfection after a contagious disease.

Lead, mercury, silver, arsenic, chlorine, and carbon all form sulfides when joined to sulfur; and when hydrogen is bubbled through melted sulfur, some hydrogen sulfide is formed. Sulfur is quite like oxygen chemically, and the sulfides correspond to oxides.

Most of today's sulfur is used to make acids and chemical products, but over one-fourth of it, about 2.5 million tons yearly, is used to make sulfuric acid for fertilizers. The making of paper requires much sulfur dioxide, made by burning sulfur. Free sulfur goes into making gunpowder, and a little goes into medicines. The use of finely divided sulfur on plants and pets to kill pests depends in part on the fact that sulfur very slowly oxidizes and forms some sulfur dioxide.

QUESTIONS

1. In what three forms is sulfur found in nature?

2. Describe in detail the changes that can be noticed when sulfur vapor cools slowly.

3. Tell how to prepare (*a*) rhombic sulfur crystals; (*b*) monoclinic sulfur crystals; (*c*) plastic sulfur.

4. Where are the world's most important supplies of sulfur located?

5. What commercial form of sulfur would be selected for making (*a*) lime-sulfur spray; (*b*) dusting sulfur for agricultural use?

6. Write formula equations for (*a*) the burning of sulfur; (*b*) union of sulfur with magnesium; (*c*) with zinc; (*d*) with iron; (*e*) with hydrogen; (*f*) with copper.

7. What is the most important use of sulfur?

8. For what purpose is sulfur used (*a*) in paper making; (*b*) in straw-hat making; (*c*) in a drugstore; (*d*) in agriculture; (*e*) by stonemasons?

9. What property of sulfur makes it a useful part of certain types of electrical apparatus? What other property of sulfur limits this use?

10. The early Spanish explorers in Mexico obtained sulfur from the mouths of volcanoes in that country. For what purpose did the Spaniards use the sulfur they obtained?

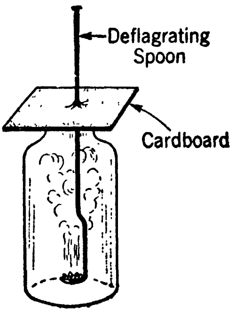


FIG. 21-5.—One of the simplest ways to make sulfur dioxide is to burn sulfur.

Sulfur Dioxide. The simplest way to make sulfur dioxide is to burn sulfur or a sulfide. (See Fig. 21-5.) Both these fuels form oxides when heated in air. Sulfur dioxide issues from volcanoes as a secondary product, but fortunately there is not much of it, for it kills vegetation.

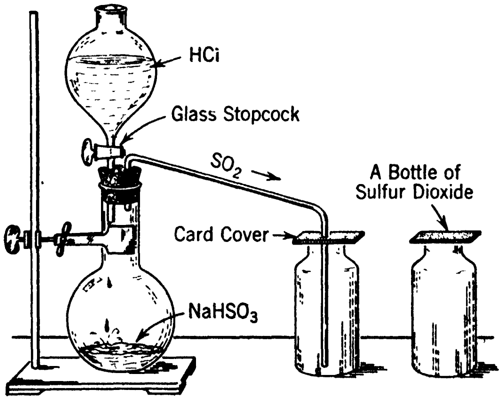


FIG. 21-6.—Any sulfite or bisulfite plus an acid yields sulfur dioxide gas. This apparatus is a suitable one in which to carry out the reaction.

Sulfurous acid in water solution can be made in several ways, one of the simplest being the action of an acid on a sodium hydrogen sulfite

$$NaHSO_3 + HCl \rightarrow NaCl + H_2SO_3$$

We make sulfur dioxide gas in the laboratory by decomposing sulfurous acid (H_2SO_3). (See Fig. 21-6.)

$$H_2SO_3 \rightarrow H_2O + SO_2\uparrow$$

The acid is quite unstable and, like carbonic acid, cannot be made and isolated in the pure state.

Hot concentrated sulfuric acid will oxidize copper and is reduced to sulfur dioxide. (See Fig. 21-7.)

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

When sulfur dioxide is made by burning sulfur, a slight amount of the hot sulfur dioxide acts on more oxygen of the air to form a higher oxide of sulfur, sulfur trioxide (SO_3).

$$2SO_2 + O_2 \rightarrow 2SO_3$$

This change is a desired one; it has been studied by chemists to discover how it may be encouraged. The metal platinum, as a catalyst, has the desired effect, but because of its high cost iron oxide (Fe_2O_3), molybdenum oxide, and vanadium oxide are also used.

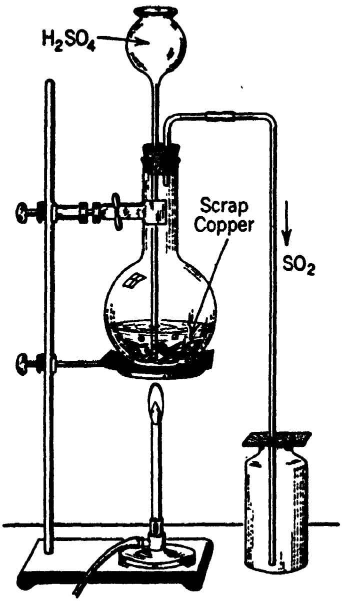


FIG. 21-7.—When hot concentrated sulfuric acid is used to attack copper, the experiment should be performed in a ventilated hood. The acid has a similar action on sulfur or carbon.

A Bleach for a Season. Sulfur dioxide in solution is essentially sulfurous acid. It acts as a mild acid, tastes sour, and acts on bases to form sulfites.

Sulfurous acid absorbs oxygen readily; it is therefore a good reducing agent.

$$H_2SO_3 + [O] \rightarrow H_2SO_4$$

Some bright-colored flowers lose their color and wilt in moist sulfur dioxide. This acid, then, is a bleaching agent. (See Fig. 21-8.) Many straw hats are bleached with sulfur dioxide or dilute sulfurous acid. The bleaching is accomplished by combination of the organic matter in the straw with sulfur dioxide, forming an unstable compound.

Now suppose a hat that has been bleached with sulfur dioxide is worn for a season. Sun-

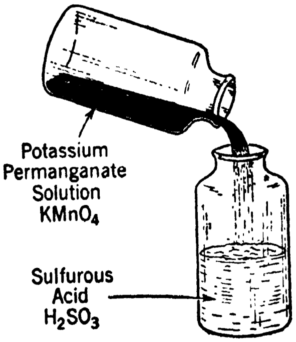


FIG. 21-8.—When purple potassium permanganate solution is mixed with sulfurous acid, a startling loss of color develops. The permanganate ion (MnO_4^-) is reduced, and the sulfite ion is oxidized. Colorless products are formed.

shine helps decompose the unstable compound, liberating sulfur dioxide slowly. The yellow-brown color of the original straw returns, even if the hat is kept carefully clean.

Sulfur dioxide changes orange shellac to white and bleaches dried fruits, flour, silk, and feathers. It is sometimes added to molasses, dried fruits, and canned corn, but the effect on health of the use of sulfur dioxide in foods is questioned by some observers.

The chief use of this colorless gas is for making sulfuric acid, but much of it is used as a refrigerant in household refrigerators because it readily changes to a liquid. The choking, sharp-odored gas is quite soluble in water; the refrigerator serviceman can therefore temporarily protect himself against escaping gas by using a damp cloth over the nose. Sulfur dioxide is dense and tends to settle. One liter weighs over twice as much as a liter of air at the same temperature and pressure.

QUESTIONS

11. Write equations for three ways of making sulfur dioxide.

12. Write formula equations for the actions of sulfur dioxide on (*a*) water; (*b*) sodium hydroxide solution; (*c*) active oxygen.

13. List four physical properties of sulfur dioxide.

14. State four uses of sulfur dioxide.

15. Contrast the chemistry of bleaching by the use of sulfurous acid with that by hypochlorous acid.

Modern Methods of Making Sulfuric Acid. The acid of the greatest importance is sulfuric acid. Very little of it is stored. The tonnage of sulfuric acid produced each month, therefore, is a reliable index of general business conditions in an industrial nation.

Two general methods are used for making sulfuric acid. These will be considered in turn. They are: (1) the contact process; (2) the chamber process.

1. The contact process for making sulfuric acid, or ***oil of vitriol,*** gets its name from the fact that a mixture of sulfur dioxide and oxygen changes to sulfur trioxide rapidly when it comes in contact with the catalyst. The steps in the process essentially are: (*a*) producing sulfur dioxide by burning sulfur or a sulfide in air; (*b*) cleaning the gas from dust and impurities that would tend to "poison" the catalyst; (*c*) passing sulfur dioxide with more air at the right temperature over a catalyst and obtaining sulfur trioxide; (*d*) absorbing the sulfur trioxide formed. Equations for the reactions are

$$\begin{aligned} &(a) \quad S + O_2 \rightarrow SO_2 \\ &(c) \quad 2SO_2 + O_2 \rightarrow 2SO_3 \\ &(d) \quad SO_3 + H_2O \rightarrow H_2SO_4 \end{aligned}$$

In actual practice the construction and operation of a sulfuric acid plant require much more attention to details than the diagram suggests. (See Fig. 21-11.) The equation (*d*), for example, shows that the sulfur trioxide is absorbed in water. It is found to be better economy, however to use concentrated sulfuric acid instead of water, obtaining fuming sulfuric acid, or ***oleum*** ($H_2SO_4 \cdot SO_3$), as a product, for the sulfur trioxide escapes through a spray of water as a mist. The addition of dilute sulfuric acid to oleum makes the resulting acid of any desired concentration.

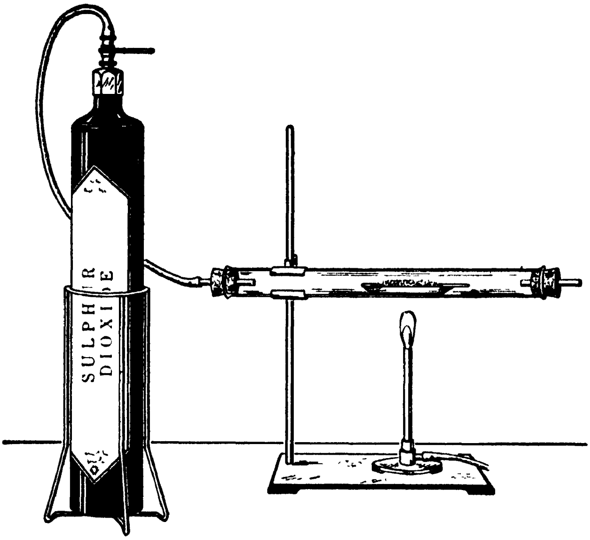


FIG. 21-9.—With this apparatus, the action of sulfur dioxide on iron is carried out.

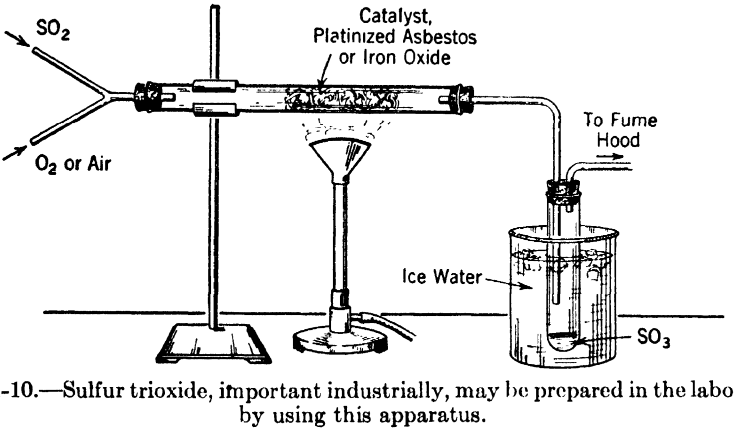


FIG. 21-10.—Sulfur trioxide, important industrially, may be prepared in the laboratory by using this apparatus.

2. The lead-chamber process takes its name from the lead room, or chamber, in which the action occurs. (See Fig. 21-12.) Sheets of lead

about as thick as this book and as large as a table top are melted together at the edges and supported from steel girders by wires to form a room about twice the size of a large schoolroom. Sulfur dioxide and air are introduced into this room along with steam and oxides of nitrogen. The oxides of nitrogen serve as the catalyst, or carrier, of oxygen. They are recovered, for the most part, and used time and time again with only a little loss. The action in the lead chambers is complicated, but essentially the following equations represent it:

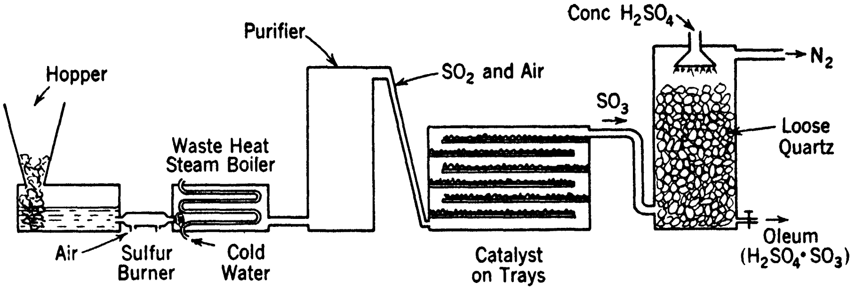


FIG. 21-11.—A simplified diagram of a contact sulfuric acid plant shows the steps in the process. Many such plants are manufacturing this important acid in huge quantities daily.

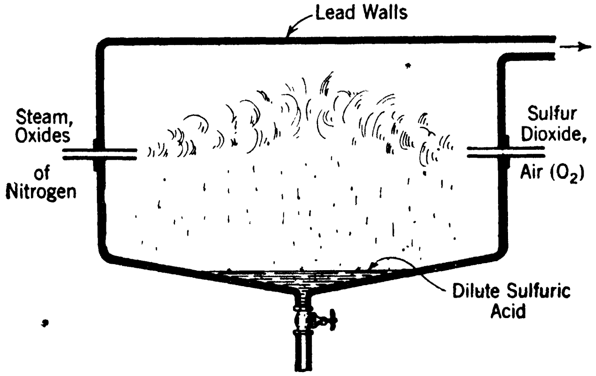


FIG. 21-12.—The broth from the sulfurous witches' brew shown above gathers on the leaden floors of the chamber. Chemists call this method of making sulfuric acid the chamber process.

(a) $S + O_2 \rightarrow SO_2$

(b) $SO_2 + H_2O \rightarrow H_2SO_3$
(from steam)

(c) $H_2SO_3 + [O] \rightarrow H_2SO_4$
(from oxides of nitrogen)

Inside the chamber a sour drizzle of acid falls slowly and collects on the floor, ready to be drawn off for use.

Many industrial processes, such as smelting metals, produce sulfur dioxide. This gas would be wasted if it could not be sent into a lead chamber and converted into sulfuric acid, and this is done in many industrial establishments. The contact method is not used, for the impure gas would "poison" the catalyst. Often the acid is used directly by the company producing it.

Comparison of Contact and Lead-chamber Sulfuric Acid. Most of the modern installations for making sulfuric acid are of the contact type because the process is simple, cheap, and compact. A contact plant can be erected on the space occupied by a large dwelling house and can be clean and attractive enough for an afternoon fancy-dress bridge party. Also, the contact process makes concentrated acid that is useful for many purposes, such as the manufacture of dyes and explosives.

The liquid product of the lead chambers is called "chamber acid." Chamber acid is dilute and is extensively used for fertilizer making. If concentrated acid is needed from the lead-chamber product, the dilute acid is heated in suitable vessels until the right amount of water has evaporated. A purer acid can be made by the contact process, the chamber acid often containing small amounts of lead sulfate, arsenic oxide, and oxides of nitrogen. Contact acid can be made having a density of 1.84 g per ml, (93 per cent H_2SO_4 by weight), while the chamber product has a density of 1.5 to 1.6 g per ml (60 to 70 per cent H_2SO_4 by weight).

Sulfuric Acid, the Dr. Jeykl and Mr. Hyde of Chemistry. Dilute sulfuric acid is a typical acid. It shows the actions of all good sources of protons:

$$H_2SO_4 \rightleftarrows 2H^+ + SO_4^{--}$$

It acts on blue litmus to turn it pink; it attacks active metals like zinc and liberates hydrogen gas; it changes metal oxides, hydroxides, and carbonates to sulfates.

The presence of sulfate ions can be proved by uniting them with barium ions. A white precipitate of barium sulfate forms immediately. Barium sulfate is insoluble in common acids. These facts serve as a test for identification of the sulfate ion (SO_4^{--}) in solution and to distinguish it from sulfite ion (SO_3^{--}) since barium sulfite ($BaSO_3$) dissolves in acids. The following are used for testing for sulfate ion:

$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{(insoluble in acid)}}{BaSO_4\downarrow} + 2HCl \quad \text{(formula equation)}$$

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4\downarrow \quad \text{(ionic equation)}$$

Concentrated sulfuric acid has vastly different properties from the dilute. This oily liquid is almost twice as dense as water (1.84 g per ml) and is a vicious liquid to use. First and foremost, it has a terrific thirst. It seeks water from almost any source with such vigor that the heat produced may change the water into steam and cause an explosion. In fact, acid flying from this cause is an altogether too common accident. For this reason we repeat the warning that it is necessary to pour the denser acid into water with much stirring when the acid is diluted, ***never*** in the reverse order. (See Fig. 21-13.) The mixture is allowed to cool before being used. Because of its strong tendency to combine with moisture, concentrated sulfuric acid is often used in ***desiccators,*** containers in which materials are dried and kept dry.

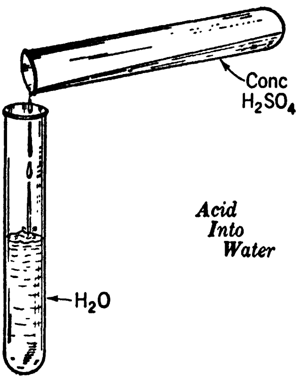


FIG. 21-13.—The correct method of mixing sulfuric acid and water can be recalled by the letters:
acid
n
water
o

The elements of water are extracted by concentrated sulfuric acid from wood, sugar, or paper, leaving black carbon. (See Fig. 21-14.) In like manner, water is extracted when concentrated acid is left for even a short time on the hands, causing a painful burn.

Second, concentrated sulfuric acid differs from dilute in that the concentrated sulfuric acid is an oxidizing agent. Thus, the action may be considered to be

$$H_2SO_4 = H_2O + SO_2 + [O]$$

For this reason we were able to use concentrated sulfuric acid to attack copper in making sulfur dioxide.

$$2H_2SO_4 + Cu \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

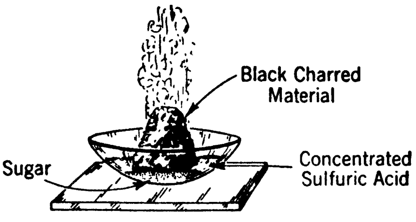


FIG. 21-14.—The thirst of sulfuric acid for water is emphasized by its making a charred black biscuit from a teaspoonful of sugar.

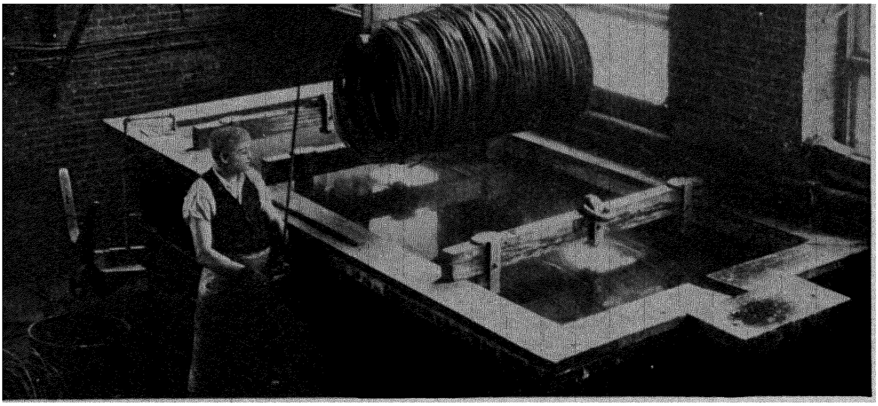
Third, in spite of these vigorous actions, concentrated sulfuric is not dissociated into ions. The pure liquid does not conduct electricity and when cold does not affect metals like iron. It is shipped in steel tank cars.

Fourth, concentrated sulfuric acid has a high boiling point, 338°C for 98 per cent pure acid. This temperature of boiling is higher than that of almost all other acids, and for this reason sulfuric acid may be used in their preparation. We shall examine the making of other acids in detail after a brief description of the uses of sulfuric acid.

Uses of the King of Acids. A paper clip and a barbed-wire fence both need sulfuric acid in the processes of their manufacture. When a batch of steel wire is annealed (softened) in an oven and withdrawn, the oxygen of the air forms a film of iron oxide on the surface of the wire.

Before the wire can be drawn into smaller sizes, this oxide coating must be removed or the wire will not be strong and uniform. "Pickling" in sulfuric acid removes the coating. (See Fig. 21-15.) Afterward lime is used to neutralize any acid remaining on the steel.

The refining of metals, electroplating, the making of many chemicals, the refining of petroleum, and the making of rayon, smokeless powder (guncotton), TNT, and many other explosives all need sulfuric acid. Gases are dried by bubbling them through concentrated sulfuric acid. Chlorine, oxygen, hydrogen, or nitrogen may be so treated; but if ammonia is bubbled into the acid, crystals of ammonium sulfate [$(NH_4)_2SO_4$], an important fertilizer, form. Chief among the uses of sulfuric acid is its action on certain salts to produce other acids (see page 357).



Courtesy of The B. F. Goodrich Company and Pennsylvania Salt Manufacturing Company

FIG. 21-15.—The oxide scale on this copper wire is to be removed by dunking the metal in a bath of dilute sulfuric acid. In order to prevent the tank from being attacked also, it has been lined with rubber and acid-resisting bricks.

QUESTIONS

16. Write the formula that represents (*a*) oleum; (*b*) oil of vitriol; (*c*) dilute sulfuric acid; (*d*) concentrated sulfuric acid.

17. By what processes is sulfuric acid produced commercially?

18. Review the chief steps in the newer method of making sulfuric acid.

19. Review the chief steps in the older method of making sulfuric acid.

20. Compare sulfuric acid made by the two chief methods in respect to (*a*) purity; (*b*) concentration; (*c*) uses.

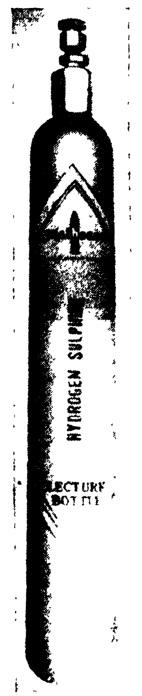
21. Describe a test by which (*a*) sodium sulfide can be distinguished from sodium sulfate; (*b*) sodium sulfite from sodium sulfate.

22. In two parallel columns list four properties of dilute sulfuric acid and four of concentrated sulfuric acid.

23. Tell the correct method of diluting concentrated sulfuric acid, and point out the reason for doing the job in the manner described.

24. Write formula equations for the action of dilute sulfuric acid on (*a*) potassium hydroxide; (*b*) potassium carbonate; (*c*) zinc oxide; (*d*) calcium hydroxide; (*e*) ammonia.

25. What is the percentage of hydrogen in sulfuric acid? Of sulfur?



Courtesy of Matheson Company

FIG. 21-16.—A steel bottle that contains hydrogen sulfide gas for use in the laboratory.

Hydrogen Sulfide. When dilute sulfuric acid, or hydrochloric acid, is placed on solid iron sulfide, an odorous gas is evolved. It is this gas, hydrogen sulfide (H_2S), more than any other that has given the odorous reputation to chemical laboratories.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S\uparrow$$

The fact that this gas is noticed when eggs age and decay and that it is present in the evil-smelling waters of sulfur springs gives an ample idea of its fragrance. It is used extensively in chemical analysis and therefore merits our study. It can also be made conveniently by adding water to aluminum sulfide or by heating together powdered rosin or paraffin and sulfur.

Hydrogen sulfide is a colorless gas that dissolves moderately well in water and is slightly denser than air. When inhaled it is not only disagreeable but ***extremely poisonous,*** almost equal to the treacherous carbon monoxide in its death-dealing effects. This gas is more gentlemanly than carbon monoxide, however, for it gives warning by its odor.

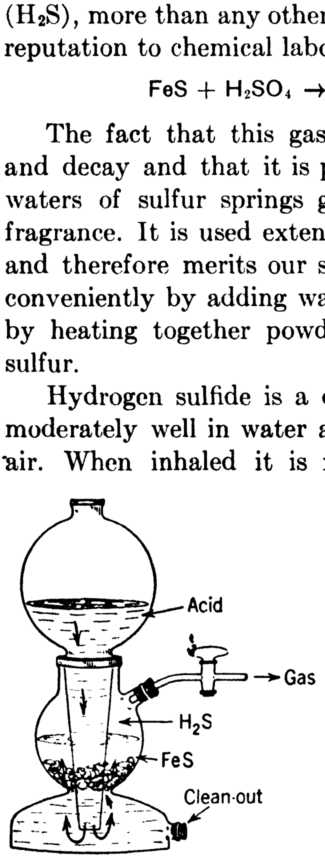


FIG. 21-17.—This generator automatically stops the gas coming from the source as soon as the supply is not in use. Many such types of apparatus have been devised.

In laboratories it may be used from a cylinder equipped with proper valves or may be made by automatic gas generators. Several designs of automatic gas generators are used, but all depend on the pressure of the gas acting on the surface of the liquid acid to push it away from the solid, thus stopping further chemical action until more gas is withdrawn from the generator. (See Fig. 21-17.)

As we have learned, this gas burns in two steps (see page 62). The first step may be seen when the flame is cooled against a glass surface. Yellow sulfur deposits, and beads of moisture collect.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

When hydrogen sulfide is burning freely, the products are those expected of complete burning, sulfur dioxide and water.

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

In solution with water, hydrogen sulfide dissociates in two steps, splitting off two protons, one at a time.

$$H_2S \rightleftarrows H^+ + HS^- \rightleftarrows H^+ + S^{--}$$

The solution is weakly acidic, containing hydronium ions (H_3O^+) due to the presence of these protons, and is called hydrosulfuric acid.

Many metal sulfides are insoluble in water. We find in nature a number of metal sulfides that are important ores. These include lead sulfide, galena (PbS); zinc sulfide, sphalerite (ZnS); and copper sulfide, chalcocite (Cu_2S). Pyrite (FeS_2), or fool's gold, is an ore of sulfur.

When hydrogen sulfide gas is bubbled into a solution containing ions of a metal, if the acidity is not high, the metal and the sulfide ions may unite, forming an insoluble sulfide. In some cases these sulfides are the same as the natural sulfide ores. For example,

$$\begin{array}{rcll}
2AsCl_3 + 3H_2S & \rightarrow & As_2S_3\downarrow + 6HCl & \text{(formula equation)} \\
2As^{+++} + 3S^{--} & \rightarrow & As_2S_3\downarrow & \text{yellow precipitate (ionic equation)} \\
2Sb^{+++} + 3S^{--} & \rightarrow & Sb_2S_3\downarrow & \text{orange precipitate (ionic equation)} \\
2Ag^+ + S^{--} & \rightarrow & Ag_2S\downarrow & \text{black precipitate (ionic equation)} \\
Cu^{++} + S^{--} & \rightarrow & CuS\downarrow & \text{black precipitate (ionic equation)} \\
Pb^{++} + S^{--} & \rightarrow & PbS\downarrow & \text{black precipitate (ionic equation)}
\end{array}$$

All these precipitates form in solutions that are feebly acid and some even in strong hydrochloric acid. The last one listed is often used as a test for the presence of the sulfide ion, for lead compounds in solution easily turn black when they meet hydrogen sulfide. Some states require that manufactured household fuel gas shall contain enough hydrogen sulfide to cause a blackening of paper moistened with lead acetate solution. The hydrogen sulfide in fuel gas causes a stench that warns people when there is a leak.

$$\underset{\text{lead acetate}}{Pb(C_2H_3O_2)_2} + H_2S \rightarrow \underset{\text{(black)}}{PbS\downarrow} + \underset{\text{acetic acid}}{2HC_2H_3O_2}$$

Sulfides of iron and zinc do not precipitate if the solution is more than slightly acidic. With an alkaline solution of ammonium sulfide a white precipitate of zinc sulfide and a black precipitate of iron sulfide can be formed readily.

$$(NH_4)_2S + ZnCl_2 \rightarrow 2NH_4Cl + \underset{\text{(white)}}{ZnS\downarrow}$$

Sodium, potassium, and calcium sulfides are very soluble and do not precipitate from water solution.

When hydrogen sulfide is bubbled through hydrogen peroxide or a similar oxidizing agent, a milky precipitate of sulfur, which may become slightly yellow, forms.

$$H_2O_2 + H_2S \rightarrow 2H_2O + S\downarrow$$

If ferric chloride solution is used and hydrogen sulfide gas bubbled through it, a precipitate of sulfur forms likewise.

$$\underset{\substack{\text{ferric}\\\text{chloride}}}{2FeCl_3} + H_2S \rightarrow \underset{\substack{\text{ferrous}\\\text{chloride}}}{2FeCl_2} + S\downarrow + 2HCl$$

This is clearly a case of electron transfer, or oxidation and reduction. The S^{--} ion loses two electrons, one to each of two ferric ions (Fe^{+++}), converting them into two ferrous ions (Fe^{++}). The ferric chloride is as much the oxidizing agent in this case as was the hydrogen peroxide that furnished oxygen in the previous equation. Hydrogen sulfide in both illustrations furnishes sulfide ions, which act as the electron-lending, or reducing, agent (see page 503).

QUESTIONS

26. Can hydrogen sulfide be prepared readily (*a*) by the action of hydrochloric acid on copper sulfide; (*b*) by the action of nitric acid on iron sulfide?

27. When hydrogen sulfide is bubbled through hydrogen peroxide, a fine white powder forms as a precipitate. Name the precipitate.

28. Write formula equations for (*a*) the action of water on aluminum sulfide; (*b*) the action of ferrous sulfide and hydrochloric acid; (*c*) the action of ferrous sulfide and dilute sulfuric acid; (*d*) incomplete burning of hydrogen sulfide; (*e*) complete burning of hydrogen sulfide.

29. Tell how to collect sulfur dioxide in the laboratory; hydrogen sulfide.

30. List five sulfide precipitates with their colors.

31. Classify as strong or weak all the acids so far mentioned in this chapter.

32. Tell how to form iron sulfide by precipitation.

33. Show by equations how hydrogen sulfide can be changed into sulfuric acid.

34. Show by equations how hydrogen sulfide can be produced, starting with iron, sulfur, common salt, and sulfuric acid as raw materials.

35. From the formulas, find the density of each of the following gases: sulfur dioxide; hydrogen sulfide; methyl mercaptan (CH_3SH) vapor. How many times as dense as air is each?

The Action of Sulfuric Acid on Common Salt—Hydrogen Chloride. When sulfuric acid (H_2SO_4) is added to common salt, a foam forms made of bubbles of a sharp, choking gas that fumes foglike in moist air. This disagreeable gas is called hydrogen chloride, and its solution in water is named ***hydrochloric*** acid in chemical laboratories and sometimes ***muriatic*** acid in industries. The gas leaves the reaction mixture at room temperatures, since its boiling point is low, −83.7°C. Examination of the solid remaining in the flask shows that just one hydrogen atom of the sulfuric acid has been replaced and that sodium hydrogen sulfate (sodium acid sulfate or bisulfate) is the other product.

$$\underset{\text{salt}}{\mathrm{NaCl}} + \underset{\substack{\text{sulfuric acid}\\\text{(concentrated)}}}{\mathrm{HHSO_4}} \rightarrow \underset{\substack{\text{sodium hydrogen}\\\text{sulfate}}}{\mathrm{NaHSO_4}} + \underset{\substack{\text{hydrogen chloride}\\\text{gas}}}{\mathrm{HCl}\uparrow}$$

This compound contains some of the hydrogen originally present in the acid; therefore, it is sometimes called an ***acid salt.*** The HSO_4^- ion is an acid.

At a higher temperature, sodium hydrogen sulfate will also act on common salt.

$$\underset{\text{salt}}{\mathrm{NaCl}} + \underset{\substack{\text{sodium hydrogen}\\\text{sulfate}}}{\mathrm{NaHSO_4}} \rightarrow \underset{\substack{\text{sodium sulfate}\\\text{(normal salt)}}}{\mathrm{Na_2SO_4}} + \underset{\substack{\text{hydrogen chloride}\\\text{gas}}}{\mathrm{HCl}\uparrow}$$

Another method of making hydrogen chloride is by joining the elements hydrogen and chlorine directly.

$$\mathrm{H_2 + Cl_2 \rightarrow 2HCl}$$

Both elementary gases can be obtained by the electrolysis of salt water (see page 374). They join vigorously, liberating much heat as they burn with a pale green flame.

Nature makes this acid in the stomachs of some animals, using a temperature no higher than that of the body, and omits the sulfuric acid. Chloride ions are gathered from salt in the food that we eat, and some small amount (0.5 per cent) of hydrochloric acid is present normally in the digestive fluid of the stomach, gastric juice, where it aids digestion of food.

If a person swallows a piece of bone, oyster shell, eggshell, or any similar hard object that is part carbonate, the acid in the stomach attacks it, rendering it harmless.

$$\underset{\text{(in shell)}}{\mathrm{CaCO_3}} + \underset{\text{(in gastric juice)}}{\mathrm{2HCl}} \rightarrow \underset{\substack{\text{a soluble}\\\text{compound}}}{\mathrm{CaCl_2}} + \mathrm{H_2O} + \mathrm{CO_2}\uparrow$$

Hydrogen chloride as a ***dry*** gas or liquid fails to change the color of blue litmus paper and is indifferent to zinc or magnesium, hydroxides, and carbonates. This inactive gas quickly changes its reactions to those of hydrochloric acid when moisture is present. The gas readily dissolves in water, 442 volumes to 1 volume of water at room temperature. A solution of hydrogen chloride, containing 20.24 per cent of hydrogen chloride, has a boiling point of 110°C and is more dense than water. It is called "constant-boiling" hydrochloric acid and can be distilled at normal pressure with no change in composition.

Chemical Activity of Hydrochloric Acid. Hydrochloric acid is widely used in laboratories and in commercial work because it is very active chemically. It is a strong acid, dissociating 100 per cent in dilute solutions. Indicators, such as litmus paper, respond to it. This acid, like others, turns blue litmus paper red.

Hydrochloric acid readily attacks fairly active metals, such as zinc, magnesium, or aluminum, but not copper.

$$\mathrm{Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow}$$
$$\mathrm{2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow}$$

Sheet-metal workers use this acid to remove oxides from metals in order to prepare a clean surface for soldering. Copper oxide film is neatly removed from copper, and the fresh metal surface sticks well to the solder. The same is true for zinc. Aluminum, however, does not solder well. The chlorides formed are vaporized in the heat of the soldering "iron" (made of copper).

$$\mathrm{CuO + 2HCl \rightarrow CuCl_2 + H_2O}$$
$$\mathrm{ZnO + 2HCl \rightarrow ZnCl_2 + H_2O}$$

Carbonates are easily attacked by this or other acids. If a stain on marble ($CaCO_3$) is to be removed, this acid will take it out by removing the part of the stone that is stained.

$$\mathrm{CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow}$$

Hydrochloric acid neutralizes alkalies. When milk of magnesia is swallowed as a medicine, the amount of hydrochloric acid in the stomach is diminished.

$$\mathrm{Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O}$$

Testing for Chlorides. How can the chemist prove that the substance he is using is a chloride, that is, contains chloride ions (Cl^-)? By experiment he finds that all the common metal chlorides except three dissolve well in water. These exceptions are lead chloride ($PbCl_2$), mercurous chloride (Hg_2Cl_2), and silver chloride (AgCl). Silver chloride is selected as the best material to use for identification of a chloride ion. Silver ions, present in silver nitrate solution, are brought together with chloride ions, present in hydrochloric acid or any soluble chloride. The insoluble solid, silver chloride (AgCl), precipitates as a curdy, cottage-cheesy, white substance. A solid forms in the mixed solutions and settles out, or precipitates.

$$\mathrm{AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3} \qquad \text{(formula equation)}$$
$$\mathrm{Ag^+ + Cl^- \rightarrow AgCl\downarrow} \qquad \text{(ionic equation)}$$

Any soluble chloride acts in this way with silver nitrate solution, but some other substances also form white precipitates when silver nitrate solution is added to them. With sodium carbonate, for example, silver carbonate precipitates. If the precipitate remains after nitric acid (HNO_3) is added, we can be sure that a halide is really present, for carbonates dissolve in acid. To distinguish silver chloride from silver bromide, we place each in some ammonium hydroxide (NH_4OH); the former dissolves in a little ammonium hydroxide, the latter requires much. This second part of the test for a chloride is called the confirming test and is necessary to avoid confusion. Other tests may be used to distinguish chlorides from bromides (see page 308).

Uses of Hydrogen Chloride and Hydrochloric Acid. As already mentioned, hydrochloric acid is used for cleaning metals that are to be soldered, for cleaning limestone, marble, or other carbonates, and also as a medicine in cases where the human stomach fails to produce the acid in sufficient quantity. In addition to these uses, this acid finds an interesting use in the wool industry. Sheep's wool, mixed with vegetable burrs that have clung to the sheep as they graze, or "shoddy" (cotton and wool mixed in a fabric) are treated with the gas (HCl). The vegetable matter becomes "carbonized," or brittle, and in a condition in which it can be crushed easily and blown away. The wool fibers remain unchanged and are worked by regular woolworking machinery.

Carboys, or large bottles, of hydrochloric acid are shipped daily about the streets of any large city. In addition, chemical manufacturing companies use great tanks full of the solution. Many widely different uses are made of the acid. It is involved in the making of aluminum, zinc, and other chlorides, in making glue, dyes, and drugs, in cleaning iron, and in changing starch to glucose. The total value of this acid used in 1 year in the United States is about 1 million dollars.

QUESTIONS

36. Write the formula for muriatic acid; muriate of soda; muriate of potash; muriate of lime.

37. Write formula equations for (*a*) action of concentrated sulfuric acid on calcium chloride; (*b*) sodium hydrogen sulfate and common salt; (*c*) burning of hydrogen in chlorine; (*d*) common salt and cold concentrated sulfuric acid.

38. Write equations for the action of hydrochloric acid on (*a*) sodium hydroxide; (*b*) sodium carbonate; (*c*) sodium hydrogen carbonate; (*d*) magnesium; (*e*) copper oxide.

39. Assume that a piece of lead to be soldered has a thin coating of lead oxide (PbO). What is the effect of the acid on the oxide? What is the effect of the heat of the soldering iron on the products resulting from the action of the acid?

40. Common salt and Glauber's salt are both white solids. Tell how to identify each by chemical tests.

41. List five uses of hydrochloric acid.

42. Account for the fact that dilute hydrochloric acid is active, while hydrogen chloride gas is relatively inactive.

43. Write formula equations for the action of dilute hydrochloric acid on (*a*) aluminum hydroxide; (*b*) calcium hydroxide; (*c*) metallic zinc; (*d*) ferrous oxide; (*e*) calcium hydrogen carbonate.

44. Show by an equation how (*a*) hydrogen chloride in water dissociates into ions; (*b*) hydrogen sulfate in water dissociates into ions.

45. Why may sulfuric acid be considered a more important acid than hydrochloric?

The Action of Sulfuric Acid on Saltpeter. Among the experiments performed by the alchemists, we find one which was widely used, that of making ***aqua fortis,*** or strong water, a liquid so called because of its powerful dissolving action on metals. "Heat oil of vitriol (H_2SO_4) with saltpeter (KNO_3) in a retort, and distill the vapors arising into a cooled vessel," said the alchemists. This same ancient discovery is still used today, except that Chile saltpeter ($NaNO_3$) is used instead of saltpeter (KNO_3) because it is cheaper and more easily obtained.

Nitric Acid, or Hydrogen Nitrate. A modern apparatus for making nitric acid is made of stainless steel, Pyrex glass, or stoneware. Sulfuric acid is heated gently with sodium nitrate. (See Fig. 21-18.) The nitric acid vapors, which have a normal boiling point of 86°C, are helped to leave the mixture by reducing the pressure on it and are condensed in a cool vessel.

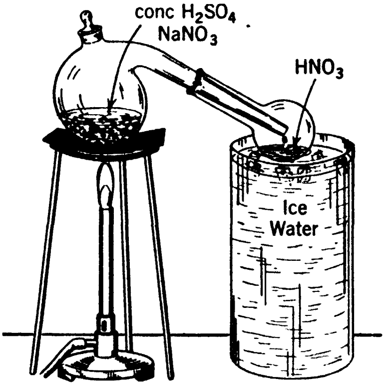


FIG. 21-18.—In the laboratory preparation of nitric acid, good ventilation is needed. Note that no rubber or cork stoppers are used—they react with nitric acid.

$$\underset{\text{Chile saltpeter}}{NaNO_3} + \underset{\text{sulfuric acid}}{HHSO_4} \rightarrow \underset{\text{sodium hydrogen sulfate}}{NaHSO_4} + \underset{\text{nitric acid}}{HNO_3\uparrow}$$

We should notice how similar this action is to that of sulfuric acid on common salt (page 358). At a higher temperature sodium hydrogen sulfate will act on more sodium nitrate, but the nitric acid decomposes. The first action in this case is the practical limit.

As a result of much work by skillful experimenters, synthetic ammonia is now made cheaply and in large quantities. This gas is a suitable substance for making most of today's nitric acid. A platinum screen, at a proper temperature, has been found to act as a catalyst in changing a continuous stream of mixed ammonia and air into nitric acid.

$$\underset{\text{ammonia}}{NH_3} + \underset{\text{from air}}{2O_2} \rightarrow \underset{\text{nitric acid}}{HNO_3} + \underset{\text{water}}{H_2O}$$

Nature makes some nitric acid in every thunderstorm. Hundreds of these disturbances daily give the earth a bath of very dilute nitric acid, restoring fertility to the soil. The energy of the lightning spark forms oxides of nitrogen from the elementary nitrogen and oxygen of the air, for example.

$$N_2 + O_2 \rightarrow 2NO$$

This nitric oxide readily joins more oxygen, and with the water of the storm nitric acid develops.

$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow NO + 2HNO_3$$

Man's attempts to imitate nature's method of making nitric acid are successful, but the cost of the electricity to make the spark is so great that only in Norway has the process been profitable. Here the cheap electricity generated by the abundant water power is used to make a huge electric spark, spread out by magnets. Air passed through the spark and suddenly cooled is found to contain oxides of nitrogen.

QUESTIONS

46. Distinguish pure nitric acid from the concentrated nitric acid of commerce.

47. Write a formula equation for the action of concentrated sulfuric acid on saltpeter, or potassium nitrate.

48. A pupil prepared a sample of nitric acid in the laboratory. The sample was light brown and showed by test that sulfate ions were present. Account for the color and for the presence of sulfate ions in the prepared sample.

49. State a use for sulfuric acid for which neither nitric nor hydrochloric acid can be used as an equivalent substitute.

50. Write formula equations for (*a*) preparation of nitric acid from Chile saltpeter; (*b*) preparation of nitric acid from ammonia; (*c*) action of nitric acid on calcium hydroxide; (*d*) on copper oxide; (*e*) on magnesium carbonate.

How to Recognize Nitric Acid. Nitric acid is a liquid at room temperature and is colorless when pure. In sunlight it easily decomposes into oxides of nitrogen. These dissolve in the nitric acid and color it amber or brown. Nitric acid is about half again as dense as water, and the concentrated nitric acid that is purchased for most chemical use contains 68.6 per cent of HNO_3.

The formula weight of nitric acid is

$$H + N + 3O = 1 + 14 + (3 \times 16) = 63.$$

Of these 63 parts by weight, 48 are oxygen, or about three-quarters. The large percentage of oxygen is not remarkable, for water, for example, has 88.81 per cent oxygen. The activity of the oxygen in pure nitric acid, however, is notable. Here we have a card-house compound, one ready to tumble down.

Let us put concentrated nitric acid on smoldering pencil sharpenings or sawdust. Oxygen from the nitric acid causes a vigorous flame to burst out. Then let us add one part of concentrated nitric acid to three parts of concentrated hydrochloric acid. This mixture, called ***aqua regia,*** will dissolve even gold.

$$\begin{array}{ll} & HNO_3 + 3HCl \rightarrow [3Cl] + 2H_2O + NO\uparrow \\ & Au + [3Cl] \rightarrow AuCl_3 \\ \hline \text{or} & Au + HNO_3 + 3HCl \rightarrow AuCl_3 + 2H_2O + NO\uparrow \end{array}$$

The equation below the line represents the sum of the two actions above it.

If nitric acid is placed on copper, a metal less active than hydrogen and not attacked by hydrochloric acid, the copper is oxidized to copper oxide and the copper oxide is attacked by more nitric acid. This action is similar to that of concentrated sulfuric acid on copper (see page 348).

$$\begin{array}{ll} & 3Cu + 2HNO_3 \rightarrow (3CuO) + H_2O + 2NO\uparrow \\ & (3CuO) + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 3H_2O \\ \hline \text{or} & 3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow \end{array}$$

Dilute nitric acid will produce such an attack on copper; but if concentrated nitric acid is used, brown nitrogen dioxide is produced.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2\uparrow$$

In fact, the products of an action with nitric acid depend on the conditions, especially the concentration of the acid. In general, no hydrogen is formed, for it is oxidized to water. With zinc, a strong reducing agent, some nitric acid may even be reduced to ammonia (the opposite action of its production by the catalytic method), and one of the products will be ammonium nitrate.

Nitric acid, then, readily dissolves metals (not aluminum), their oxides, and, of course, metal carbonates and hydroxides to form nitrates. It is a strong acid, dissociating ions well, and a vigorous acid in its wild, unrestrained supplying of energetic oxygen.

Notable among the chemical actions of this acid is its ready attack on living, or organic, matter. The skin, which contains protein or complex nitrogen compounds, becomes colored yellow by it. So does silk, wool, and egg white. The yellow color is deepened to orange by the addition of ammonium hydroxide (NH_4OH). This is one test for a protein.

Testing for a Nitrate. Nitric acid contains the group of elements —NO_3, called the nitrate radical. This group, present in all nitrates and in nitric acid, may be identified in the laboratory by a test that requires skill and care. The solution to be tested for the presence of the nitrate radical is mixed in a test tube with some freshly prepared ferrous sulfate solution ($FeSO_4$). A long-stemmed funnel is placed in the test tube and concentrated sulfuric acid poured slowly into the funnel, so that it goes to the bottom of the tube. The acids form two layers, the denser sulfuric acid on the bottom. If a brown ring forms just above the acid, a nitrate must be present; for all nitrates act in this way, and no substances not nitrates give the brown ring test.

We Use Nitric Acid. When we drive to the "movies" in an automobile, we come in contact with many articles prepared through the use of nitric acid. The lacquer paint on the car may be made from cotton treated with nitric acid. The cushions on which we sit, if they are imitation leather, are made from cloth coated with nitrated cotton. Also, the film on which the motion pictures are printed is made of nitrated cotton; and if we see a newsreel of battle-fleet target practice, we may hear that highly nitrated cotton is used to propel shells and that nitrated toluene ($C_6H_5CH_3$), as the explosive inside the shells, causes them to burst as they strike their objectives. This explosive probably is TNT, trinitrotoluene [$C_6H_2{\cdot}CH_3{\cdot}(NO_2)_3$].

Nitrating of cotton is accomplished by treating cotton with concentrated nitric acid, with some concentrated sulfuric acid present to remove water. Most of the nitric acid made is used for nitrating, which is a very dangerous process in unskilled hands. Adding nitric acid to phenol (C_6H_5OH), commonly called carbolic acid, produces trinitrophenol, or picric acid [$C_6H_2{\cdot}OH{\cdot}(NO_2)_3$], a high explosive and a yellow dye. Nitrating glycerin [$C_3H_5(OH)_3$, glycerol] forms glycerin nitrate, popularly called nitroglycerin [$C_3H_5(NO_3)_3$] or "soup" in detective stories. Glycerin nitrate is a sensitive explosive and is also used as a medicine for heart trouble. Alfred Bernhard Nobel of Sweden found that glycerin nitrate could be soaked up in sawdust and molded into a stick which was a much more satisfactory explosive for farm and road work than others employed, being less sensitive to shock. This invention of ***dynamite*** was the cornerstone of his great fortune and led to the founding of the famous Nobel prizes in literature, medicine, peace, physics, and chemistry—five human enterprises Nobel thought worth encouraging.

Nitric acid is used to etch (eat into) metals. By using this acid, copperplates are prepared from which pictures can be printed. The original plate from which the picture of Madame Curie on page 2 was printed was prepared in this way. Nitric acid is also used to make nitrate fertilizers; of course, the acid is not used directly on plants. Useful in peace, essential in war, nitric acid has attracted the attention of every military and civic leader, for no picture of national resources is complete without considering this acid.

QUESTIONS

51. Describe in detail the test used to identify the nitrate radical.

52. Write the formula equations of the action of dilute nitric acid on (*a*) copper, (*b*) silver; of concentrated nitric acid on (*c*) copper, (*d*) ammonium hydroxide.

53. What chemical treatment will change glycerin into glycerin nitrate?

54. Point out that nitric acid is necessary in peace and indispensable in war.

55. What percentage of nitric acid is nitrogen? Hydrogen?

Oxides of Nitrogen. When dilute nitric acid acts on copper chips in a test tube, a gas bubbles up through the blue solution of copper nitrate that forms. Close examination shows that the gas is colorless within the solution but that upon striking the air it becomes brown. Care should be taken to avoid breathing either gas, for they are both poisonous. The colorless gas is nitric oxide (NO), and the brown gas is called nitrogen dioxide (NO_2).

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + \underset{\substack{\text{nitric oxide}\\ \text{colorless}}}{2NO\uparrow}$$

$$2NO + \underset{\text{from air}}{O_2} \rightarrow \underset{\substack{\text{nitrogen dioxide}\\ \text{brown}}}{2NO_2}$$

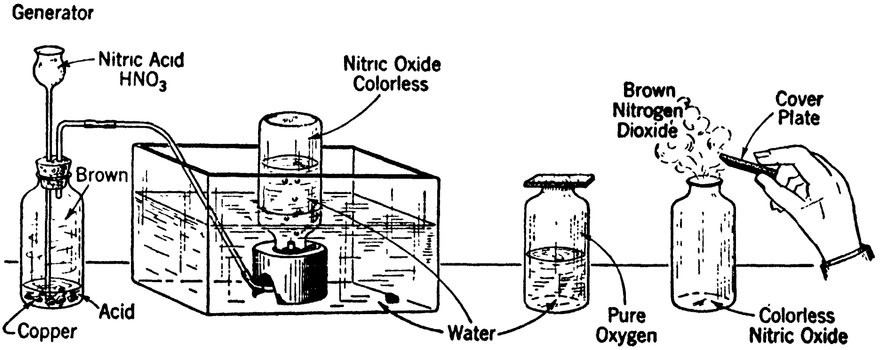


Fig. 21-19.—Nitric oxide is prepared by reducing dilute nitric acid with copper chips. The resulting colorless gas darkens when exposed to air or pure oxygen.

If the experiment is repeated in a generator bottle and the gas collected over water (see Fig. 21-19), we notice (1) that the generator bottle fills with brown gas because of the air present at the start and (2) that the brown gas does not collect in the receiver but a colorless gas does. Apparently the brown nitrogen dioxide is readily soluble in water, and the colorless nitric oxide is much less soluble. After all the air has been swept out of the generator, we are ready to collect a measured bottleful of pure, colorless nitric oxide. If the bottle of nitric oxide gas is now withdrawn from the water and the cover plate lifted, the brown fumes form again almost mysteriously where the gas meets the air.

If we wish an even more startling experiment, we can add slowly to the colorless nitric oxide a half bottle of pure oxygen. With each addition of oxygen, the brown nitrogen dioxide appears, but it soon dissolves in the water.

Nitrogen Tetroxide. If we chill a closed tube containing brown nitrogen dioxide, we notice that its color becomes lighter and that its density increases. Cooled in Dry Ice, nitrogen tetroxide forms a pure white solid (m.p. $-9.3°C$). These effects are explained by assuming that in any given amount of nitrogen dioxide, some colorless nitrogen tetroxide (N_2O_4) is present with which it is in equilibrium.

$$\underset{\text{brown}}{2NO_2} \xrightleftharpoons[\text{favored by warming}]{\text{favored by cooling}} \underset{\text{colorless}}{N_2O_4}$$

The tendency of molecules, such as nitrogen dioxide, to cluster into larger groups is called ***polymerization,*** and the cluster is called a ***polymer.*** Nitrogen tetroxide is a polymer of nitrogen dioxide.

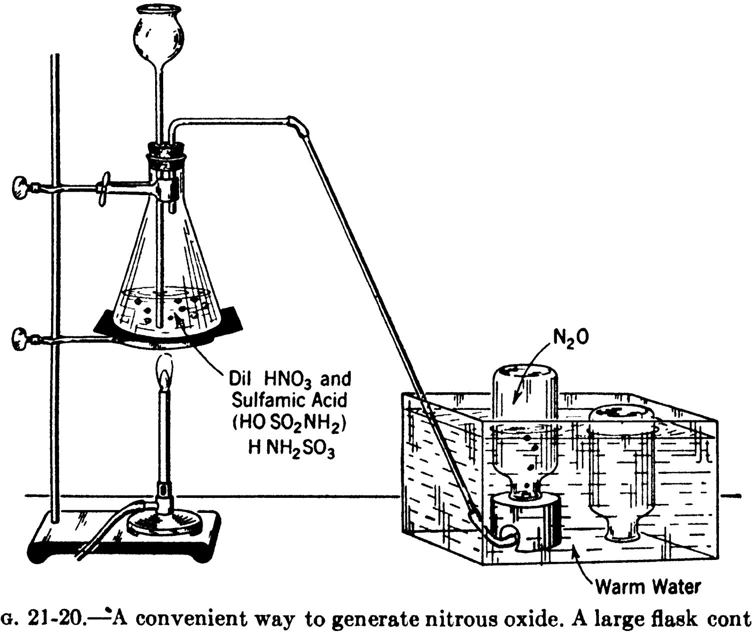


FIG. 21-20.—A convenient way to generate nitrous oxide. A large flask containing a little ammonium nitrate, clamped horizontally and equipped with a single delivery tube, may be substituted for the generator shown.

Laughing Gas. If dilute nitric acid is saturated with ammonia, a slush of ammonium nitrate crystals can be separated from the mixture.

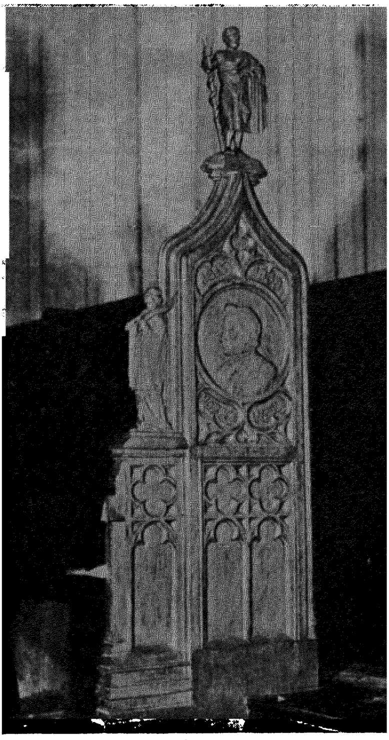
$$HNO_3 + NH_3 \rightarrow \underset{\text{ammonium nitrate}}{NH_4NO_3} \qquad \text{(formula equation)}$$

From the chemical point of view, ammonium nitrate with its two nitrogen atoms per formula has two points of weakness in its structural design. (1) It breaks apart so easily and nicely that it is used in some explosives. (2) We must use reasonable caution when we heat this compound. When this is done carefully, nitrous oxide (N_2O), or dinitrogen oxide, escapes as a gas. (See Fig. 21-20.)

$$NH_4NO_3 \rightarrow 2H_2O + \underset{\text{nitrous oxide}}{N_2O\uparrow}$$

Nitrous oxide is a rather dense but colorless gas that may be collected over warm water; it dissolves very little in hot water. It is used by doctors and dentists as an anesthetic in putting patients to sleep. It may be given to a patient before using ether for an anesthetic. In some cases of dental work that require grinding a tooth cavity, the patient may have a supply of this gas, which he can give to himself as needed, producing only partial anesthesia. Often nitrous oxide is used with one-quarter oxygen mixed with it.

The gas was first prepared by Joseph Priestley and its physiological properties discovered by Sir Humphry Davy. It was first used in a dental operation in 1844 by Dr. Horace Wells (1815–1848) (see Fig. 21-21), who wrote his last will and testament before trying it on himself. Previous to this time it had been used for purposes of entertainment. People acted strangely while recovering from its effects. Some fought wildly, some cried, others became nervous and laughed hysterically (for this reason it has been called ***laughing gas***), and a few died. This last result was unexpected and stopped its use for entertainment.



Courtesy of Trinity College

FIG. 21-21.—This pew end in Trinity Chapel, Hartford, Connecticut, was dedicated to Dr. Horace Wells (1815–1848), the first person to use nitrous oxide in a dental operation. The carved figure on top is that of Aesculapius, god of healing.

Whipped-cream ejectors at soda fountains contain cream under pressure with nitrous oxide. When the ejector valve is opened, the cream spurts forth, fully whipped and filled with bubbles of the gas.

Burning substances continue to burn in nitrous oxide just as well as or perhaps a little better than in air but not so well as in pure oxygen.

QUESTIONS

56. In a column, list the three most important oxides of nitrogen. Make a table of (*a*) their names; (*b*) their formulas; (*c*) their colors; (*d*) their solubility in water; (*e*) their densities as calculated from the formulas.

57. Bromine vapor and nitrogen dioxide are both dark-brown gases. Contrast their behavior when (*a*) cooled; (*b*) placed in cold water; (*c*) passed into potassium iodide solution.

58. Compare the effect of putting a lighted candle into a bottle containing (*a*) air; (*b*) pure oxygen; (*c*) nitrous oxide.

59. What is the effect of cooling without pressure change on (*a*) iodine vapor; (*b*) nitrogen dioxide; (*c*) nitrogen?

60. What volume of oxygen is required to convert $\left\{\begin{matrix}10\\17\end{matrix}\right.$ cubic feet of nitric oxide into nitrogen dioxide at the same temperature and pressure?

Phosphoric Acid. Common phosphoric acid is a siruplike liquid containing some water. Without water, phosphoric acid (H_3PO_4) is a white solid that melts at 42.3°C and has a density of 1.83 g per ml. Most of it is made by treating the natural rock phosphate with sulfuric acid and allowing the gypsumlike sludge of calcium sulfate to settle to the bottom of the container. Later the phosphoric acid is drawn off the top.

$$\underset{\substack{\text{natural}\\\text{phosphate}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{sulfuric}\\\text{acid}}}{3H_2SO_4} + 6H_2O \rightarrow \underset{\text{gypsum}}{3(CaSO_4\cdot 2H_2O)} + \underset{\substack{\text{phosphoric}\\\text{acid}}}{2H_3PO_4}$$

A purer grade is obtained by burning the elementary phosphorus as it comes from the electric furnace where it is made. The phosphorus pentoxide formed by the burning is dissolved directly in water.

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

Phosphoric acid may be used as a substitute for sulfuric acid in some cases, since it has a high boiling point, but it is a weaker acid. It breaks off three protons, one at a time. In orthophosphoric acid (H_3PO_4) solutions, three sorts of negative ions are in equilibrium with each other. Under certain conditions we can represent the situation as

$$H_3PO_4 \rightleftarrows \begin{array}{c} H^+ \\ \text{and} \\ H_2PO_4^- \\ \substack{\text{27 per cent}\\\text{dihydrogen}\\\text{phosphate ion}} \end{array} \rightleftarrows \begin{array}{c} H^+ \\ \text{and} \\ HPO_4^{--} \\ \substack{\text{0.2 per cent}\\\text{monohydrogen}\\\text{phosphate ion}} \end{array} \rightleftarrows \begin{array}{c} H^+ \\ \text{and} \\ PO_4^{---} \\ \substack{\text{0.0002 per cent}\\\text{phosphate ion}} \end{array}$$

Consequently, phosphoric acid forms three sorts of salts. All three of the sodium salts and the calcium salts are used commercially.

Sodium dihydrogen phosphate (NaH_2PO_4) is an acid in baking powders; disodium hydrogen phosphate (Na_2HPO_4) is the compound sold in drugstores for medicinal sodium phosphate; and normal, or trisodium, phosphate (Na_3PO_4), or T S P, is used extensively to soften water, to treat water for boilers, and in household cleaning powders. Its solution is very alkaline, nearly as strong as that of lye (NaOH).

A large amount of phosphoric acid is joined directly to ammonia to form ammonium phosphate fertilizers.

SUMMARY

Sulfur (brimstone) is found free in volcanic regions of Sicily, Japan, Greece, and Mexico and underground in Texas and Louisiana. This element is also found combined with many metals as metallic sulfides and sulfates.

Physical properties: Sulfur is a yellow nonmetal; it is insoluble in water and soluble in carbon disulfide; when heated it undergoes a series of changes. Sulfur has several allotropic forms, rhombic, monoclinic, and plastic.

Chemical properties: Sulfur burns with a pale-blue flame; it joins metals to form metal sulfides; it is similar to oxygen in many chemical actions.

Sulfur is used to make sulfur dioxide and sulfuric acid, for an insecticide, and for an agricultural spraying agent.

Sulfur dioxide occurs in some volcanic gases. It is prepared by

1. Burning sulfur or a sulfide
2. Decomposition of sulfurous acid, made from a sulfite (or hydrogen sulfite) and hydrochloric acid
3. Reduction of hot concentrated sulfuric acid by copper

Sulfur dioxide is a colorless, irritating gas at room temperature. It is quite dense, very soluble in water, and easily changed to a liquid by an increase in pressure. These are physical properties.

The chemical properties of sulfur dioxide are that it

1. Joins water to form sulfurous acid
2. Oxidizes to form sulfur trioxide
3. Reacts with bases to form sulfites

The chemical properties of sulfurous acid (solution) are as follows:

1. It is a mild acid.
2. It joins oxygen to form sulfuric acid.
3. It is a good reducing agent.

Sulfur dioxide is used as a refrigerant, to make sulfuric acid, and as a food preservative. Sulfurous acid is used as a bleaching agent.

Sulfuric acid (oil of vitriol) is prepared commercially by the contact and chamber methods. In the contact method sulfur burns, forming sulfur dioxide. Sulfur dioxide is in turn oxidized in the presence of a solid catalyst, forming sulfur trioxide. The resulting sulfur trioxide is absorbed to make concentrated sulfuric acid. In the chamber method a lead-lined room is used into which steam, sulfuric dioxide, and oxides of nitrogen are introduced. A mist of sulfuric acid forms, producing dilute sulfuric acid.

The properties of dilute sulfuric acid are different from those of the concentrated acid. The dilute acid is strong, similar in strength to hydrochloric acid. Concentrated sulfuric acid is an un-ionized acid. When mixed with a small amount of water, the concentrated acid dissociates one proton more readily than two. $H_2SO_4 \rightarrow H^+ + HSO_4^-$. Concentrated sulfuric acid is a strong dehydrating agent and an oxidizing agent when hot. The concentrated acid should be diluted by stirring ***into*** water with great care. Much heat is evolved in the process. Concentrated sulfuric acid acts on salts, forming other acids.

Sulfuric acid has many uses. Among them are pickling scale from steel products, making fertilizer, preparing other acids, electroplating, refining petroleum, dehydrating, and manufacturing explosives. Its use is very general, and it is a most important chemical substance in an industrial civilization.

Hydrogen sulfide is a very poisonous gas. It occurs in decaying sulfur-containing organic matter and in some volcanic gases. Its laboratory preparation is by action of hydrochloric or dilute sulfuric acid on ferrous sulfide.

The physical properties of hydrogen sulfide are that it is a colorless gas with a disagreeable odor, it has a greater density than air, and has moderate solubility in water.

Its chemical properties are as follows: It burns, either completely or partially. It is a weak acid in solution. It acts with solutions of many metal salts, forming sulfide precipitates. It is a good reducing agent. Hydrogen sulfide is used extensively in chemical analytical work.

Hydrochloric acid (muriatic acid) occurs in dilute solution in the stomach of some animals. The gas is prepared

1. By action of sulfuric acid on common salt
2. By action of sodium hydrogen sulfate on common salt
3. By direct synthesis, burning hydrogen in chlorine

The physical properties of hydrogen chloride are that it is a colorless gas with a sharp odor, is very soluble in water, is denser than air, and produces a fog in moist air.

Hydrogen chloride is inactive chemically when in the form of dry gas. In solution (hydrochloric acid) it shows marked chemical activity. Its actions are typical of acids on hydroxides, oxides, carbonates, and active metals.

Hydrogen chloride or its solution is used in cleaning metals for soldering, carbonizing cotton in mixed textiles, changing starch to glucose, manufacturing drugs and dyes, and testing for Ag^+ ion. It is one of the most widely used laboratory reagents.

Nitric acid (aqua fortis) is prepared by the action of sulfuric acid on a nitrate and by oxidation of ammonia in the presence of a catalyst (Ostwald method). Some is formed in lightning storms.

The properties of nitric acid are that it is unstable, that is an oxidizing agent, and that it dissolves metals, such as silver and copper, evolving oxides of nitrogen—but not hydrogen. Nitric acid has the typical actions of a strong acid on hydroxides, carbonates, and oxides; also, it changes protein to a yellow color. Nitrates are identified by the following test: A brown ring is formed when ferrous sulfate solution and concentrated sulfuric acid are added to a solution of the sample. Nitric acid is used in making explosives, lacquers, dyes, and fertilizers.

Nitric oxide is prepared by the action of copper on nitric acid. Its physical properties are that it is colorless, slightly soluble in water, and a little denser than air. Its most notable chemical property is the immediate change to brown nitrogen dioxide when in contact with oxygen.

Nitrogen dioxide is a brown, irritating gas; it is denser than air, is in equilibrium with N_2O_4, and is soluble in water.

Nitrous oxide (laughing gas) is prepared by decomposition of ammonium nitrate by gentle heating. Its physical properties are that it is a colorless gas with a faint odor and is insoluble in hot water. It resembles oxygen in chemical actions but is not so vigorous an oxidizing agent. It is used as an anesthetic and in making whipped cream at soda fountains.

Phosphoric acid is prepared

1. By action of sulfuric acid on rock phosphate
2. By action of phosphorus pentoxide with water

Phosphoric acid forms three series of salts. It is a moderately strong acid. It is extensively employed to make fertilizers and in general chemical manufacturing.

QUESTIONS

61. What is the percentage of P_2O_5 in phosphoric acid? In rock phosphate?

62. Write formula equations for the neutralization of phosphoric acid by (*a*) sodium hydroxide; (*b*) calcium hydroxide; (*c*) potassium carbonate; (*d*) zinc oxide; (*e*) aluminum hydroxide.

63. Show by equations how to prepare phosphoric acid (*a*) using elementary phosphorus prepared in an electric furnace; (*b*) using rock phosphate and sulfuric acid.

64. Write the formulas and names of three different potassium salts of phosphoric acid.

65. Name the product formed when (*a*) a little $\left\{\begin{matrix}\text{soda lye}\\ \text{potash lye}\end{matrix}\right.$ is added to phosphoric acid; (*b*) when more lye is added; (*c*) when excess lye is added.

UNIT FIVE-------------CHAPTER XXII

THE BASIC HEAVY CHEMICALS

After a lesson on soapmaking in his chemistry class, a pupil with an eye to economy was eager to make soap at home. For a few cents he purchased a 13-oz can of lye at a grocery store. He enlisted the aid of his mother, and in a few weeks she had saved from cooking and stored in jars 6 lb of fat. Then he dissolved some lye in 1 qt of water. While he waited for the lye solution to cool off, he cleaned the fat by melting it and skimming off the dirt and absorbed the coloring matter from the fat by cooking a few slices of potato in it. Then he mixed the warm liquid fat and the lye solution while stirring. A change into soap and glycerin took place. When the mixture was ready to harden, he poured it into cardboard boxes for molds. When hardened, he cut the molds into small cakes, putting them aside to dry out a bit before use. He had made 12 cakes of soap suitable for laundry use that would certainly retail at 10 cents each.

When soap is made at home, it is necessary to use an iron kettle—never aluminum or enamel ware, for a solution of lye acts chemically on these vessels.

Imagine a train made up of 20 heavy steam locomotives. Such a train would have an enormous weight, practically equal to the weight of the lye (sodium hydroxide or caustic soda) made each day in the United States. Yet, among alkalies, sodium hydroxide ranks third in order of importance as a commercial base; sodium carbonate and lime are both ahead of it.

When we think of bases, we consider sodium hydroxide first for it is the compound that is used most extensively as a base in the chemical laboratory.

Manufacture of Sodium Hydroxide (NaOH). Commercially, sodium hydroxide (lye) is made by two processes, both of almost equal importance: (1) the electrolytic method; (2) the chemical method.

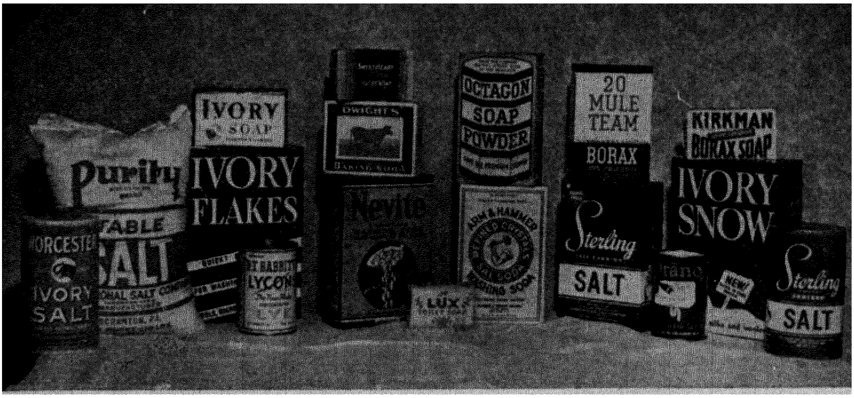
New Terms

stalactite
stalagmite
kiln
limewater
slake
synthetic ammonia

1. The electrolytic method is carried out by passing an electric current through a salt-water solution in a cell specially designed to keep the chlorine that is liberated at the anode separated from the lye that is formed at the cathode. The reaction in the cell may be summed up as follows:

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2\uparrow + Cl_2\uparrow$$

This action has already been considered (see page 302) for the preparation of chlorine. If sodium hydroxide is the chief product, chlorine is a by-product. The value of the chlorine lowers the cost of the sodium hydroxide.



Photograph by Philip Acquaviva

FIG. 22-1.—An assortment of sodium compounds in different forms can be obtained at grocery stores. They include salt, baking soda, washing soda, lye, borax, and soap.

2. The chemical method is carried out in iron kettles. A suspension of calcium hydroxide is mixed with a solution of sodium carbonate

$$\underset{\text{milk of lime}}{Ca(OH)_2} + \underset{\text{sodium carbonate}}{NaCO_3} \rightarrow \underset{\text{precipitated chalk}}{CaCO_3\downarrow} + \underset{\text{lye}}{2NaOH}$$

The mixture is stirred by blowing steam through it for some time. Then it is allowed to settle, and the solution of sodium hydroxide is drawn off or filtered away from the solid calcium carbonate or precipitated chalk. The lye solution is concentrated or crystallized by evaporating the water.

Both the electrolytic and the chemical methods make a somewhat impure lye, but the products are suitable for many purposes.

How Sodium Hydroxide Acts. Sodium hydroxide is a white, innocent-looking material. If a little of it is placed on the fingers, it feels slippery; the compound changes the oils on the skin to a soap, which, of course, is slippery. However, if lye remains in contact with the skin, it causes a painful burn. Lye is also given the name caustic soda because of its corrosive action. It destroys animal matter, and a hot solution dissolves wool or silk. These actions are all caused by the hydroxyl ion (OH^-).

Sodium hydroxide can be purchased in the form of brittle sticks, flakes, pellets that resemble well-worn tips of billiard cues, a solid mass in a steel drum, or a saturated solution in a tank car. All forms must be kept tightly sealed, for the compound absorbs both moisture and carbon dioxide from the air. Exposed to air, a part of the lye changes into sodium carbonate (Na_2CO_3).

$$2NaOH + H_2CO_3 \rightarrow 2H_2O + Na_2CO_3$$

Being a typical base, sodium hydroxide acts readily with strong acids.

$$2NaOH + H_2SO_4 \rightarrow 2H_2O + Na_2SO_4$$

Sodium hydroxide is used in making rayon and photographic films. Petroleum is freed from odorous sulfur compounds by the use of lye. Lye is employed extensively in producing soap and chemicals. Cooking wood chips in caustic solution is part of the process of making them into paper. John Mercer (1791–1866), an English cotton spinner, found that cotton cloth treated under tension with a lye solution became lustrous and stronger. His discovery made the first ***mercerized*** cotton in 1850.

How Potassium Hydroxide Acts. Potassium hydroxide (KOH), also called potash lye or caustic potash, is similar to sodium hydroxide in its chemical actions. Both are very soluble in water, and both are excellent sources of hydroxyl ions, although potassium hydroxide is somewhat more costly. The soap made with the potassium compound is softer than that made with sodium hydroxide. Potassium hydroxide serves as a material for absorbing carbon dioxide.

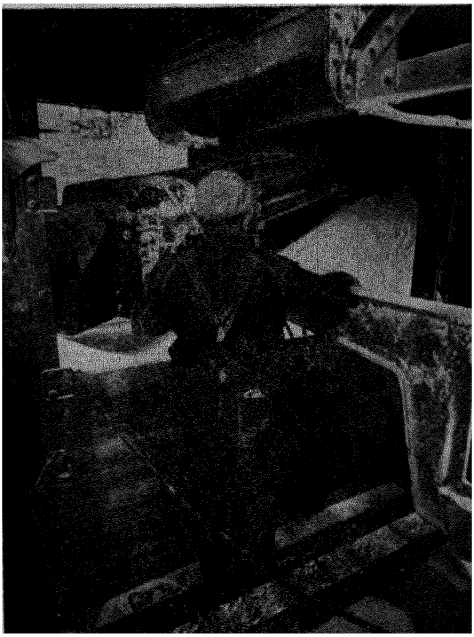
If it is desired to make a biological model of the blood vessels in a freshly killed cat, quick-drying liquid plastic is injected into the tissue selected. The cat is then placed in concentrated potassium hydroxide; all animal matter dissolves, and the hardened plastic keeps the mold of the tissues into which it was injected.

Sodium Carbonate (Soda Ash). Most of the world's supply of sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) is made by a process that Ernest Solvay (1838–1922), a Belgium chemist, patented in 1864. Soda ash, as sodium carbonate is called commercially, is the most important heavy basic chemical. Essentially, it is produced from sodium hydroxide and carbon dioxide.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

It is easier to handle than sodium hydroxide since it is not so corrosive. Also, as soon as it meets a strong acid, it loses carbon dioxide gas.

The Solvay Process. Solvay's raw materials were four simple common substances, water, salt, carbon dioxide, and ammonia. The steps in the process are essentially as follows: (1) Ammonia and carbon dioxide are bubbled into a saturated solution of brine. Both gases first join with water and then join together.



Courtesy of The Mathieson Alkali Works, Inc.

FIG. 22-2.—This workman is loading a box car with soda ash. Industrial chemicals are manufactured in large tonnages.

$$\begin{array}{llll} H_2O + CO_2 & \rightleftarrows & H_2CO_3 & \\ NH_3 + H_2O & \rightleftarrows & NH_4OH & \\ \hline NH_4OH + HHCO_3 & \rightleftarrows & \underset{\text{ammonium hydrogen carbonate}}{NH_4HCO_3} & + H_2O \end{array}$$

(2) When the solution containing the ammonium hydrogen carbonate acts with an excess of common salt under the proper conditions, the moderately soluble sodium hydrogen carbonate ($NaHCO_3$) precipitates.

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3\downarrow + NH_4Cl$$

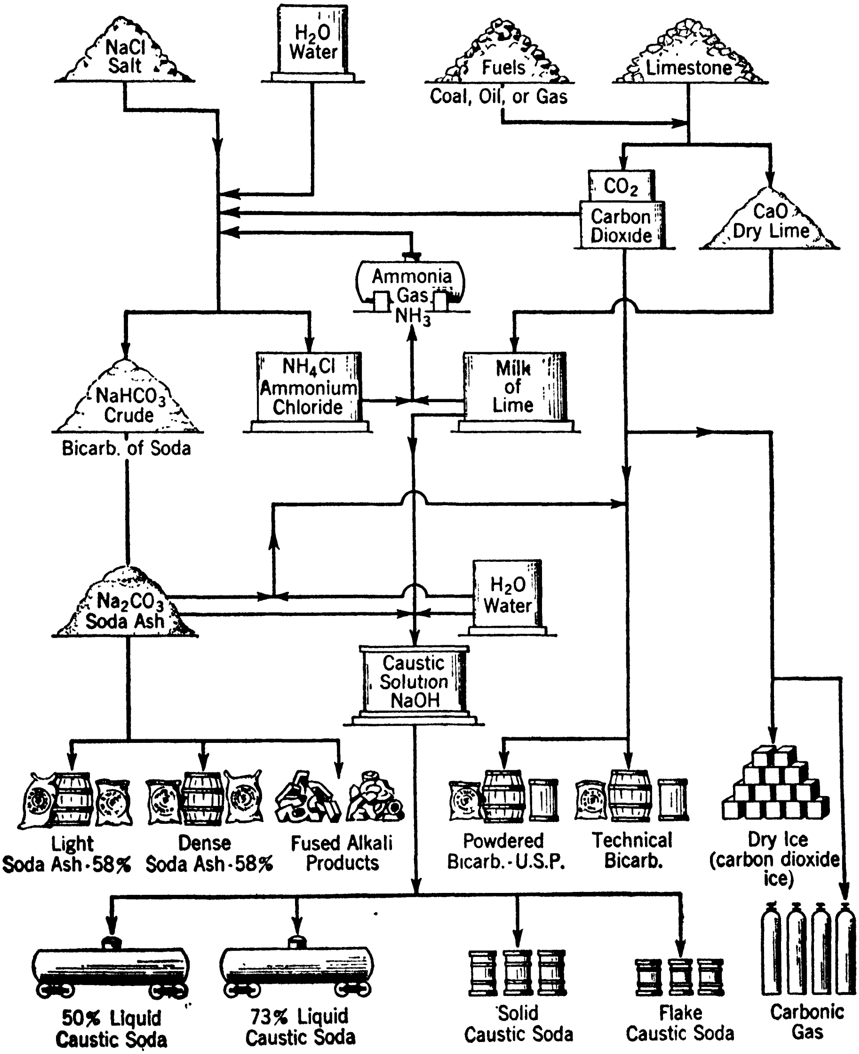
(3) Most of the dried sodium hydrogen carbonate is heated, driving off carbon dioxide and making anhydrous sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\uparrow$$

The ammonia in this process is far more expensive than the sodium compounds; therefore, the ammonium chloride is recovered by evaporation. Then limestone is heated to lime and carbon dioxide, and the lime is slaked to form calcium hydroxide (see page 382). The ammonium compound is then treated with this cheap basic material, freeing ammonia gas for use once more.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3\uparrow + 2H_2O$$

As has been said, the raw materials for the Solvay process are water, salt, carbon dioxide, limestone, and a little ammonia to make up for some loss. The products are either sodium hydrogen carbonate or sodium



Courtesy of The Mathieson Alkali Works, Inc.

FIG. 22-3.—Flow chart of ammonia soda operations.

carbonate, chiefly the second, and a by-product, calcium chloride. Little use has been found for the calcium chloride aside from moistening gravel roads and thus laying the dust. (See Fig. 22-3.)

The Mild Soda. The "baking soda" on the pantry shelf at home is sodium hydrogen carbonate ($NaHCO_3$), or commonly ***bicarbonate of soda.*** This white powder dissolves moderately well in water. Among its household uses are as a relief for indigestion; with cream of tartar, as a leavening agent for making cakes; with sour milk, as a leavening agent for biscuits or gingerbread; and, with aluminum, as a mild alkali for cleaning silverware. This is the sodium compound which is used in the soda-acid type of fire extinguisher (see page 74), in effervescent tablets, and in baking powders (see Appendix). All these uses are similar in chemical action. The sodium hydrogen carbonate neutralizes acids and releases carbon dioxide. A simple example is

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2\uparrow$$

The Strong Soda. The powdered white material, sodium carbonate (Na_2CO_3, soda ash), is the usual form of this compound in commerce. It is easily dissolved in water. For household use, however, the compound is allowed to form washing soda crystals ($Na_2CO_3 \cdot 10H_2O$), or ***sal soda*** (the soda from salt). These crystals lose water easily and become a crumbly powder if the package is left open to the air.

Sodium carbonate is used for washing greasy pots and pans, for cleaning automobile cooling systems, and for softening water, a laundry aid. It is also used in many scouring powders. Among its most important uses in the industrial world are in the making of glass, soap, and other chemicals; in the neutralizing of acids; and in the treatment of textiles.

A relatively small amount of sodium carbonate is made from natural deposits of the dry material in Owens Lake and Searles Lake in California.

The sodium hydrogen carbonate forms the normal carbonate on heating, driving off water and carbon dioxide. This chemical change was mentioned as a part of the Solvay process.

The carbonate can be changed into the hydrogen carbonate by reversing the process. A solution of sodium carbonate is treated with an excess of carbon dioxide. Sodium hydrogen carbonate forms

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

QUESTIONS

1. Rank the four most important basic heavy chemicals in order of their importance.

2. Give two commercial names for sodium hydroxide.

3. Name two by-products of the preparation of sodium hydroxide by the electrolysis of common salt solution.

4. Tell how sodium hydroxide is obtained in solid form in its preparation by the chemical method.

5. Lye is sometimes shipped as a concentrated solution and sometimes as a solid. State one advantage and one disadvantage of each method of shipping.

6. Write formula equations for the reactions of (*a*) sodium hydroxide and (*b*) potassium hydroxide on (1) carbonic acid; (2) nitric acid; (3) acetic acid; (4) sulfuric acid (eight different equations).

7. Compare sodium hydroxide with potassium hydroxide, giving two points of likeness and two of difference.

8. Write a set of six equations to represent the Solvay process, including recovery of ammonia.

9. On a weight basis, which is the more effective alkali, sodium hydroxide or potassium hydroxide? HINT: Which has the larger percentage of hydroxide?

10. Compare Na_2CO_3 with $NaHCO_3$ in respect to scientific name, common name, and two uses.

Lime from Limestone. The cheapest of the basic heavy chemicals is calcium oxide, or lime. Its story starts with a limestone quarry. Limestone is an abundant material among the surface rocks of the earth. Chemically, it is impure calcium carbonate ($CaCO_3$) mixed with sand, clay, iron oxide, or other impurities. Probably at some earlier era it was formed by the deposits of shells or skeletons of sea creatures. The famous white cliffs of Dover, England, were certainly formed in this way, for when examined under a microscope the chalk fragments are seen to be composed of microscopic shells. We believe that inland mountains, thousands of feet thick, which are composed chiefly of limestone, were at one time likewise under the sea. Support for this view comes from the fact that they frequently contain fossils and that almost all sea shells and skeletons of marine creatures are comprised of calcium carbonate. Coral and pearls are also made of this material.

Fine crystals of calcium carbonate in minerals are called calcite. A transparent form, or Iceland spar, is almost pure. Marble is a form of limestone that has had a more rugged geological history and has been partly recrystallized. It will take a high polish and is useful for ornamental building stone and statutes.

When a limestone quarry yields building stones, as many do in Indiana and elsewhere, many unimportant chunks of rock are taken out along with the well-cut stones. These chunks may be sent to the limekiln to be "burned." Actually, in the strict sense, they are heated rather than burned, but the term "lime burning" has been used for centuries.

Some sort of kiln (pronounced "kil") is provided. A simple one is made like a tall vertical chimney. When the fire from the fuel heats the contents to about 1000°C, the limestone decomposes.

$$CaCO_3 \rightleftarrows CaO + CO_2\uparrow$$

At this temperature the chemical action is reversible, but the carbon dioxide has no chance to reunite with the lime, for it is forced away by a strong draft. The white, crumbly lime is removed from time to time at the bottom of the kiln. The poorer grades may contain the ashes from the fuel, but not if the kiln is properly designed. (See Fig. 22-4.)

Another type of kiln is a horizontal revolving tube, sloping slightly toward the exit end. Crushed limestone is fed into a hopper at one end, and fire enters at the center of the other. The limestone descending into the kiln meets the fire ascending. The lime is removed at the lowest spot. (See Fig. 22-5.)

Chunks of limestone are also used for building roads. Ground limestone is spread on the soil to counteract soil acids. Chunks of limestone are used for flux in furnaces where metals are refined. The limestone acts together with sand at the high temperature in the furnace to form a liquid that absorbs many worthless impurities.

$$\underset{\text{limestone}}{CaCO_3} + \underset{\text{sand}}{SiO_2} \rightarrow \underset{\text{calcium silicate}}{CaSiO_3} + CO_2\uparrow$$

For the same reason furnaces are sometimes lined with dolomite ($CaCO_3 \cdot MgCO_3$).

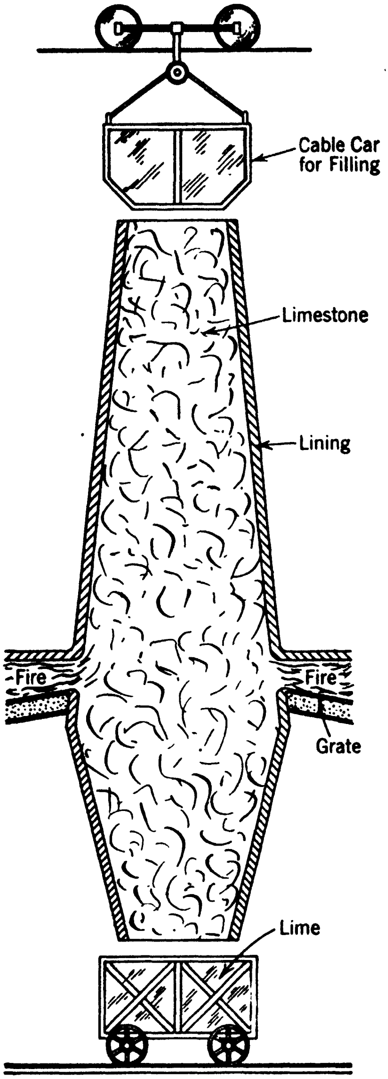
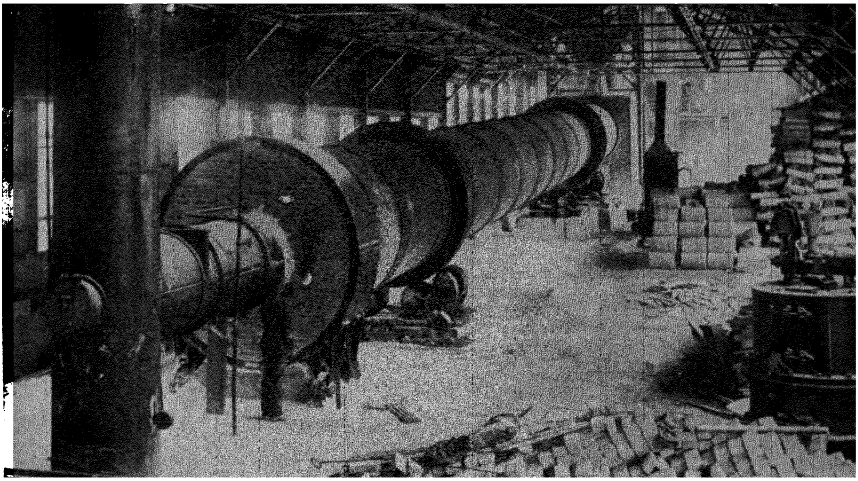


FIG. 22-4.—Lime to make wall plaster for the earliest houses in America was made in kilns that resemble this one. Limestone was fed into the top of the chimney. Huge fires roared up the stack, heating the limestone. The finished, or "burned," lime was taken from the bottom.

Limestone Caves. Just as sodium carbonate can be converted into sodium hydrogen carbonate by an excess of carbon dioxide solution, so calcium carbonate can be changed into calcium hydrogen carbonate by water and carbon dioxide.

$$\underset{\text{insoluble}}{CaCO_3} + H_2CO_3 \rightarrow \underset{\text{slightly soluble}}{Ca(HCO_3)_2}$$

Since calcium hydrogen carbonate is moderately soluble in water, soil water that contains carbon dioxide will dissolve limestone slowly. The effect on the water is to make it "hard" (see page 606). The effect on the rock is to leave an empty space. Many large caves have been formed in this way. Mammoth Cave in Kentucky, Luray Caverns in Virginia, and the Carlsbad Caverns in New Mexico are all examples of limestone caves that have been formed by dissolving limestone.



Courtesy of Vermont Marble Company

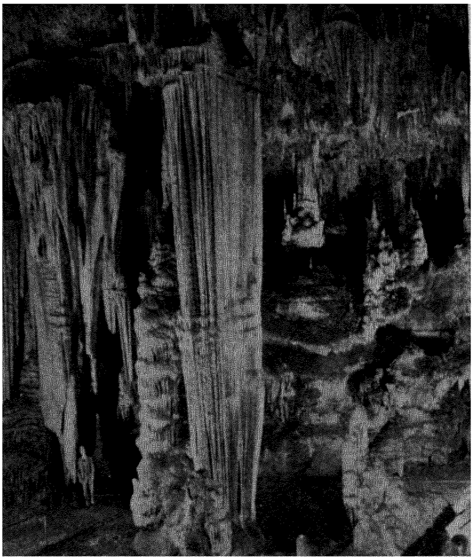
FIG. 22-5.—A horizontal rotating kiln illustrates the counter-current principle. The flames go up while the limestone tumbles down slowly. Notice the hopper for feeding limestone, the pipe to supply oil for the fire, the duct for air, the workman examining the interior of the kiln through a peep hole, and the bricks (foreground) used for relining.

As in the case of the corresponding sodium compounds, the carbonate–hydrogen carbonate change is reversible. If moisture and carbon dioxide are lost, the insoluble carbonate of calcium forms once more.

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

A drop of water hanging from a projection in the roof of a cave evaporates and loses some carbon dioxide. A tiny bit of limestone deposits. The next drop falls to the floor. Very gradually from the roof of the cave an icicle-like ***stalactite*** is built, and from the floor of the cave a similar but pinnacle-like growth called a ***stalagmite*** is formed. Several centuries later, these may unite to form a column to support the cave roof. (See Fig. 22-6.)

We Make Chalk. In spite of the fact that so many different forms of calcium carbonate are available in nature (see Fig. 22-7), artificially made calcium carbonate (whiting, or precipitated chalk), finds many uses, competing with finely ground marble. It is made by the action of sodium carbonate solution on calcium chloride solution. The precipitated chalk formed is filtered from the salt water (also formed), washed, and dried.



Courtesy of Luray Caverns Corporation and Virginia Conservation Commission

FIG. 22-6.—Grotesque limestone formations within Luray Caverns, Virginia, dwarf a man observer.

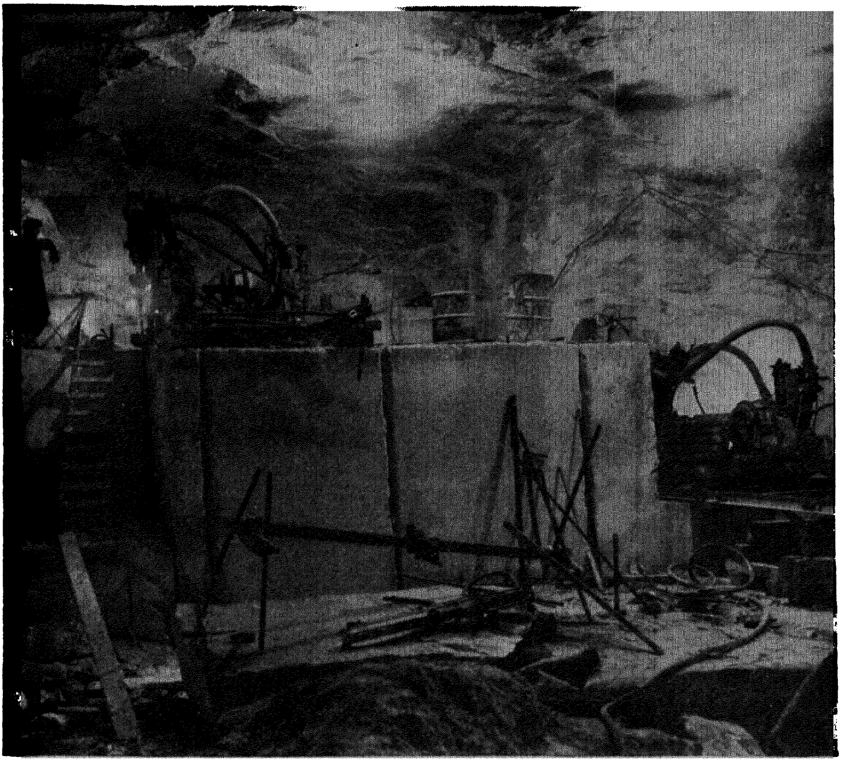
$$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3 \downarrow$$

Mixed with linseed oil, it is called putty. It is used in some paints and is the scouring agent in most tooth-powder mixtures. Chemically, it is simply rather pure limestone.

Calcium Oxide (CaO, Quicklime). The ancient term "quick" means "live." Live lime, or quicklime, is thirsty. When its thirst is quenched, or slaked (not slacked), the substance acts very much alive—moving, swelling, and crumbling. In fact, it becomes so hot that it may cause fires.

$$CaO + H_2O \rightarrow Ca(OH)_2 \text{ (+ heat)}$$

The water-slaked lime, calcium hydroxide [$Ca(OH)_2$], is a white paste if prepared without much regard to the amount of water being added;



Courtesy of Vermont Marble Company

FIG. 22-7.—Power-driven saws cut huge blocks of marble in this Vermont quarry. From such sources, we obtain stones for the architect's design or for the sculptor's chisel.

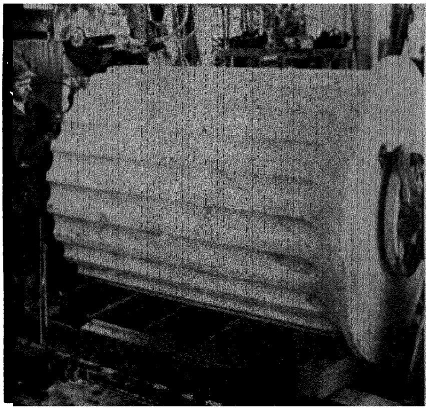
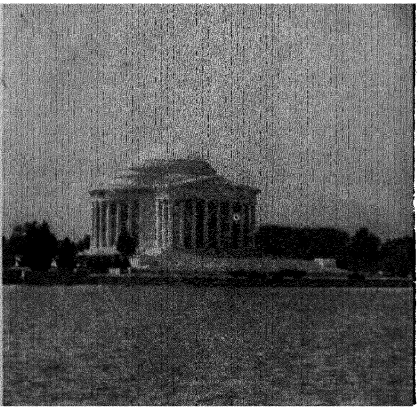


FIG. 22-8.—Here a huge fluted marble column is being made from a block of marble. Notice the power-driven abrasive wheel used to cut the flutings.



Courtesy of Vermont Marble Company

FIG. 22-9.—One of the most stately buildings in the world is made from white marble. Can you identify this building?

with the right amount of water it is a white powder. In the latter form slaked lime is supplied to builders for making plaster walls and mortar. Mortar is made with one part of slaked lime and three or four parts of sand, with sufficient water to make a workable paste. Cement is used more than lime mortar today, but most brick walls of older structures were laid up with lime mortar. Lime mortar becomes hard owing to drying and absorption of carbon dioxide.

Courtesy of Buffalo Museum of Science

FIG. 22-10.—Indiana limestone, chiefly calcium carbonate, is used extensively as a building stone. Visitors to Buffalo are always welcomed at the Buffalo Museum of Science in Humboldt Park. This structure has a limestone exterior.

Slaked lime is used for taking hair off hides in tanneries; extensively for sweetening acid soils for crops; and making paper, sodium hydroxide, some sorts of bricks, and bleaching powder.

Limewater. If a suspension of calcium hydroxide in water, milk of lime, is filtered, a clear solution comes through the filter paper. This is called ***limewater,*** and it is used in medicine. Although the calcium hydroxide present in this solution is ionized and is a source of hydroxyl (OH^-) ions, very little calcium hydroxide dissolves and the solution is only a rather mild source of hydroxyl ions.

When the stopper is left off a limewater bottle, a crust forms on top of the solution. The carbon dioxide of the air is absorbed and forms calcium carbonate, a milky precipitate. This chemical action is the well-known laboratory test for the presence of carbon dioxide.

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

Tom Sawyer's Fence. In the famous story, *Tom Sawyer*, by Mark Twain, Tom had to whitewash a fence; or, rather, he had to get a fence whitewashed. Let us assume that we, like Tom, have induced our friends to do the work of whitewashing for us so that we can sit back and consider the composition of whitewash. Whitewash is primarily a suspension of calcium hydroxide with some gluing material. When air acts on the calcium hydroxide, forming insoluble calcium carbonate, the action is described by the preceding equation. This action is deliberate; that is, it takes place slowly. In a thin coat, such as that on Tom's fence, the action is practically completed within a few days. In an ordinary brick wall, however, 25 years may be needed, and in the walls of some plastered houses almost 300 years may elapse before all the action in the plaster is complete. Of course, the setting action proceeds rapidly at first, then more and more slowly. Much wall plaster is slaked lime mixed with sand and cheap fibers and water. The finish wall plaster, the outer layer, is made from gypsum ($CaSO_4 \cdot 2H_2O$) and is usually applied as plaster of Paris ($2CaSO_4 \cdot 1H_2O$).

QUESTIONS

11. Name four natural materials that are chiefly calcium carbonate.

12. State two chemical actions that are common to all forms of calcium carbonate.

13. Write formula equations for (*a*) slaking lime; (*b*) setting of lime plaster; (*c*) formation of limestone caves; (*d*) formation of stalactites in a cave; (*e*) formation of slag from silica in a dolomite-lined furnace.

14. When lime is kept open to the air, it "air slakes." Of what two compounds is it then composed?

15. What use is made of precipitated chalk in (*a*) tooth-paste manufacturing; (*b*) papermaking; (*c*) paint manufacturing; (*d*) setting glass in window sash?

16. Copy and complete the following table for forms of calcium carbonate (do not duplicate any common name, *and do not write in this book*):

Common name	Formula	Use
Limestone	—	—
—	—	Building stone
—	$CaCO_3 \cdot MgCO_3$	—
Lime	—	—
—	$Ca(OH)_2$	—
—	—	Testing for CO_2

17. What is the value of putting slaked lime into a compost heap?

18. Why should ammonium sulfate fertilizer not be added to a field that has been treated recently with slaked lime?

19. Explain in what sense this statement is true: Most houses are torn down before the plaster is dry.

20. Calcium chloride is approximately 36 per cent calcium. What weight of anhydrous calcium chloride must be decomposed by electrolysis in order to produce $\begin{Bmatrix}3.6\\7.2\end{Bmatrix}$ pounds of metallic calcium?

Ammonia. Strictly speaking, ammonia is not considered a heavy basic chemical. In fact, it is a gas as we usually meet it, although sometimes it comes to the market as a liquefied gas, or in a water solution. Ammonia is included here, however, because, like hydroxides, carbonates, and other bases, it neutralizes acids. Ammonia may have received its name from the oasis of Jupiter Ammon, at Siwa in the Sahara Desert, where it arose from decomposing camel dung.

Sources of Ammonia. The odor of ammonia may be noticed near a manure pile or from a bottle of household ammonia. Ammonia gas (NH_3) forms from the decay of nitrogen-containing organic matter. Nitrogen-containing compounds found in living organisms are called proteins, and their decay produces ammonia.

Proteins formed in plants ages ago are a modern commercial source of ammonia. When these plants were changed to coal, some of the protein remained in the coal. A ton of soft coal, heated in a modern by-product coke oven, may produce as much as 6.5 lb of ammonia. After purification, the ammonia is run into sulfuric acid. Here it unites with protons from the acid until a mush of ammonium sulfate crystals is formed.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

These are whirled dry in a centrifuge basket, making them ready to be sold as fertilizer to the grower of cotton and other crops.

Synthetic Ammonia. Ammonia is such a useful and necessary substance that many attempts have been made to synthesize it from its two elements. The chemical equation for the synthesis looks simple on paper.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The practical difficulty to be overcome in order to produce more than a slight trace of ammonia is to make the lazy nitrogen join with hydrogen. In general, we have learned that substances become more active chemically when they are heated. The idea then presents itself that a warmed mixture of nitrogen and hydrogen in volume proportions of 1 to 3 might give a satisfactory yield of ammonia. Such, however, is not the case. Study shows two reasons for this. (1) When ammonia is formed, heat is liberated. Raising the temperature, therefore, would hinder the formation of ammonia. (2) At a raised temperature, ammonia decomposes easily. This may be predicted from the first point.

$$2NH_3 \rightarrow N_2 + 3H_2$$

We are dealing with an equilibrium, or reversible, chemical action—one that does not tend to go to completion by itself in the desired direction.

An increase of pressure is the next obvious aid, for four volumes of mixed elementary gases change to two volumes of ammonia. Experiments show that high pressure is indeed a help in producing ammonia. From laboratory experiments we learn that, from a 3 to 1 mixture of hydrogen and nitrogen at a certain temperature and at the pressure of the air, 15.3 per cent ammonia is formed; at 10 times air pressure, 50.66 per cent; at 100 times air pressure, 81.54 per cent; and, at 1000 times air pressure, 98.29 per cent.

These high values are obtained only after waiting for the equilibrium to establish itself. A successful commercial process must be both rapid and continuous. To take care of this lag we now call in our third reserve, the catalyst. A catalyst is selected that hastens most the establishment of the equilibrium at the conditions of temperature and pressure chosen.

The Haber Process. The Haber process, developed in Germany in 1912, is the fundamental process for making ammonia from the elements. Many variations are used, but all are based on Haber's synthesis. The development and improvement of this process were problems that were attacked from two angles, (1) the manufacture of the gases hydrogen and nitrogen and (2) the uniting of the gases to form ammonia. For this process, a method of converting a mixture of nitrogen and hydrogen into ammonia was developed by Fritz Haber (1868–1934); and the successful production of the raw materials, nitrogen and hydrogen, was developed by Karl Bosch (1874–1940).

1. To produce the nitrogen and hydrogen, steam is passed over hot coke to form a mixture of hydrogen and carbon monoxide, called water gas (see page 527).

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

This gas mixture in turn is mixed with producer gas which is chiefly nitrogen and carbon monoxide. These three gases are further mixed with steam and passed over a catalyst to change the carbon monoxide and steam into hydrogen and carbon dioxide.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The carbon dioxide is removed from the mixture by forcing it into water under pressure, and the last traces are scrubbed out by washing with sodium hydroxide solution. A mixture containing hydrogen and nitrogen remains. The nitrogen comes originally from the air and the hydrogen from water.

2. The mixture of nitrogen and hydrogen is run over a suitable second catalyst at proper temperature and pressure, forming a small amount of ammonia. A minute later the ammonia is removed by liquefying it. The unchanged elementary gases are recirculated to pass once more over the catalyst.

The American Process. The Fixed Nitrogen Laboratory of the U.S. Department of Agriculture at Washington, D.C., recommends iron oxide promoted by 1 per cent potassium oxide and 3 per cent aluminum oxide, prepared in a special way, as a catalyst for the making of ammonia. Other catalysts are used, but iron oxide is the principal material.

In the American process air is mixed with an excess of hydrogen and the mixture burned. The water formed is condensed out, leaving a mixture of nitrogen and hydrogen. This process uses a much higher pressure (900 to 2000 times air pressure) than that of the original Haber process. The hydrogen may come from the electrolysis of water and the nitrogen from boiling liquid air.

After the gases are passed over the catalyst, the pressure is reduced somewhat and the mixture cooled. Fairly pure ammonia separates out as an anhydrous liquid. It is ammonia in liquid form, without water.

The Cyanamide Process. The method of making ammonia at the famous Muscle Shoals plant on the Tennessee River in Albama starts with lime and coke in an electrically heated furnace. Calcium carbide is produced.

$$\underset{\text{lime}}{CaO} + \underset{\text{coke}}{3C} \rightarrow \underset{\text{calcium carbide}}{CaC_2} + CO\uparrow \tag{1}$$

The calcium carbide is then placed in an electrically heated tank and supplied with nitrogen from boiling liquid air. The lazy nitrogen is captured in a compound called calcium cyanamide. The pure compound is a colorless substance, but it is blackened by the carbon that remains mixed with it.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \tag{2}$$

The cyanamide may be used directly on the soil as a fertilizer, but it can be made to produce cyanides when heated with coke and salt.

$$\underset{\text{salt}}{2NaCl} + \underset{\text{coke}}{C} + \underset{\substack{\text{calcium}\\ \text{cyanamide}}}{CaCN_2} \rightarrow \underset{\substack{\text{calcium}\\ \text{chloride}}}{CaCl_2} + \underset{\substack{\text{sodium}\\ \text{cyanide}}}{2NaCN}$$

Most of the cyanamide, however, is treated with steam under pressure to form ammonia.

$$\underset{\text{cyanamide}}{CaCN_2} + \underset{\text{steam}}{3H_2O} \rightarrow \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\text{ammonia}}{2NH_3} \tag{3}$$

The ammonia in turn produces solid fertilizer when passed into sulfuric or phosphoric acid (see page 290). The numbered equations (1), (2), and (3) show the chemical changes in the ***cyanamide process.***

Description of Ammonia. Once a person with a normal sense of smell detects the pungent penetrating odor of ammonia, he is able to recognize it again. Such a definite odor is said to be characteristic or identifying. Small amounts of ammonia are detected also by the ability of the gas to turn moist pink litmus paper blue.

Ammonia is colorless, either as a gas or a liquid. One liter of the gas weighs 0.76 g, about one-half the weight of air. Very large amounts of ammonia dissolve in a relatively small amount of water, 500 volumes to 1.

To show this experimentally let us fill a ***round-bottomed*** flask with ammonia gas and close the flask by a two-holed stopper that has a medicine dropper full of water through one hole and a long glass tube tapered at the upper end through the other. (See Fig. 22-11.) The flask is now inverted and supported in such a fashion that the outer end of the glass tube dips into a vessel of water to which phenolphthalein has been added. The water is squirted out from the medicine dropper. Action follows immediately. The small amount of water injected thus into the flask dissolves so much ammonia that the pressure within the flask is suddenly decreased. The pressure of the air on the surface of the open vessel of water into which the glass tube extends forces the liquid up the tube, making a miniature geyser or fountain. The phenolphthalein turns bright pink when it reaches the ammonium hydroxide formed in the flask.

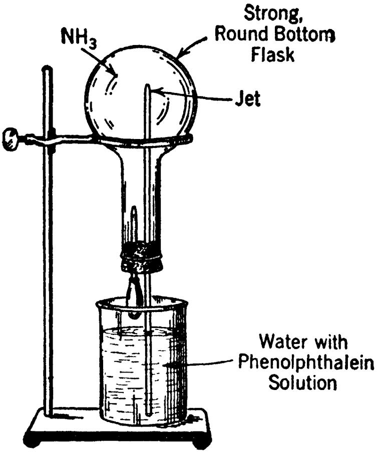


FIG. 22-11.—The ammonia fountain experiment illustrates the extreme solubility of ammonia in water. A similar experiment can be performed with hydrogen chloride or sulfur dioxide.

Ammonia gas can be changed into a liquid rather simply by pressure. The liquid boils again when the pressure is released, taking in heat. The boiling point of ammonia at atmospheric pressure is −33.5°C. Boiling and condensing ammonia is the cycle used in the refrigerating system for ice making, cooling meat counters in stores, cooling drinking water in large buildings, and keeping entire buildings (food-storage warehouses) cold.

How We Make Ammonia in the Laboratory. The commercial methods of making ammonia need too much apparatus to be used in most laboratories. We can obtain ammonia easily by boiling household ammonia. The dissolved gas leaves the solution when the temperature is raised. Water-vapor molecules also leave with the ammonia gas, and these are separated by some material that absorbs them but that does not act on the ammonia. For this purpose, anhydrous calcium sulfate, commercial Drierite, is one suitable material (see Fig. 22-12); soda-lime mixture (NaOH and CaO), another.

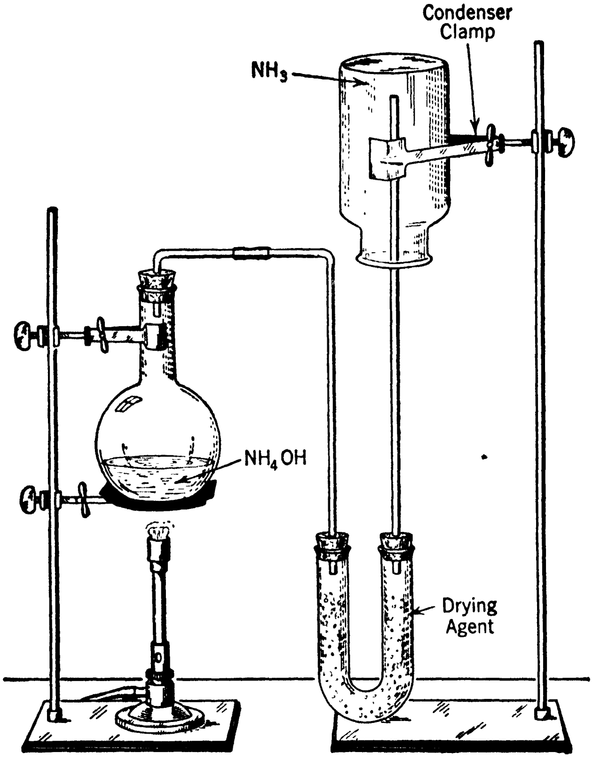


FIG. 22-12.—Ammonium hydroxide decomposes into ammonia gas and water when heated. If the vapors are dried, ammonia alone remains.

Larger amounts of ammonia may be produced easily by warming an ammonium compound mixed with an alkali in a flask as in Fig. 22-13. The alkali neutralizes the acid with which the ammonia has joined to form the ammonium compound, leaving the free gas. Examples are

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3\uparrow + H_2O$$
$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NH_3\uparrow + 2H_2O$$

All ammonium compounds release ammonia gas when they are heated with an alkali. The ammonia gas can be identified by its odor; therefore, heating with an alkali is a means of testing a substance for the presence of the ammonium ion (NH_4^+).

Chemical Actions of Ammonia. Ammonia gas dissolved in water contains some ammonium hydroxide. It acts alkaline; ammonia is a base.

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$$

As soon as the hydroxyl ions are all combined with grease, as they might be, for example, when household ammonia is used for washing windows, more ammonia acts with the water to produce additional ammonium hydroxide. We can think of ammonium hydroxide as a good source of hydroxyl ions (OH^-) and at the same time as a mild base.

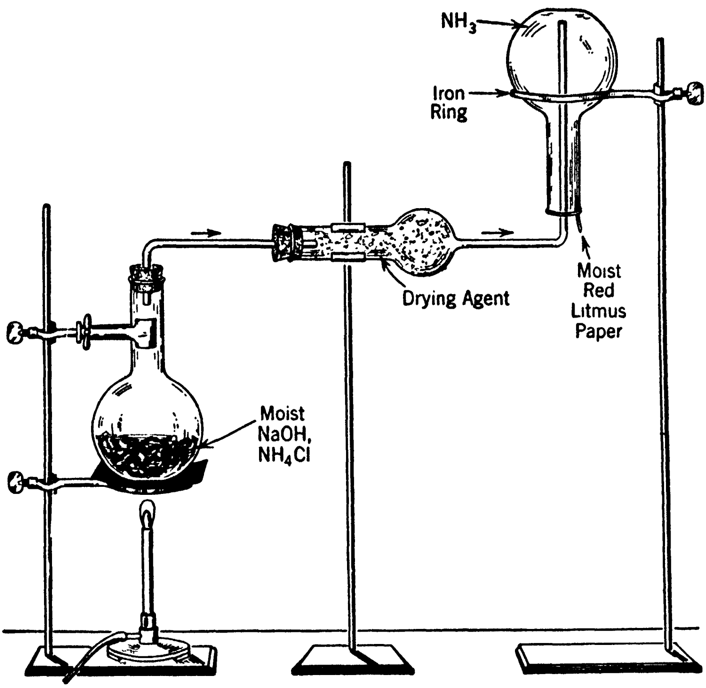


FIG. 22-13.—This is the apparatus for preparing and collecting a flask of dry ammonia gas. Moisture from the generator is retained in the tube of drying agent.

Of course, ammonia acts with acids, also; that is, it annexes protons easily. For example,

$$\underset{\text{ammonia}}{NH_3} + \underset{\substack{\text{phosphoric}\\\text{acid}}}{HHHPO_4} \rightarrow \underset{\substack{\text{ammonium}\\\text{dihydrogen}\\\text{phosphate}}}{NH_4HHPO_4}$$

Many metal ions become ammoniated readily. Silver (Ag^+), copper (Cu^{++}), and mercury (Hg^{++}) are examples. When ammonia water is added to a solution of copper sulfate, a beautiful deep-blue color of the tetrammine copper ion $[Cu(NH_3)_4]^{++}$ is formed.

$$\underset{\text{light blue}}{[Cu(H_2O)_4]^{++}} + 4NH_3 \rightarrow \underset{\text{rich deep blue}}{[Cu(NH_3)_4]^{++}} + 4H_2O$$

Ammonia is oxidized to nitric acid (see page 362) with a heated platinum wire screen for a catalyst.

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

In fact, when pure oxygen is bubbled through a solution of concentrated ammonia, the mixture of gases emitted will explode when ignited.

The ammonia can be easily decomposed into its elements at moderate temperature by using the proper catalyst.

$$2NH_3 \rightarrow 3H_2 + N_2$$

Hot magnesium will act with ammonia, releasing hydrogen,

$$2NH_3 + 3Mg \rightarrow Mg_3N_2 + 3H_2$$

but a good oxidizing agent, heated copper oxide for example, removes the hydrogen, freeing nitrogen.

$$2NH_3 + 3CuO \rightarrow 3H_2O + 3Cu + N_2$$

Ammonium Compounds. Most of the ammonium compounds are white, resembling salt or sugar in appearance. Exceptions are those which are colored because of a colored negative ion. Ammonium dichromate [$(NH_4)_2Cr_2O_7$], for example, a strong oxidizing agent, is colored a brilliant orange. Ammonium salts also decompose rather easily when heated, and in most cases the mixed vapors above the heated materials cool and form the ammonium compound again.

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

All ammonium salts dissolve well in water. These solutions have the ammonium ion (NH_4^+) in them and are acidic. A price list of the important chemicals on the drug and chemical market lists 14 ammonium compounds. Four of the more common are listed in the table below.

FOUR COMMON AMMONIUM COMPOUNDS

Name	Formula	Uses
Ammonium carbonate	$(NH_4)_2CO_3$	In smelling salts
Ammonium chloride ("sal ammoniac")	NH_4Cl	In dry cells, as flux for soldering
Ammonium nitrate	NH_4NO_3	As fertilizer; in explosives and fireworks; to make "laughing gas"
Ammonium sulfate	$(NH_4)_2SO_4$	As fertilizer

SUMMARY

Sodium hydroxide, commercial lye, or caustic soda is prepared (1) by electrolysis of common salt in water and (2) by interaction of calcium hydroxide solution and sodium carbonate. Sodium hydroxide, a caustic substance, is corrosive to animal matter. It absorbs carbon dioxide, forming sodium carbonate. It is used in the manufacture of rayon, paper, and soap, for refining petroleum, and in the treatment of textiles.

Potassium hydroxide is similar to sodium hydroxide. Sodium carbonate, soda ash, sal soda, or washing soda (hydrated) is prepared by the Solvay process. The raw materials used in the Solvay process are salt, water, carbon dioxide, and ammonia. Sodium carbonate is used in the manufacture of soap, glass, and cleansing powders. It is a neutralizer for acids.

Sodium hydrogen carbonate, baking soda, or sodium bicarbonate is prepared by the Solvay process. It is used in baking powders, in cooking, in the soda-acid fire extinguisher, and as a medicine.

The natural forms of calcium carbonate are found widely distributed on the earth as limestone, marble, shells, calcite, and coral. Calcium carbonate neutralizes acids, forms lime when heated strongly, forms slag when heated with sand, and forms limestone caves by action of soil water (weak carbonic acid).

Precipitated chalk is prepared by putting solutions of calcium chloride and sodium carbonate together. The calcium carbonate precipitates. This insoluble compound is used to make putty and tooth powder.

Lime, or quicklime (CaO, calcium oxide), is prepared by heating limestone in a kiln. $CaCO_3 \rightarrow CaO + CO_2$. When slaked with water, lime evolves much heat and forms slaked lime, or calcium hydroxide. A suspension of slightly soluble calcium hydroxide in water, called milk of lime, is used in the manufacture of paper, in making bleach powder, in making mortar and plaster, and for sweetening the soil. The clear solution of calcium hydroxide, called limewater, is used to test for presence of CO_2 and in medicine.

Ammonia is formed naturally from the decay of proteins. It is a by-product of the destructive distillation of soft coal. It is manufactured by direct synthesis, by using the Haber method. $N_2 + 3H_2 \rightarrow 2NH_3$. Any strong alkali and any ammonium compound heated together produce ammonia. This is the common laboratory method for its preparation. It is also manufactured synthetically by the cyanamide process.

Ammonia is colorless, has a pungent odor, is very soluble in water, is easily liquefied, and is about three-fifths as dense as air. Ammonia water is a solution of ammonia in water. Some ammonium hydroxide forms in this solution. Ammonia adds to acids, forming ammonium compounds, and it adds to some ions, forming ammoniated complex ions. In the Ostwald synthesis, ammonia combines with oxygen in the presence of platinum catalyst to form nitric acid. When heated, ammonia decomposes into nitrogen and hydrogen.

Ammonium compounds decompose when heated, but the products of heating recombine in some cases. Ammonium compounds are used for fertilizers and for a variety of special purposes.

QUESTIONS

21. List three sources of ammonia.

22. How is ammonium chloride manufactured from ammonia? How is ammonia manufactured from ammonium chloride?

23. In the synthesis of ammonia from its elements, what three factors are controlled in order to increase the yield?

24. Write four equations for the Bosch-Haber process of producing ammonia, including preparation of the elementary gases.

25. Write three equations showing the synthesis of ammonia by the cyanamide process.

26. List five physical properties of ammonia.

27. In the ammonia-fountain experiment (page 389), a flat-bottomed flask, used by mistake, broke explosively. What was the cause of the accident?

28. Write formula equations for reactions between the following substances: (*a*) ammonium sulfate and sodium hydroxide; (*b*) ammonium chloride and potassium hydroxide; (*c*) ammonium phosphate and calcium hydroxide; (*d*) ammonium nitrate and lithium hydroxide.

29. State two uses for household ammonia.

30. Point out the importance of being able to manufacture ammonia synthetically.

31. Write formula equations for the decomposition of the following compounds when heat is applied: (*a*) ammonium chloride; (*b*) ammonium nitrate; (*c*) ammonia; (*d*) sodium nitrate; (*e*) ammonium nitrite.

32. What is the penetrating odor that comes from a bottle of smelling salts? Write an equation for the decomposition of the ammonium compound.

33. Compounds can be made in which a hydrogen atom of ammonia is substituted. One of these, hydroxylamine, has one atom of hydrogen in ammonia replaced by the hydroxyl radical. Write the formula of (*a*) hydroxylamine; (*b*) hydroxylammonium chloride; (*c*) hydroxylammonium sulfate.

MORE CHALLENGING QUESTIONS

34. Construct a model cell for the electrolysis of hot brine. Measure the electrical input and the amount of chemicals produced; calculate the efficiency of the cell.

35. Investigate the process for preparing mercerized cotton. Make some of this cotton. Compare it for tensile strength with unmercerized thread of the same size. Exhibit samples showing the cotton before and after treating.

36. Make a table, listing name, formula, and important uses of (*a*) caustic soda; (*b*) potash lye; (*c*) sal soda; (*d*) ammonia water; (*e*) bicarbonate of soda; (*f*) limestone; (*g*) quicklime; (*h*) milk of lime.

37. Clear crystalline calcite is notable for its property of double refraction. Using the geometrical method, determine the indices of refraction for a sample of crystalline calcite. Refer to a physics laboratory manual for the method.

38. Investigate the history of the Colosseum in Rome, Italy. For what purpose was the building used? Of what material was it made? What became of the stones taken from its walls after the building was abandoned?

UNIT FIVE - - - - - - - - - - - - CHAPTER XXIII

THE SILICATE INDUSTRIES

The silicate industries are those which make bricks, cement, pottery, chinaware, glass, and similar products. These materials are quite common in our homes and take an important part in everyday life. Silicate houses are made of bricks held together by concrete mortar; windows are glass made of transparent mixed silicates; sunrooms have special glass panes made of high-silica glass that let in the sun's health-promoting ultraviolet rays. The glass bricks that are sometimes set into the walls of buildings allow light to penetrate into an otherwise dark corner.

Walls of rooms are covered with lime plaster that contains much sand or silica in it. Basement walls and sidewalks are concrete—more silicates. Glass is used extensively within the house: mirrors, light bulbs, and baking dishes are all made of different sorts of glass. Ordinary chinaware is made from clay and glazed; clay is a complex silicate. Pottery for tableware and ornamental vases are also silicates. In the kitchen, the enamelware pots and pans have a silicate glass coating over steel, and a similar glazed surface is seen on bathroom furnishings. Altogether, these serviceable silicate industries provide practical and decorative articles that make life more enjoyable. (See Fig. 23-2.)

Courtesy of Owens-Corning Fiberglas Corporation

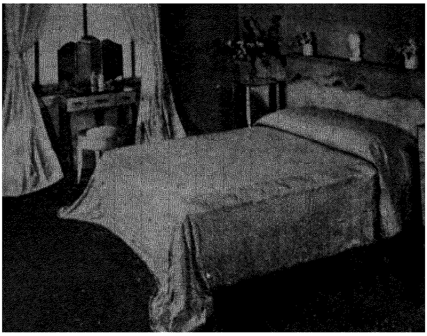
FIG. 23-1.—Winding fine filaments of glass onto a spool calls for workers with steady hands. Glass fibers are newcomers in the textile industry.

The use of silicates is one of the earliest arts of mankind. Clay pottery making is found among primitive peoples in many parts of the world.

New Terms

infusorial, or diatomaceous, earth
feldspar
kaolin
biscuit ware
glass
water glass

Writing on clay tablets was the ancient Assyrian way of keeping records. Glassmaking has a long and fascinating history. From our standpoint, it is interesting to see how each of these branches of the silicate industries has profited by the application of chemistry. One example will serve as illustration: Strong glass dishes have been available for many years, but such dishes broke in hot water. Recently, however, glass dishes have been made in which the housewife can even bake food in the oven. Furthermore, now we have glass dishes that will withstand an open flame on the stove top. Other developments, such as flexible glass, shatterproof glass, nonexpanding glass, tempered glass, and bullet-resisting glass, are either commonplace or are mentioned as coming developments.



Courtesy of Sterns Textile Manufacturing Company

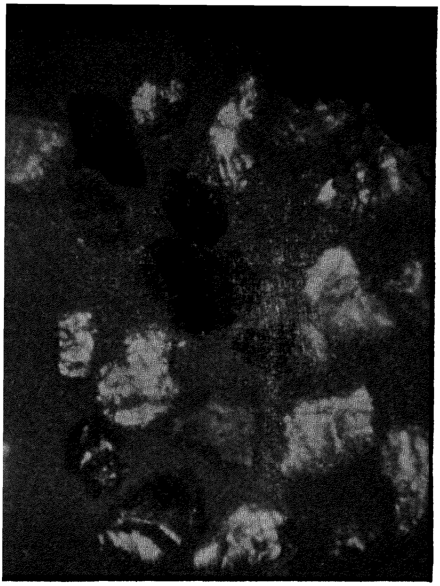
FIG. 23-2.—A lustrous bedspread shown here was made from spun-glass fibers. Careful examination of the picture will show other articles made of glass that help to make the room attractive.

Courtesy of Corning Glass Works

FIG. 23-3.—Borosilicate glass, such as Pyrex brand glassware, is one of the most rugged types of glass. Here we see a strong electrical insulator made of glass being inspected.

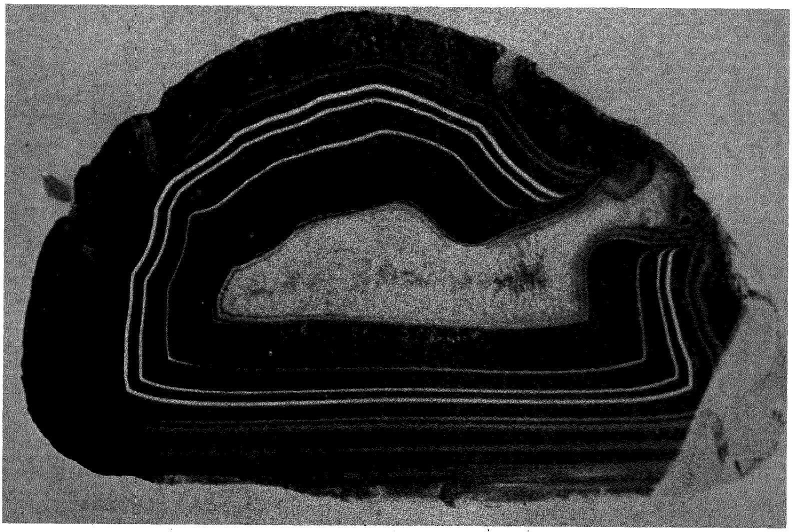
Silica. The basis of the silicate industries is silica. Chemically, the substance is silicon dioxide (SiO_2), an inactive, water-insoluble compound. This material is known to everyone, for it is the white sand or quartz rock found in nature. (See Fig. 23-4.) Brown sand is silica with impurities, usually iron oxide, in it. Mineral collectors recognize many sorts of quartz and impure silica. Among them are smoky quartz, pink rose quartz, and purple amethyst. These may be found in six-sided crystals, many beautiful specimens of which are available. Silica is the ***most common*** mineral in the earth's crust.

Semiprecious varieties of silica are agate, jasper, onyx, and opal as well as amethyst. These possess beautiful colorings and when polished are used for jewelry. (See Fig. 23-5.)



Courtesy of The Travelers Insurance Company

FIG. 23-4.—Small grains of sand, such as these shown here under polarized light and magnified fifty times, make "the pleasant land."

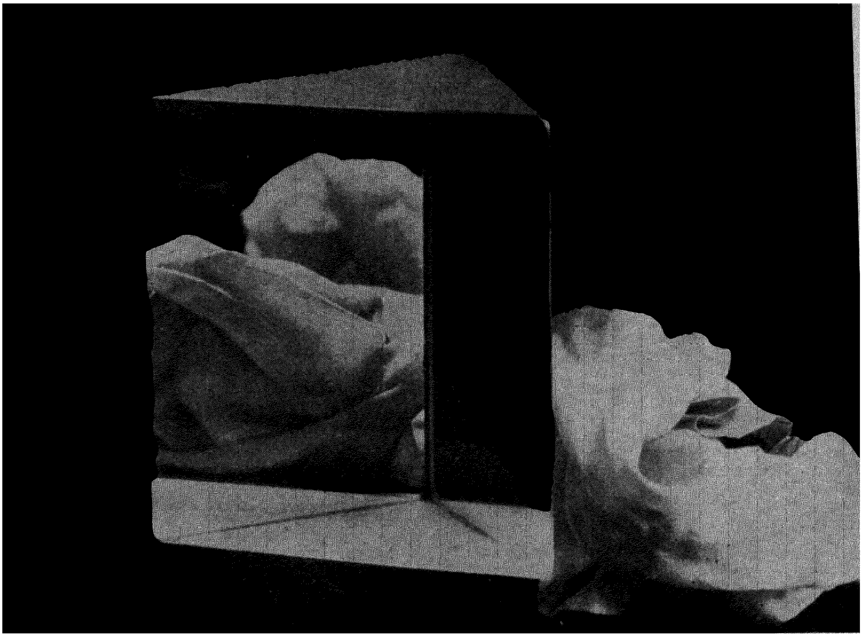


Courtesy of Journal of Chemical Education

FIG. 23-5.—This cut and polished opal shows bands and a mass of crystals in the center.

Indians and other people used much silica, especially quartz and flint, for chipping material from which to fashion stone knives, arrow points, drills, and other tools. Many museums, as well as individuals, have extensive collections of these interesting implements made of silica.

Sandstone is silica held together by some natural cementing material. When some deposits of extremely fine silica are examined under the microscope, it is apparent that they were once part of the skeletons of tiny creatures. This material is called ***infusorial*** or ***diatomaceous*** earth. It is used for adsorbing undesired colors from liquids and for a scouring agent. One type of silver-polish cream is a suspension of fine infusorial earth in a soapy gel.



Courtesy of General Electric Company

FIG. 23-6.—This 60-degree quartz prism shows almost perfect total reflection of the cloth on the right of it.

The element silicon is the second most abundant in the earth's crust. Some plants, straw and bamboo for example, have a small amount of the oxide, or silica.

Pure silica (SiO_2), called rock crystal or quartz, was once used extensively in ornamental work, on lighting fixtures in formal ballrooms for example. Today the chief use of high-quality quartz is in making optical instruments and laboratory vessels. (See Fig. 23-6.) Modern torches can readily melt this material at its rather high melting point, 1710°C, into a highly transparent glass that transmits ultraviolet light. Laboratory vessels made of fused quartz glass expand so little that they can be taken from the heart of a flame and plunged suddenly into cold water without cracking. Thin sheets of quartz crystal are used in controlling the frequencies of radio transmitters and other electronic devices.

Silica (silicon dioxide) is the oxide of a semimetal. Chemically, carbon dioxide resembles silicon dioxide in a general way, and carbonates have a similarity to silicates. Silica will not act easily with most acids or bases, but at high temperatures it joins oxides of metals.

$$Al_2O_3 + 3SiO_2 \rightarrow Al_2(SiO_3)_3$$

Hydrofluoric acid corrodes it slowly.

$$4HF + SiO_2 \rightarrow SiF_4\uparrow + 2H_2O$$

Silica is not attacked by strong oxidizing agents. Only very strong reducing agents will free the element silicon from its oxide. Carbon in an electric furnace will do this (see page 251), or powdered magnesium.

$$2Mg + SiO_2 \rightarrow 2MgO + Si$$

The uses of sand in building and road construction are well known to everyone. Good grades of white sand are used for making glass.

Soluble Silicates. When sand is heated with sodium carbonate or potassium carbonate, a chemical action occurs.

$$\underset{\text{sand}}{SiO_2} + \underset{\substack{\text{sodium carbonate}\\ \text{"soda ash"}}}{Na_2CO_3} \rightarrow \underset{\substack{\text{sodium metasilicate}\\ \text{"water glass"}}}{Na_2SiO_3} + CO_2\uparrow$$

The sodium metasilicate formed, after treatment with steam, dissolves readily in water. Prepared for the market, it is a sticky, thick sirup called ***water glass.*** Soluble silicates are used to glue corrugated cardboard boxes together, to repair broken glass and pottery, and at home to preserve eggs by filling the pores and thus preventing oxidation. Cloth treated with water-glass solution becomes fireproof. Sodium silicate solution is used as a water softener.

When an acid is added to water-glass solution, a thick jellylike paste forms. This material is silica with more or less water loosely attached to it. It is sometimes called silicic acid. When dried it is called silica gel, a porous solid that is extensively used in refrigeration and in adsorbing valuable vapors.

QUESTIONS

1. List 10 uses for glass.
2. List five products of silicate industries that are used at home.
3. What difference in composition distinguishes pure quartz from amethyst?

4. What properties of flint caused primitive people to use it for making tools and weapons?

5. What advantage has a windowpane of pure silica over one of common quartz? What disadvantage?

6. Write formula equations for three different chemical reactions, each involving silica.

7. What percentage of clay ($H_4Al_2Si_2O_9$) is silica?

8. Write an equation to represent (*a*) the action of hydrochloric acid on sodium silicate solution; (*b*) the effect of strongly heating the silica-containing product of reaction (*a*).

9. How can water glass be used so that money is saved on the family grocery bill?

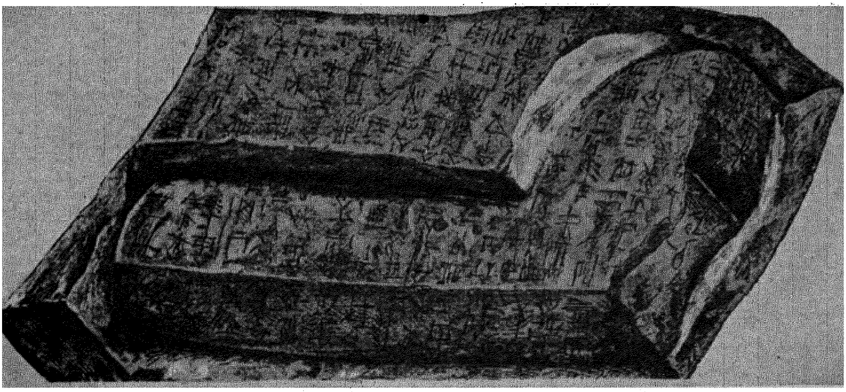
10. Write a formula equation for the action between (*a*) sodium hydroxide and silica; (*b*) potassium carbonate and silica; (*c*) calcium carbonate and silica; (*d*) aluminum oxide and silica.

Common Clay. Ordinary clay started as a hard rock called **feldspar** ($KAlSi_3O_8$). Feldspar can be considered a compound made of potassium, aluminum, and silicon oxides ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$). Exposed to the weather, feldspar decays by the action of water and carbon dioxide, permitting its potassium oxide to become available for plant growth. The resulting compound is clay ($H_4Al_2Si_2O_9$). Very pure clay is white and is called ***kaolin,*** after the name of a Chinese emperor, Kao, who encouraged its use in his realm for making chinaware. Brown clay has organic matter, iron oxide, and sometimes sand mixed in with it.

Bricks. Red housebricks are usually made near a clay pit. The clay is taken to the brickyard, where it is mixed with water, sand, and feldspar, unless these are already in the clay. The plastic mass is screened and then pressed into molds of the proper shape. The molded blocks of clay are placed on racks to dry. After drying, the bricks are piled loosely over small tunnellike arches. When the pile is complete, it is covered loosely with clay. Newer techniques stack the bricks in a circular permanent kiln. Fires are burned in the arches or in the kiln, for several days. The bricks lose water and melt a little (sinter) during the firing, becoming honeycombed with tiny holes. Iron oxide (ferric) formed during the firing accounts for the red color.

Many sorts of fancy bricks are made for special purposes. The composition of the mixture may be different or the temperature of the firing altered. A higher temperature will melt the outside of the bricks, producing a vitrified nonporous surface. A simple way of getting a smooth, water-shedding surface on clay products is to throw salt onto the fire of the kiln when it is hot. The vapors of the salt deposit and react on the outside of the ware, producing a glasslike coating. This is called a salt glaze and is seen on jugs and earthenware.

Firebricks for lining furnaces may be made of nearly pure silica for acidic linings and of magnesia (MgO) or alumina (Al_2O_3) for basic lining. Some are also made of aluminum silicate.



Courtesy of General Ceramics Company

Fig. 23-7.—Before the invention of paper, Babylonian businessmen used baked clay tablets in baked clay envelopes for their records.

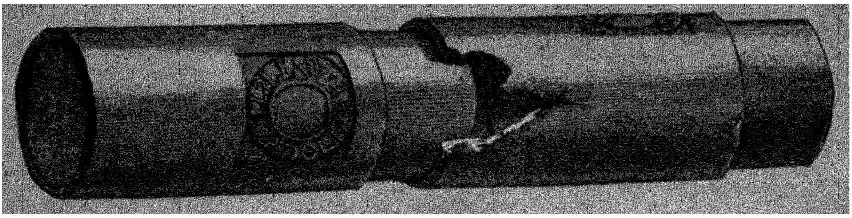
Roofing and drain tiles are made in a manner similar to bricks. Sewer pipes are also made from clay, sometimes quite coarse. The surfaces of these products are made nonporous by means of various glazes.

Pottery. Pottery is made from carefully selected clays that are mixed with water and purified. The mixture may be used as a thick fluid that is poured into plaster-of-Paris molds to form the ware. Another method of forming the ware is to place a blank of stiffer clay on a revolving potter's wheel and to shape it by a tool.

After drying, the ware is fired in a kiln. It comes out hard, light gray, rough-surfaced, and porous. At this stage it is called ***biscuit ware.*** Next it is glazed; that is, a glaze mixture, consisting for example of feldspar, borax, lead oxide, crushed quartz, whiting, and clay, is suspended in water and applied to the surface of the ware. Then the ware is fired again, the glaze melting easily and giving the biscuit a glassy surface.

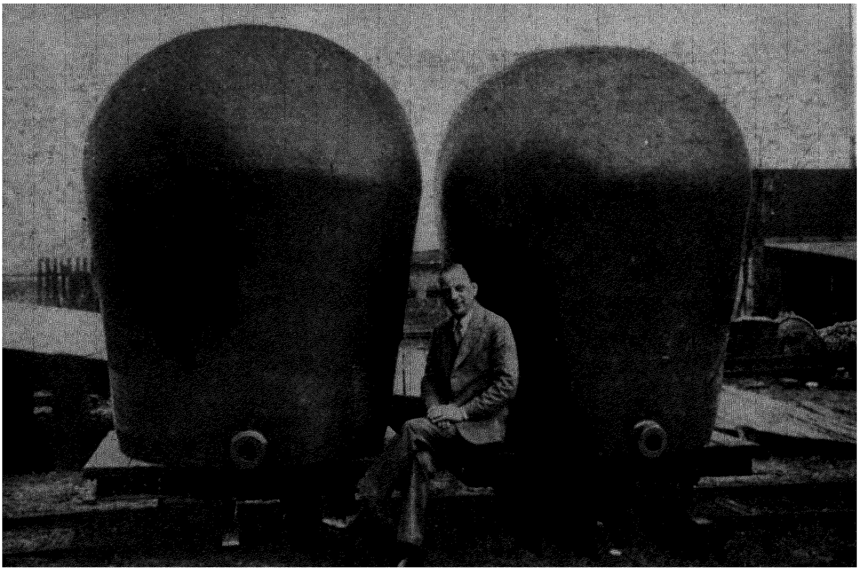
Let us melt some borax ($Na_2B_4O_7 \cdot 10H_2O$) in a loop on the end of clean platinum or iron wire inserted in a glass handle. (See Fig. 23-10.) Let us then touch the edge of the glassy bead thus formed in the loop to a small amount of manganese dioxide and remelt the bead. When cool, a clear transparent purple bead is formed. The oxide has dissolved in the glassy material and has colored it purple.

In a similar manner colors in pottery and glass are obtained. Some material, usually an oxide, is dissolved in the glass or the glaze. Cobalt oxide produces blue; uranium, orange; and iron, red or green. Decorations are put on either under or over the glaze and melted in. Transfer-paper patterns or hand painting are both used.



Courtesy of General Ceramics Company

FIG. 23-8.—This piece of ancient Roman drain tile was once part of the famous Appian Way, the road from Rome to Brundisum, now Brindisi. The road was begun by Appius Claudius Caecus about 312 B.C.



Courtesy of General Ceramics Company

FIG. 23-9.—Until the job of making these vessels was completed, this gentleman didn't rest as easily as he is shown here. These are the largest stoneware vessels ever made. They are used for holding acids.

Tableware and Porcelain. Better quality dinner plates and other dishes for the table are made from china clay, feldspar, and ground flint mixed with water. This ware is shaped, dried, and "burned" to form the biscuit ware in the manner employed for making pottery. The pattern and the glaze are applied to the biscuit again as in the manner for pottery. Dinnerware and porcelain are thus special types of pottery.

Porcelain has a glasslike interior. The clay mixture for its manufacture contains a relatively large amount of feldspar. The temperature of firing porcelain is higher than that for ordinary dinnerware. Because of the glasslike interior, porcelain allows some light to pass through it. It is translucent, but not transparent like glass. Much laboratory apparatus is made from "chemical" porcelain. Porcelain was "discovered" in Meissen, Germany, in 1709 in an attempt to make better crucibles for the alchemical transmutation of base metals to gold, but porcelain had been made by the Chinese many centuries before.

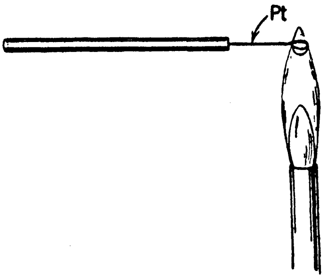
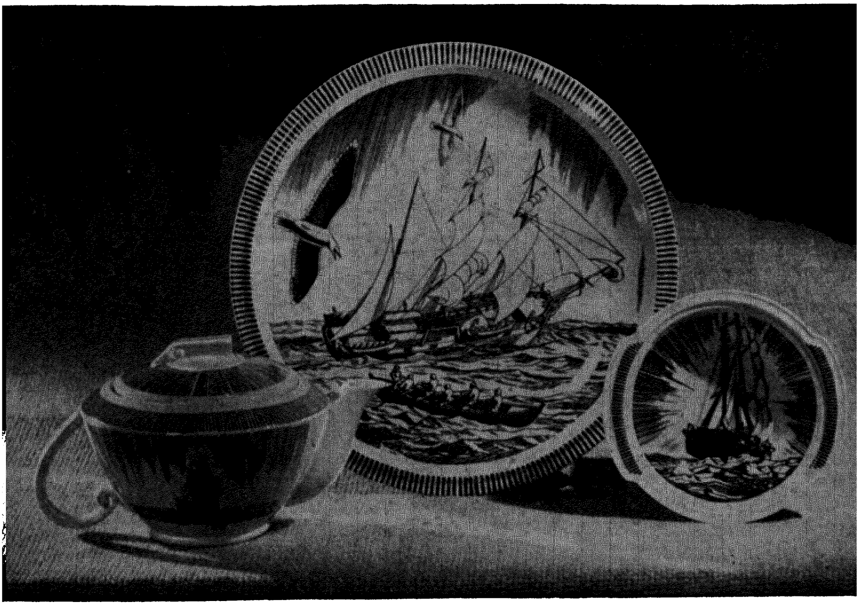


FIG. 23-10.—Melted borax dissolves metallic oxides and forms colored beads. A platinum wire with a loop at the outer end, mounted in a holder, is a suitable piece of apparatus for making borax-bead tests.



Courtesy of Vernon Kilns

FIG. 23-11.—Designer Rockwell Kent has put scenes from the famous sea story, "Moby Dick," onto a set of dinnerware.

A few years ago no satisfactory laboratory porcelain was made except in central Europe. When by necessity the porcelain makers of the United States were faced with a demand for this product, they studied and investigated. Eventually the Coors plant in Colorado produced a porcelain that is superior to the European in resistance to heat and chemicals and in mechanical strength. Moreover, the quality of the American product has been improved constantly.

The making of porcelain electrical insulators and spark-plug porcelain are other specialized industries that have profited by the application of chemical knowledge.

So many sorts of ceramic products are possible that the field offers great opportunity for the expression of artistic and decorative skill. The variety of colors, designs, glazes, and clays is almost without end. Many people adopt potterymaking as a hobby. Some have found the hobby growing into an interesting and profitable business.

Enamelware. Enameled kitchenware has a glasslike coating over steel. The coating is similar to the glaze applied to pottery, but more problems are involved in producing satisfactory goods. A foremost consideration is that the metal must be scrupulously clean. Then, the vitreous enamel coating must expand at just the same rate as the metal. Also, the coating must be applied evenly and have no holes.

The glaze is baked onto the metal base, as with pottery. Bathroom sanitary ware is made in this way. Refrigerators, stoves, signs, and sinks are only a few of the common articles coated with enamel. Dissolved oxides or colloidal materials suspended in the glaze impart colors.

QUESTIONS

11. What element, valuable to plant growth, is made available through the weathering of feldspar?

12. What is the cause of the coloration in brown sand? What treatment may help whiten the sand?

13. Describe the process of making a common flowerpot.

14. Which of these products usually has a vitrified surface: roofing tile; vinegar jug; laboratory porcelain crucible; water jug; flowerpot, sewer tile; drain tile; enamelware; electrical porcelain; tableware?

15. What properties of porcelain make it useful as part of a spark plug?

16. List three compounds that should not be heated in laboratory porcelain ware.

17. Glass stoppers of bottles containing sodium hydroxide or ammonium hydroxide solution sometimes "freeze in" tightly. Account for this action.

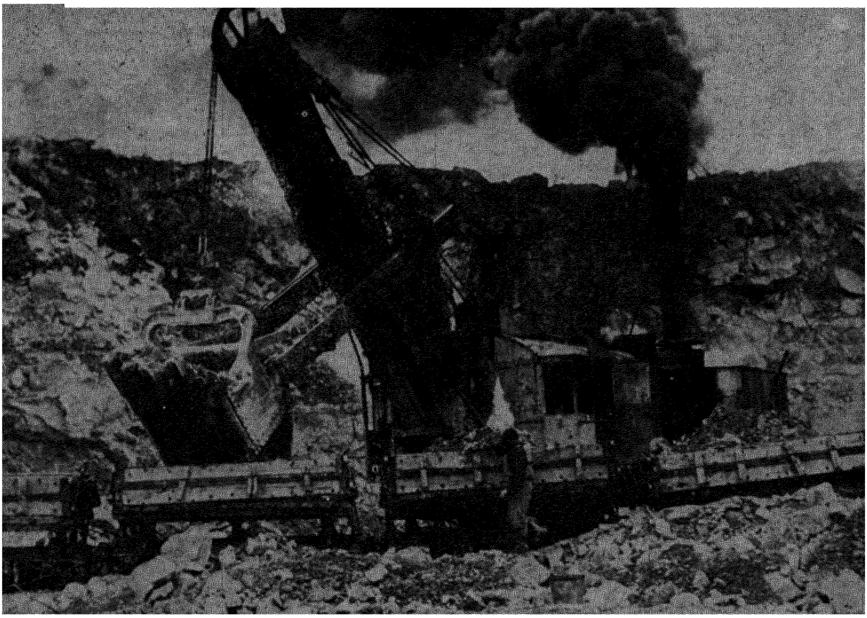
18. Tell how to distinguish a paste diamond (glass) from rock crystal (quartz) and also from a real diamond.

19. Glass could be manufactured more quickly and cheaply if the products of the glass-molding machine could be cooled, racked, and packed immediately.

Instead, the products pass through a long lehr, cooling slowly. Why is the last step in the process necessary?

20. Why is the use of chipped or cracked table chinaware inadvisable from a health standpoint?

Portland Cement. Lime mortar (see page 384) "sets" only in air with ample carbon dioxide. The search for a mortar that would harden under water led John Smeaton of England in 1756 to discover the first cement of modern times, Portland cement. Actually, he rediscovered a cement similar to one that had been used centuries before by the Romans.

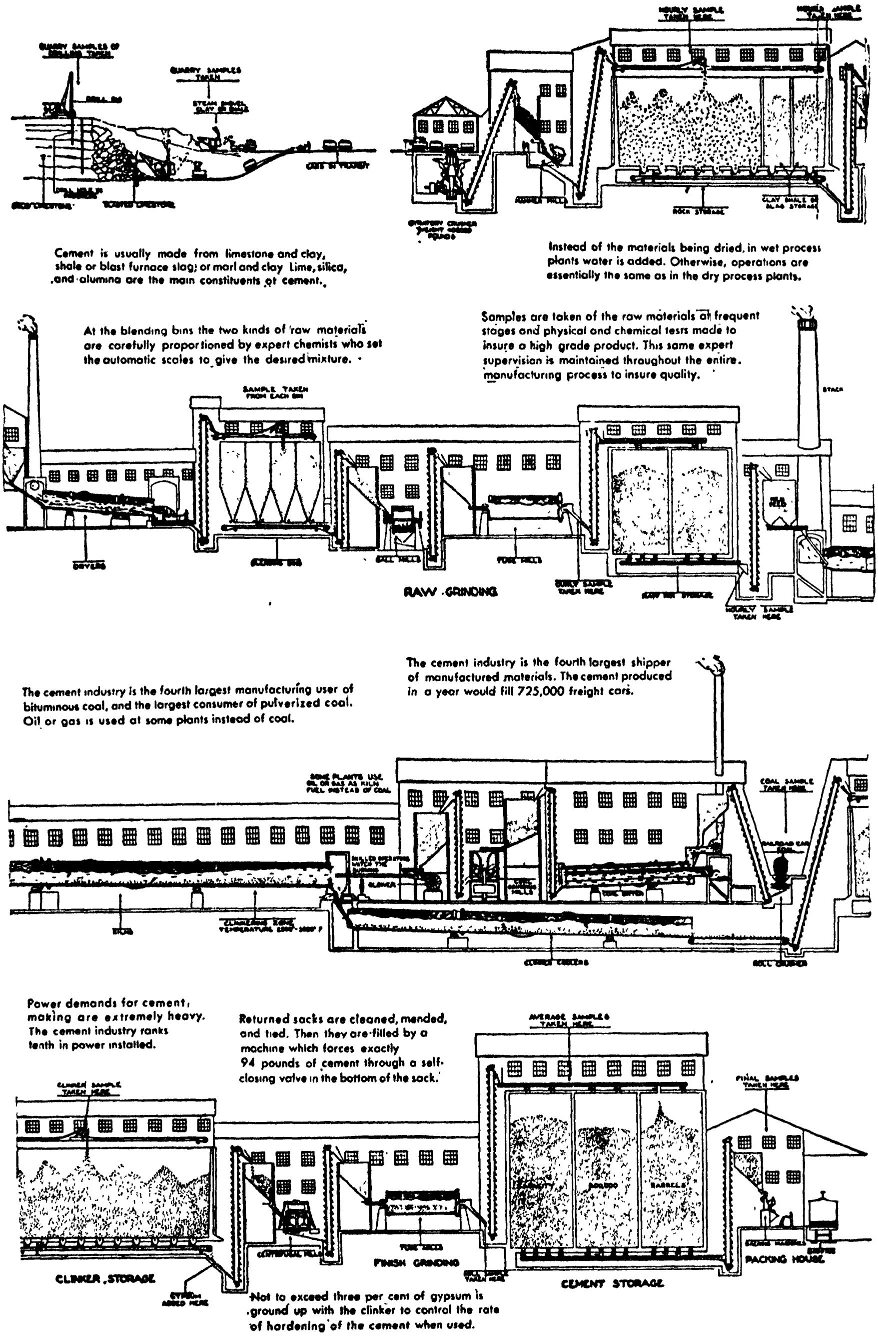


(Courtesy of Portland Cement Association)

FIG. 23-12.—Portland cement starts as rock in a quarry.

Portland cement is made from a mixture of clay, or shale, and limestone. Cement rock (which is equivalent to limestone and shale in one stone) or slag may also be used. (See Fig. 23-12.) The raw material is ground to a powder and introduced into the upper end of a rotating kiln. This kiln is a nearly horizontal firebrick-lined cylinder, one end of which is slightly raised and projects into the stack. (See Fig. 23-14.) It is almost as long as a football field and so large in diameter that a tall basketball center could run through it, holding his long arms up over his head, without touching the top.

A fire hotter than that needed to melt steel (1425°C) melts the powdered rock as it tumbles down the slowly turning tube. The rock melts



Cement is usually made from limestone and clay, shale or blast furnace slag; or marl and clay. Lime, silica, and alumina are the main constituents of cement.

Instead of the materials being dried, in wet process plants water is added. Otherwise, operations are essentially the same as in the dry process plants.

At the blending bins the two kinds of raw materials are carefully proportioned by expert chemists who set the automatic scales to give the desired mixture.

Samples are taken of the raw materials at frequent stages and physical and chemical tests made to insure a high grade product. This same expert supervision is maintained throughout the entire manufacturing process to insure quality.

The cement industry is the fourth largest manufacturing user of bituminous coal, and the largest consumer of pulverized coal. Oil or gas is used at some plants instead of coal.

The cement industry is the fourth largest shipper of manufactured materials. The cement produced in a year would fill 725,000 freight cars.

Power demands for cement making are extremely heavy. The cement industry ranks tenth in power installed.

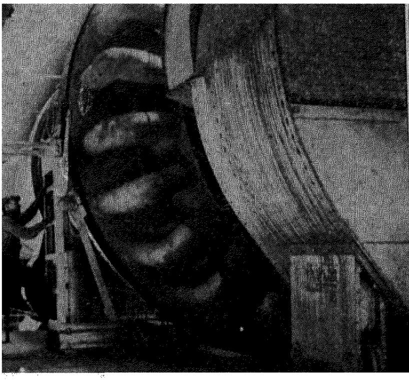
Returned sacks are cleaned, mended, and tied. Then they are filled by a machine which forces exactly 94 pounds of cement through a self-closing valve in the bottom of the sack.

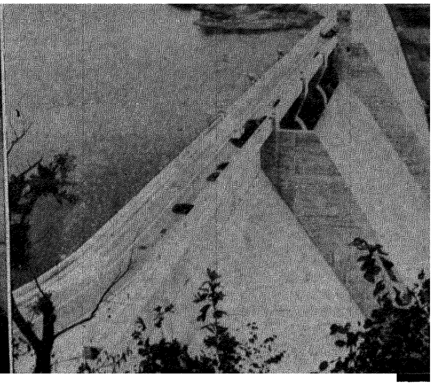
Not to exceed three per cent of gypsum is ground up with the clinker to control the rate of hardening of the cement when used.

Courtesy of Portland Cement Association

FIG. 23-13.—The manufacture of cement—how rocks are converted into this versatile material.

together, forming rough, gray clinkers of about the size of large peas. In this form cement will keep indefinitely. The cement of commerce is made by powdering the clinker and adding to it 2 or 3 per cent of gypsum, to control the time needed for the cement to "set."

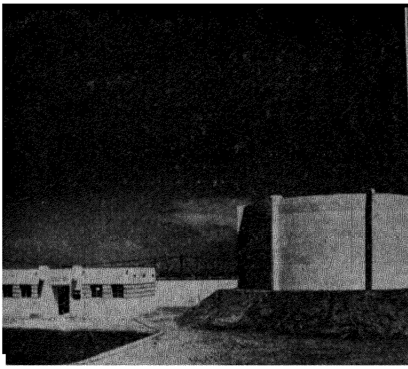


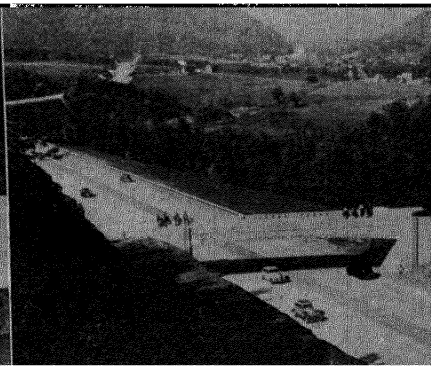


Courtesy of Portland Cement Association

FIG. 23-14.—The burner foreman is about to inspect the hot end of a Portland-cement kiln.

FIG. 23-15.—Norris Dam on the Clinch River, Tennessee, is built of reinforced concrete.





Courtesy of Portland Cement Association

FIG. 23-16.—The sewage treatment plant at Huntington Beach, California, has an exterior made chiefly from reinforced concrete. A progressive community treats its sewage.

FIG. 23-17.—The Pennsylvania turnpike between Harrisburg and Pittsburgh is an excellent example of the artistic and practical use of reinforced concrete.

Chemically, Portland cement is a mixture of silicates of calcium, aluminum, and a few other metals. Tricalcium silicate is the compound most desired in the cement for quick setting. Cement "sets" by the addition of water only. Water attaches itself firmly to the powdered cement and forms a hard material. The process is not completely understood, but evidence points to the formation of crystals by the reaction with water as one important part. Colloidal material is present in the "green," freshly poured cement, probably formed by the action of the water on silicates and aluminates.

When cement is reheated with additional limestone in exact proportions, a new cement is formed that has the property of high early strength. It is quick setting and does not change much in volume when it "sets." Such "doubly burned" cement is high in tricalcium silicate. It will stand traffic 24 hours after being poured.

Cement two parts, sand three parts, and crushed stone six parts mixed with water forms a satisfactory concrete. Its strength to withstand heavy loads and mechanical shocks is greatly improved by embedding iron rods or wires in it. For this reason the cement for roads is poured over a steel-rod mesh; floors, too, of a reinforced-concrete building, such as those in many modern schoolhouses, are a maze of steel bars before the concrete is poured over them. The concrete must be kept moist for several days, while gradually it increases in strength. (See Figs. 23-15, 16, and 17.)

QUESTIONS

21. Compare the setting of lime mortar with the setting of cement. Which mortar would be used for laying up bricks that must later be covered with water?

22. What raw materials are needed for cementmaking?

23. Explain the necessity for embedding pipes of a refrigerating system in the concrete at Boulder Dam when it was being built.

24. Distinguish Portland cement; concrete; sand; reinforced concrete.

25. List four important structures made of reinforced concrete.

Glass. Chemists take a particular interest in glass. They use this material extensively for their tools and vessels. It is light, strong, and inactive chemically, and above all it is transparent. This fact, together with its thousands of practical uses, accounts for its importance. Many chemists are skilled glassworkers. They have practiced glassworking in order to construct special equipment for their experiments.

Glass is so common that we probably cannot raise our eyes from this page without seeing some.

No one knows who made the first glass; its story is lost in antiquity. Without doubt glass was first noticed in the ashes of a very hot fire that had been kindled on sand. Glass objects known to be over 5000 years old have been found in Egyptian tombs.

Glassmaking in America started on the Atlantic seaboard where deposits of white sand and near-by stands of wood for fuel were located. The center of glassmaking has since moved to certain regions of Ohio, New York, lower New Jersey, and near-by states, because of the cheap natural gas in this region. Carload after carload of window glass, bottles, optical glass, colored glass, and even glass bricks roll away from these glassworks daily—over 100 million dollars' worth a year!

The Glass Furnace. The usual glass furnace is a large steel tank lined with a special glass-resisting brick and heated by inexpensive fuel gas. The raw materials are mixed and powdered: these consist of limestone, sand, soda ash, salt cake (Na_2SO_4), and a little carbon, although other materials may be added for special types of glass. About an equal weight of broken glass (cullet) is also added to aid melting. Most furnaces run continuously until the lining wears out. Raw materials are placed in the furnace at one end, and liquid glass is drawn out from the other. (See Fig. 23-18.)

In glass of the ordinary type, silicates are formed in the furnace from carbonates; the glass resulting is a fused mixture of silicates of sodium and calcium with extra dissolved silica. This type is called lime-soda glass. When it cools, it does not crystallize; it remains a liquid that becomes more and more viscous, or thick, until it is essentially an amorphous solid.

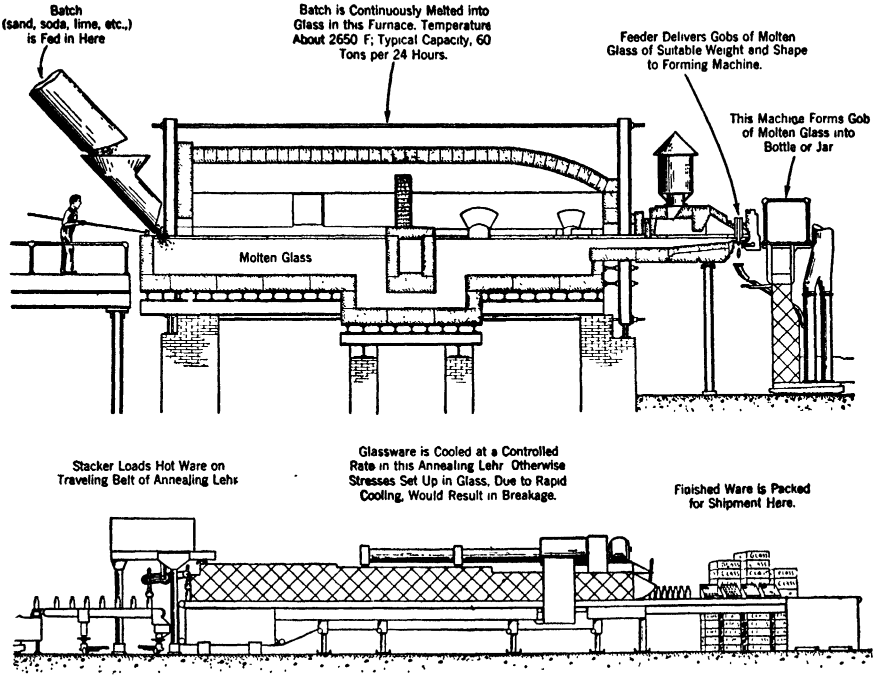
The following equations show in part some of the chemical changes that occur when a charge is melted in a glass furnace:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2\uparrow$$
$$C + 2Na_2SO_4 + 2SiO_2 \rightarrow 2Na_2SiO_3 + 2SO_2\uparrow + CO_2\uparrow$$

Window Glass. Formerly window glass was blown either mechanically or by the lungs into an elongated balloon. The ends of the balloon were cut off, and the resulting cylinder was split lengthwise. Then, by applying heat, the glass was flattened into a sheet. The outside circumference of the cylinder was a little longer than the inside circumference, and the flattened sheet formed was thus slightly irregular. These places of irregular thickness cause distorted vision when a person looks through this glass. We can notice such places in panes of window glass in all but new buildings and those furnished with the more expensive plate glass.

An improved method of making window glass was made possible by ingenious and persistent work. Today a wide ribbon of glass is drawn from a furnace of molten glass just as paper may be pulled from a roll. Attached to a bait rod that starts it, a flat band of glass passes over rolls from the furnace through an annealing lehr, or oven, where it is cooled gradually to avoid strains. Then it is cut into sheets automatically. The demand for optically plane glass for automobile windshields and windows has encouraged this development.

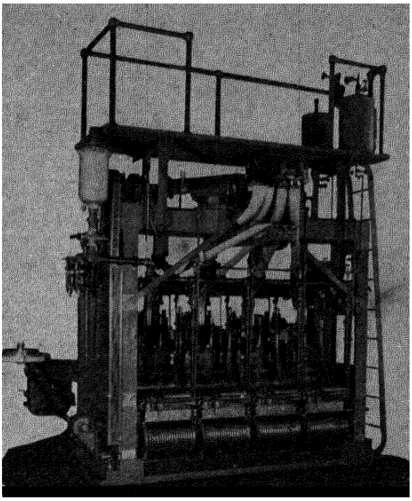
Plate Glass. In one method of making plate glass, a huge ladleful of the molten liquid is poured onto a flat-topped steel table, which has a ridge along each side. A heavy iron roller flattens the plastic glass as a rolling pin flattens piecrust. The thickness of the plate is determined by the height of the ridges. When cool, the plate is removed and, set in plaster of Paris, and about half of it (counting both sides) is ground away by emery (Al_2O_3). Then the plate is polished to a brilliant luster on both sides by rouge (Fe_2O_3). The process is somewhat wasteful and expensive, but a strong, clear, attractive glass is the result. This is the sort of glass that is used for the show windows in most large stores. Plate glass is now also made by a continuous-sheet process.



Courtesy of Hartford Empire Company

FIG. 23-18.—This diagram shows the manufacture of hollow glassware by automatic machinery. A picture of a machine that forms the ware is on the opposite page.

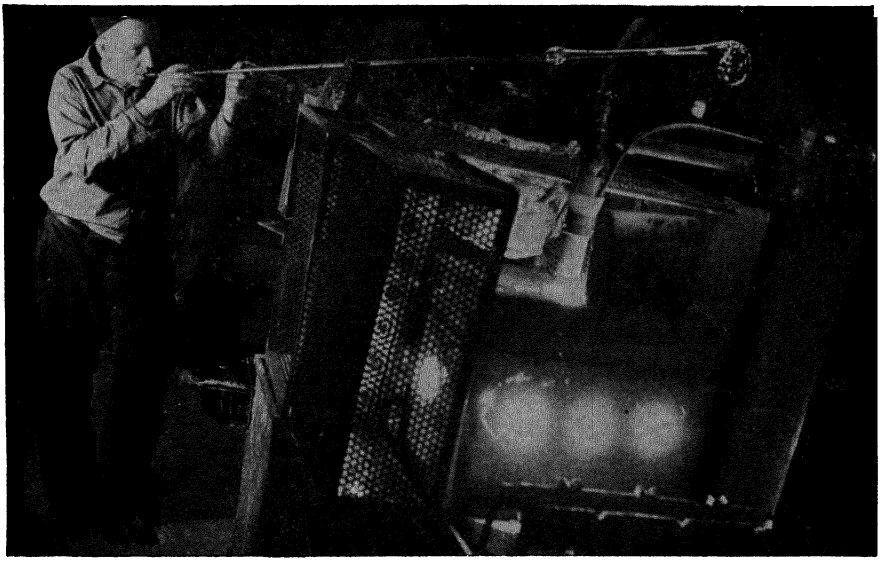
Glass Bottles and Jars. The making of glass containers is a mechanical process and an exceedingly interesting one. Let us look at a bottle containing some popular beverage and of a sort that is sold by the thousands. The story of its making is told on the outside of the glass. An automatic glass bottle-making machine has steel molds of the shape desired. (See Fig. 23-19.) A gob of molten glass falls into the mold. It is shaped and the inside blown hollow in two steps. We notice a thick place in the wall about two-thirds from the top. This place marks the end of the first step in the making. Then we note a slight ridge around the bottleneck just below the rim where the neck mold form was brought up while the liquid glass was pressed against it. A similar ridge is found at the bottom. Now we notice two vertical ridges on each side. These show where the molds opened while the finished bottle was removed. Then slowly the bottle passed through an annealing lehr, or oven, where it cooled gradually. The resulting bottle, one of 6000 made that day from one machine, is free of strains. Polarized light is used to test for these strains.



Courtesy Hartford Empire Company

FIG. 23-19.—A bottle- or jar-forming machine has four units. Gobs of liquid glass slide down tubes to molds in the center. A timing device for the automatic operation is on the cylinders shown at the bottom.

Special Glass. Special types of glass may be made in a clay pot. These pots of liquid glass are served by a team of workers, each



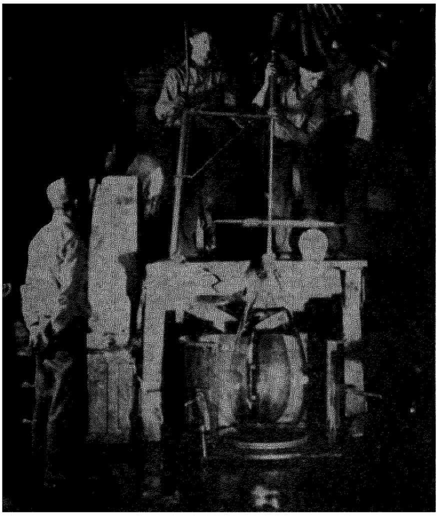
Courtesy of Corning Glass Works

FIG. 23-20.—Although much chemical apparatus is blown in molds, some pieces must be blown "off hand." This glass blower is shaping a retort.

having special duties. A "gather" of glass is often removed on the end of a blowpipe. Laboratory glass beakers and flasks, for example, are blown in a mold, by lungs or compressed air, the glass rotating while it is blown. We may see spiral marks on this type of ware. (See Fig. 23-21.)

Optical Glass. Every physics student has learned that a lens composed of crown and flint glass will prevent chromatic aberration (color-fringe error). Crown glass, like the ordinary kind used for window panes, is a lime-soda glass. Flint glass contains lead and potassium silicates. Optical glass, usually flint, is clear and brilliant; it is used for making lenses, including eyeglasses.

Colored Glass. Most sand used in making glass contains iron. Ferrous silicate, a green compound, forms in the final glass. This color may be noticed in cheap glass bottles or in very old glass. The green color is avoided, in milk bottles for example, by including some manganese dioxide (MnO_2) in the melt among the raw materials. The iron is oxidized, and light-yellow ferric silicate is formed, rather than ferrous compound. When glass containing manganese dioxide remains a long time in bright sunshine, the purple permanganate ion (MnO_4^-) forms, coloring the glass. The oxides that dissolve in and color glazes (see page 401) produce the same effect in glass.



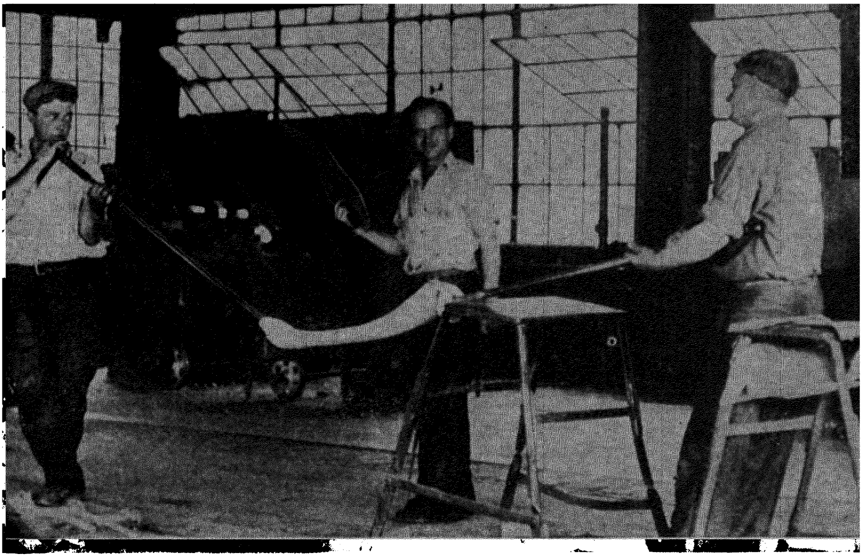
Courtesy of Corning Glass Works

FIG. 23-21.—In hand blowing a large Pyrex brand cylinder, a tear-shaped gob of glass is put into a mold for the final blowing operation.

Collodial selenium added to the raw materials makes the red-colored glass for taillights and signal lights, iron sulfide produces amber, and chromic oxide makes glass green. Ruby and purple glass for stained glass windows is made by using colloidal gold, the size of the gold particles determining the color produced.

Low-expansion Glass. "Pyrex" brand glass is well-known for its heat-resisting quality. It contains various percentages of aluminum oxide (Al_2O_3) and boric oxide (B_2O_3) and a high percentage of silica (SiO_2). Such borosilicate glass is used extensively for making kitchenware and laboratory vessels. It has the ability to resist heat changes owing to its small expansion coefficient.

Glass and Thermometer Tubing. Glass tubing is made by forcing a ring of liquid glass around a jet of compressed air, only very slight variations being possible in the diameter of the bore (lengthwise hole). (See Fig. 23-22.) Thermometer tubing is drawn from a shaped ball of glass with a bubble inside; it has a very small bore.



Courtesy of Corning Glass Works

FIG. 23-22.—Not a piccolo player, but a skilled artisan in glass about to draw out several yards of uniform thermometer tubing from the glass bubble on the end of the blowpipe.

Safety Glass. Safety glass is a sandwich. Two sheets of glass are sealed over a sheet made of a transparent plastic substance. The plastic filling of the sandwich holds the pieces of glass together in case of breakage. Many lives have been saved by this invention.

Tempered Glass. Tempered glass has a hard surface but a tough flexible interior. Its ability to bend without breaking is remarkable.

Electric Light Bulbs. The bulbs for electric lights are blown from a glass ribbon by automatic machines. A small disklike depression in the ribbon is puffed out by the compressed air into the familiar pear-shaped bulb. Thousands of bulbs can be made each day by a single machine.

Glass Cloth. Glass fibers are produced by machine. They are very fine and soft, resembling silk or wool. Since these fibers are obviously fireproof and poor heat conductors when matted, they can be used for insulating houses, refrigerators, and railroad cars. Some articles of fancy clothing are also made from glass fibers. It is not recommended, however, that the cloth be worn next to the skin.

Fibers for glass cloth are made by spraying glass onto cooling trays. These short fibers resemble staple rayon (see page 568), and they can be spun and woven in much the same manner as any fibers.

"Vycor." For special laboratory uses there is now available a type of glass that is 96 per cent silica. After the glass is shaped, the soluble compounds of sodium, calcium, and other metals are dissolved by treatment with acid. The glass is then dried and refired. In this process it shrinks to the final dimensions. This new type of glass resists vigorous chemical actions well, expands very little, and has a very high softening temperature.

Glass Blocks and Other Developments. Glass construction blocks and glass linings for tanks and chemical apparatus are well known. Other new developments in glass technology are coming onto the market rapidly. They are the result of research, hard work, and patience. Each new discovery opens up more possibilities for beginners, rather than limiting the field. Many problems await complete solution. For example, how can inexpensive window glass be made that will not give sharp edges when it breaks and that at the same time will transmit practically all the light that falls on it?

SUMMARY

Silica is a common name for the compound silicon dioxide (SiO_2). Quartz is silica in the shape of six-sided crystals, commonly colorless and transparent, but also at times found in yellow, brown, purple, green, and other shades. White sand is pure silica; brown sand, silica containing impurities. Flint is an impure variety of quartz. Silicon is the second most abundant element in the earth's crust, and its compound, silica, is a very common substance.

Silica is an inactive, water-insoluble compound. It has a high melting point (about 1710°C), is transparent to ultraviolet light, and expands only slightly with each degree increase in temperature.

At high temperatures silica joins aluminum oxide, sodium carbonate, and calcium oxide, forming silicates. It reacts with hydrofluoric acid, forming silicon tetrafluoride and water. It can be reduced to the element silicon by the reducing agent carbon in an electric furnace.

Silica is used as an abrasive; it is used in mortar, concrete, and in glassmaking. Quartz is used in making optical instruments, laboratory apparatus, and specialties such as radio crystals.

Soluble silicates include sodium and potassium silicate. Sodium silicate solution (water glass) is used as an adhesive, for fireproofing cloth, preserving eggs, and for making silica gel.

Common clay is produced by weathering feldspar; feldspar is a compound of potassium, aluminum, and silicon oxides.

White clay is kaolin, used for making chinaware. Bricks are baked clay.

Impervious coatings on bricks are obtained by melting the outside surfaces (vitrifying) or by melting common salt onto the surface. Pottery is made from mixed clay, molded and baked, forming biscuit ware. The glaze is then applied and the ware fired again. Dissolved metallic oxides give colors. Tableware is a special type of pottery made from clay, feldspar, and ground silica. The glaze and pattern are applied as for pottery. Porcelain is pottery that is fired at a higher temperature than ordinary dinnerware. Some porcelain is used for laboratory ware. Enamelware is glass-coated ironware.

To form Portland cement, shale and limestone are heated in a rotary kiln, forming a clinker; this is powdered and gypsum added to catalyze setting. Cement sets with addition of water only. Concrete is made from cement, crushed stone, and sand; sometimes it is reinforced with steel. .

Glass is made from sand, soda, and lime heated with cullet to aid in melting. There are many special types of glass. Fabricating glass is accomplished by making (1) sheets drawn or cast or (2) jars and bottles blown into molds. Colors in glass are due to dissolved oxides or colloidal suspensions of metals. Borosilicate glass has high silica and boric oxide content. Optical glass contains lead and potassium silicates. Safety glass is (1) plate glass run onto wire reinforcement or (2) glass sheets sandwiched with a plastic material between them.

QUESTIONS

26. List three transparent materials and one translucent material.

27. List four essential ingredients of a melt for making glass.

28. Write equations for two reactions that occur in the glassmaking furnace.

29. Write formula equations for the reactions between (*a*) lead oxide and sand; (*b*) barium carbonate and sand; (*c*) ferrous oxide and sand; (*d*) potassium sulfate and sand.

30. Describe briefly three methods of making window glass. Which of the three seems the most successful?

31. The most important glass articles imported into colonial America were glass beads. For what purpose were they used?

32. Old glass in an automobile may break more readily than equivalent newer glass. Account for the increase in brittleness of such glass with age.

33. What connection exists between colloid chemistry and glassmaking?

34. Explain why glass manufactured from sodium carbonate and sand alone would be unsuitable material for making window glass.

35. List five glass colors commonly seen, and tell how each is produced.

MORE CHALLENGING QUESTIONS

36. Read and make a report on (*a*) the novel *Marietta, Maid of Venice,*[1] by F. Marion Crawford; (*b*) plate glass, including pot furnaces; (*c*) cut glass; (*d*) properties and uses of glass cloth; (*e*) early American glass.

---

[1] The Macmillan Company, New York, N. Y., 1919.

37. Make a collection of colored glass. Perform tests to identify the coloring agent in each sample.

38. Investigate types of cement other than Portland cement.

39. Obtain a sample of glass wool, and make a physical test of its heat-insulating property.

40. Secure several sorts of glass squares or prisms, and measure the index of refraction of each.

UNIT FIVE . . . . CHAPTER XXIV

CHEMICAL CALCULATIONS

In the laboratory we try to answer many questions about substances. Some of these questions ask, "What sort?" The answers describe nature to us. Here we find unsuspected beauty, orderliness, and reliability.

Equally interesting are the questions that ask, "How much?" The answers to these questions show us another view of nature. Here we find the strictest economy. Nothing is utterly destroyed. Matter is saved; energy is saved; neither is lost.

The question "How much?" is asked in cooking, in making pictures, in filling a doctor's prescription, and in adjusting the controls of a radio, refrigerator, or stove. Satisfactory results depend upon the correct answer.

In a similar manner the question "How much?" is asked in chemistry. Here the answer is definite, and we can find it by simple arithmetic. In elementary chemistry laboratory, we may want to know how much of reacting substances to put together and how much of each product to expect. In industrial chemistry, the amounts of chemicals and of heat used and produced are exceedingly important and may make one operation more profitable than another.

Let us start this chapter with a discussion of the full meaning of a chemical equation.

The Complete Meaning of an Equation. Each formula for a substance that takes part in a chemical change represents a definite weight of that substance. By CO_2 we mean, not only one molecule of carbon dioxide, but 44 parts by weight ($C = 12$, $2O = 32$) of that substance. The parts by weight are usually measured in grams for laboratory purposes, but pounds, kilograms, or even tons may be used. Usually also, CO_2 means 44 g of the gas (1 mole). Likewise, H_2O signifies 18 g, or 1 mole, of water.

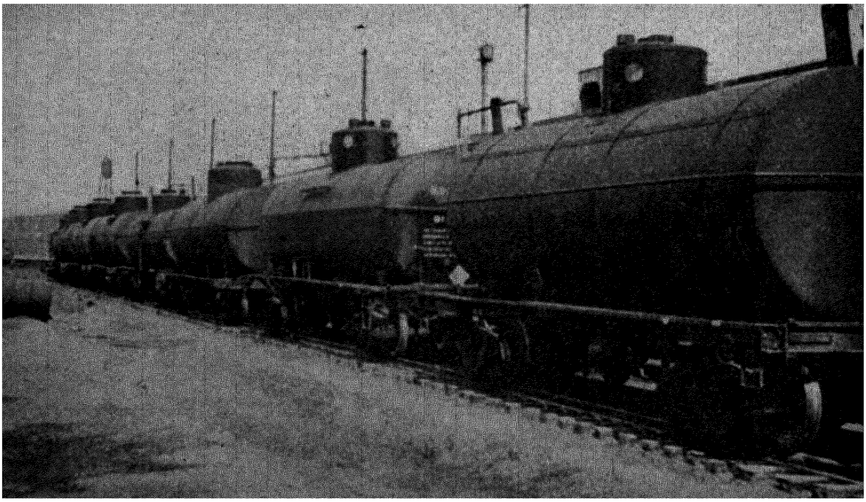
$2H_2O$	→	$2H_2$	+	O_2	(balanced equation)
2 moles water	→	2 moles hydrogen	+	1 mole oxygen	(molar equation)
$2 \times 18 = 36$ parts by weight of water	→	4 parts by weight of hydrogen	+	32 parts by weight of oxygen	(equation in terms of weights represented)
36 g water	→	4 g hydrogen	+	32 g oxygen	(gram-molecular equation)

In short,

$$\begin{array}{cccccc} 2H_2O & \rightarrow & 2H_2 & + & O_2 \\ 36\text{ g} & \rightarrow & 4\text{ g} & + & 32\text{ g} \end{array}$$

Here we see illustrated the equality expressed by the chemical equation, for the weight of the substances entering into a chemical change is equal to the weight of the products. In this case 36 g of water has been decomposed into a total of 36 g of gases (4 + 32).

How to Find the Weight of a Substance in a Chemical Change. We have just seen that 36 g of water produces 4 g of hydrogen and 32 g of oxygen. It follows that 18 g of water would produce one-half as much of each gas, namely, 2 g of hydrogen and 16 g of oxygen. One-tenth as much, or 3.6 g of water, would form 0.4 g of hydrogen and 3.2 g of oxygen. The weight relationships of the three substances are expressed by the figures 36, 4, and 32. Any amount of water produces these gases in the same proportion by weight. If 50 g of water should be decomposed into elementary gases, the weight of gas formed in each case would be found by a proportion.



Courtesy American Petroleum Institute

FIG. 24-1.—Industrial calculations involve carloads of materials. Mistakes are costly. These tank cars are being loaded with petroleum products. Chemists sample the fuel and determine its heat value when burned.

$$\begin{array}{ccccl} 50\text{ g} & & X & Y & \text{(known and desired weights)} \\ 2H_2O & \rightarrow & 2H_2 + & O_2 & \text{(balanced equation)} \\ 36\text{ g} & & 4\text{ g} & 32\text{ g} & \text{(formula weights)} \end{array}$$

If we assume that the formulas of the equation represent lines, we can make a ratio (two equal fractions) from these figures as they stand. Of course, we find the answer for the weight of each substance separately. The weight of hydrogen formed is found thus:

$$\frac{50\ \cancel{g}}{36\ \cancel{g}} = \frac{X}{4\ g}$$

Solving for X,

$$X = {}^{200}\!/_{36}\ g = 5.56\ g\ \text{hydrogen.} \quad \textit{Ans.}$$

Notice that units are cancelled out just like numbers and that the uncanceled unit goes with the answer. The weight of oxygen formed at the same time is 50 g minus 5.56 g, or 44.44 g, or

$$\frac{50\ \cancel{g}}{36\ \cancel{g}} = \frac{Y}{32\ g}$$

Solving for Y,

$$Y = {}^{1600}\!/_{36}\ g = 44.44\ g\ \text{oxygen.} \quad \textit{Ans.}$$

If we know the weight of any one substance in a chemical change, either a substance entering into the change or a product of it, then it is possible to find the weights of *all* other substances in the change, *provided* that we know the balanced equation for the reaction. The general method of finding the unknown weight of a substance in a chemical change when the weight of one is given is as follows:

1. Write the complete balanced equation, taking great care that it is correct. Every formula in the equation must be exactly right.
2. Write the given weight above the proper substance and an X above the substance whose weight is to be found.
3. Underneath these substances put their formula weights, taken as many times as the number before the formula for the substance indicates.
4. Make a proportion of these four quantities just as they stand in space, calling the equation the line.
5. Solve for the unknown quantity X by clearing fractions and dividing.
6. Express the answer in the correct units of measurement.

When aluminum is attacked by a solution of hydrogen chloride (hydrochloric acid), aluminum chloride and hydrogen are formed. What weight of aluminum is required to produce 534 g of aluminum chloride? In solving this problem the six steps outlined are followed.

(1) $2\text{Al} + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\uparrow$

(2) $\overset{X}{2\text{Al}} + 6\text{HCl} \rightarrow \overset{534\text{ g}}{2\text{AlCl}_3} + 3\text{H}_2$

(3) $\underset{2 \times 27 = 54\text{ g}}{\overset{X}{2\text{Al}}} + 6\text{HCl} \rightarrow \underset{2 \times 133.5 = 267\text{ g}}{\overset{534\text{ g}}{2\text{AlCl}_3}} + 3\text{H}_2$

(4) $\dfrac{X}{54\text{ g}} = \dfrac{534\ \cancel{\text{g}}}{267\ \cancel{\text{g}}}$

(5) $267X = 534 \times 54\text{ g}$

(6) $X = 108\text{ g aluminum.}$ *Ans.*

X may be placed on either side of the equation. Also, both the known and the unknown substances may be represented on the same side of the arrow.

As another example, a chemist has an order for 272 lb of dry zinc chloride. He is to make the compound by the action of zinc on hydrochloric acid. (*a*) How much zinc is needed, and (*b*) what weight of hydrogen chloride should be used?

(1) $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\uparrow$

(2) $\overset{X}{\text{Zn}} + 2\text{HCl} \rightarrow \overset{272\text{ lb}}{\text{ZnCl}_2} + \text{H}_2$

(3) $\underset{65\text{ lb}}{\overset{X}{\text{Zn}}} + 2\text{HCl} \rightarrow \underset{65 + (2 \times 35.5) = 136}{\overset{272\text{ lb}}{\text{ZnCl}_2}} + \text{H}_2$

(4) $\dfrac{X}{65\text{ lb}} = \dfrac{272\ \cancel{\text{lb}}}{136\ \cancel{\text{lb}}}$

(5) $136X = 272 \times 65\text{ lb}$

(6) $X = 130\text{ lb zinc.}$ *Ans.* (*a*)

(2) and (3) $\text{Zn} + \underset{73\text{ lb}}{\overset{Y}{2\text{HCl}}} \rightarrow \underset{136\text{ lb}}{\overset{272\text{ lb}}{\text{ZnCl}_2}} + \text{H}_2$

(4) $\dfrac{X}{73\text{ lb}} = \dfrac{272\ \cancel{\text{lb}}}{136\ \cancel{\text{lb}}}$

(5) $136Y = 272 \times 73\text{ lb}$

(6) $Y = 146\text{ lb hydrogen chloride.}$ *Ans.* (*b*)

QUESTIONS

(Assume STP unless otherwise stated. In each problem use the correct units. The answer should be expressed in the appropriate unit. Express weights in grams and volumes in liters unless otherwise directed.)

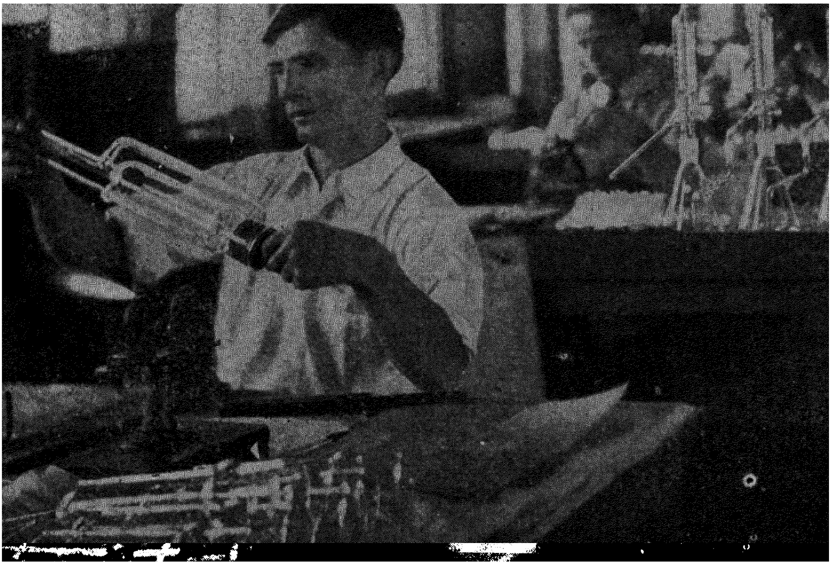
1. A ton of coal is assumed to contain $\left\{\begin{matrix}1600\\1800\end{matrix}\right.$ pounds of carbon. What weight (pounds) of carbon dioxide goes up the chimney when a ton of this coal is burned?

2. What weight (tons) of sulfur must be burned to produce $\left\{\begin{matrix}1\text{ ton}\\5\text{ tons}\end{matrix}\right.$ of sulfur dioxide?

3. What weight of copper chloride is formed by burning $\left\{\begin{matrix}127.2\\381.6\end{matrix}\right.$ grams of copper in chlorine?

4. What weight of oxygen can be made from $\left\{\begin{matrix}122.5\\367.5\end{matrix}\right.$ grams of potassium chlorate when the compound is heated?

5. How much of each of its elements is needed to produce $\left\{\begin{matrix}269.2\\67.3\end{matrix}\right.$ grams of copper chloride by direct synthesis?



Courtesy of Corning Glass Works

FIG. 24-2.—Good chemical technique requires skillful workmanship combined with a knowledge of the properties of substances. These lamp workers produce apparatus with small tolerances for size error.

Weight-volume Relationships. Recall that CO_2 represents, not only carbon dioxide, but a gram-molecular weight of that gas, or 1 mole. The ***volume*** represented by 44 g of carbon dioxide is 22.4 liters at STP (the gram-molecular volume). This is so because the gram-molecular weight of any gas is the weight in grams of 22.4 liters of it at 0°C and 1 atm pressure (see page 148).

If we ask, "How much carbon dioxide gas by volume (liters) will be produced from 4.8 g of carbon?" the method of answering the question is as follows:

(1), (2), and (3)
$$\overset{4.8\text{ g}}{\underset{12\text{ g}}{C}} + O_2 \rightarrow \overset{X}{\underset{22.4\text{ liters}}{CO_2}}$$

(4)
$$\frac{4.8\cancel{g}}{12\cancel{g}} = \frac{X}{22.4\text{ liters}}$$

(5) and (6)
$$X = \frac{4.8 \times 22.4\text{ liters}}{12} = 8.96\text{ liters}$$

carbon dioxide. *Ans.*

Instead of placing the gram-molecular weight of carbon dioxide under the formula, the gram molecular volume, 22.4 liters, corresponding to the molecular weight, is used. The portion of carbon dioxide produced will have the same relationship to 22.4 liters as the gram weight of carbon has to 12 grams, its gram-molecular weight. It is possible, therefore, to find the volume in liters at standard conditions of any ***gas*** in a chemical change by ***using 22.4 liters in place of the molecular weight of the gas.***

If more than one gram molecular weight of the gas is used or produced, the 22.4 liters will be multiplied by that number. For example, $2H_2$ represents 44.8 liters of hydrogen, and $3C_3H_8$ stands for 67.2, or 3 × 22.4, liters of propane gas.

What volume of oxygen at STP can be produced from 24.5 g of potassium chlorate when the compound is heated?

(1), (2), and (3)
$$\overset{24.5\text{ g}}{\underset{245\text{ (gram formula weight)}}{2KClO_3}} \rightarrow 2KCl + \overset{X\text{ liters}}{\underset{\substack{3 \times 22.4 = 67.2\text{ liters} \\ \text{(gram-molecular volume)}}}{3O_2\uparrow}}$$

(4)
$$\frac{24.5\cancel{g}}{245\cancel{g}} = \frac{X}{67.2\text{ liters}}$$

(5) and (6)
$$X = \frac{24.5 \times 67.2\text{ liters}}{245}$$
$$= 6.72\text{ liters oxygen.}$$ *Ans.*

QUESTIONS

6. Suppose Joseph Priestley once heated $\left\{\begin{matrix}54\\108\end{matrix}\right.$ grams of mercury oxide. (*a*) What weight of mercury did he produce? (*b*) What weight of oxygen gas was formed? (*c*) What volume (liters at STP) did this gas occupy?

7. What volume of hydrogen gas can be liberated by the action of hydrochloric acid on $\left\{\begin{matrix}108\\162\end{matrix}\right.$ grams of aluminum?

8. What volume of nitrogen gas is liberated when $\left\{\begin{matrix}256\\512\end{matrix}\right.$ grams of ammonium nitrite is heated? $NH_4NO_2 \rightarrow N_2 + 2H_2O$.

9. What weight of zinc must be burned to make $\left\{\begin{matrix}405\\1215\end{matrix}\right.$ grams of zinc oxide?

10. What volume of oxygen is necessary to join completely with $\left\{\begin{matrix}150\\100\end{matrix}\right.$ grams of hydrogen?

11. What volume of sulfur dioxide may be expected as a result of burning $\left\{\begin{matrix}3200\\4800\end{matrix}\right.$ grams of sulfur?

12. In what volume ratio should the elementary gases be furnished when it is desired to produce hydrogen chloride by direct union of the elements?

13. How many liters of hydrogen gas are needed to make $\left\{\begin{matrix}100\\500\end{matrix}\right.$ liters of ammonia gas by direct union of its elements?

14. What volume of each of the elementary gases can be made by the decomposition of $\left\{\begin{matrix}180\\540\end{matrix}\right.$ grams of water?

15. What weight of pure zinc will be needed by a chemist who is to prepare $\left\{\begin{matrix}272\\408\end{matrix}\right.$ grams of zinc chloride by the reaction between zinc and hydrochloric acid?

16. What weight of plaster of Paris can be made from $\left\{\begin{matrix}\text{1 ton}\\\text{5 tons}\end{matrix}\right.$ of gypsum?

17. The weight when packed is marked on a package of washing soda crystals. What percentage of loss in weight is permitted from such a package without cheating a customer?

18. A box of washing soda weighs $\left\{\begin{matrix}2.5\\5.0\end{matrix}\right.$ pounds when packed. What is the least weight (pounds) it may have through loss of moisture only?

19. Write the equation for the burning of octane.

20. How many liters of chlorine can be produced by electrolysis of a solution containing $\left\{\begin{matrix}585\\1170\end{matrix}\right.$ grams of common salt in water?

Volume-volume Relationships. If in a problem two substances are both gases, the same principle regarding liters applies except that in this case the gram molecular volume, 22.4 liters, should be used with both.

What volume of ammonia is needed to provide 60 liters of hydrogen?

(1), (2), and (3)

$$\overset{X}{\underset{\substack{(2 \times 22.4)\\ 44.8\text{ liters}}}{2NH_3}} \rightarrow N_2 + \overset{60\text{ liters}}{\underset{\substack{(3 \times 22.4)\\ 67.2\text{ liters}}}{3H_2}}$$

(4)

$$\frac{X}{44.8\text{ liters}} = \frac{60\cancel{l}}{67.2\cancel{l}}$$

(5) and (6)

$$X = \frac{60 \times 44.8\text{ liters}}{67.2} = 40\text{ liters ammonia.} \quad \textit{Ans.}$$

It will be noted that the common factor 22.4 liters can be canceled out; therefore, why not omit it altogether?

For example, what volume of nitrogen will be produced at the same time the 60 liters of hydrogen are formed?

(1), (2), and (3)

$$2NH_3 \rightarrow \overset{X}{\underset{(1 \times 22.4)\text{ liters}}{N_2}} + \overset{60\text{ liters}}{\underset{(3 \times 22.4)\text{ liters}}{3H_2}}$$

(4)

$$\frac{X}{1\text{ liter}} = \frac{60\cancel{l}}{3\cancel{l}}$$

(5) and (6)

$$X = \frac{60 \times 1\text{ liter}}{3} = 20\text{ liters nitrogen.} \quad \textit{Ans.}$$

Now it becomes clear why two volumes of hydrogen join one volume of oxygen to form two volumes of water vapor (see page 85). In fact, the gases concerned in a chemical change have the volume ratio of small whole numbers. This principle is precisely that stated in Gay-Lussac's law (see page 140): ***The volumes of gases in a chemical change have the volume ratio of small whole numbers, provided that all are measured at the same temperature and pressure.***

Obviously, the volumes can be read directly from the equation.

$$1CH_4 + 2O_2 \rightarrow 1CO_2 + 2H_2O$$

1 volume methane + 2 volumes oxygen yield 1 volume of carbon dioxide + 2 volumes of steam

All gases are assumed to be measured at the same temperature and pressure. In this case the temperature has to be higher than 100°C.

A Practical Problem Using English Units. What is the amount of salt (NaCl) needed to make salt cake (Na_2SO_4)? Let us assume that 500 lb of sodium hydrogen sulfate, 90 per cent pure, and salt (sodium chloride), 98 per cent pure, are used.

The reacting part of the sodium hydrogen sulfate is 90 per cent of 500 lb, or 0.90 × 500 lb = 450 lb. We can find the needed weight of ***pure*** sodium chloride by the method already described (see page 419).

$$\overset{450\text{ lb}}{\underset{120\text{ lb}}{NaHSO_4}} + \overset{X}{\underset{58.5\text{ lb}}{NaCl}} \rightarrow Na_2SO_4 + HCl\uparrow$$

Pound formula weights

$$\frac{450\cancel{\text{lb}}}{120\cancel{\text{lb}}} = \frac{X}{58.5\text{ lb}} \qquad X = \frac{450 \times 58.5\text{ lb}}{120} = 219.4\text{ lb pure sodium chloride.}$$

Since the salt used is only 98 per cent sodium chloride, we can find the weight of salt needed (100 per cent) by dividing the answer above by 0.98 (98 parts per 100 parts).

$$\frac{219.4\text{ lb}}{0.98} = 223.9\text{ lb salt.} \quad \textit{Ans.}$$

The answer may also be obtained in one operation.

$$\frac{0.90 \times 500\,\cancel{\text{lb}}}{120\,\cancel{\text{lb}}} = \frac{0.98\,X}{58.5\text{ lb}}$$

Solving for X,

$$X = 223.9\text{ lb salt.} \quad \textit{Ans.}$$

SUMMARY

A formula indicates parts by weight of a compound. Equations also indicate parts of weight of reacting substances and products. Weight-weight problems, an unknown weight of a reacting substance, are found by solving the proportion

$$\frac{X}{\text{Formula weight of unknown (g)}} = \frac{\text{given weight } (\cancel{\text{g}})}{\text{formula weight of given substance } (\cancel{\text{g}})}$$

Any weight unit may be used.

Weight-volume problems are solved conveniently by using gram weights for solids and 22.4 liters (STP) for each gram molecular weight of a gas. A typical ratio is

$$\frac{X}{\text{Formula weight of unknown (g)}} = \frac{\text{given volume of gas at STP}}{n \times 22.4\text{ liters}}$$

in which n = number of gram molecular volumes needed.

Problems of the volume-volume type are solved by using 22.4 liters for each gram molecular weight of two or more gases. Also, in this sort of example the 22.4 liters cancels as a common factor, and the coefficients used in a balanced equation express the volume relationships between gases. This is an example of applying Gay-Lussac's law.

The equations above represent the weight relationships between pure materials. When percentages are involved, the mathematical equation should be adjusted to take these into consideration.

QUESTIONS

21. How much oxygen (liters) is needed to burn $\left\{\begin{matrix}10\\15\end{matrix}\right.$ liters of methane?

22. When $\left\{\begin{matrix}50\\60\end{matrix}\right.$ liters of acetylene burns, what volume of oxygen is used? What volume of carbon dioxide is formed?

23. What volume of oxygen is needed to burn $\left\{\begin{matrix}240\\480\end{matrix}\right.$ grams of magnesium?

Assuming that the air is one-fifth oxygen, what volume of air is needed to supply the oxygen? (Omit any chemical action involving nitrogen in this problem.)

24. What volume of air is needed to burn $\left\{\begin{matrix}50\\150\end{matrix}\right.$ liters of carbon monoxide? What volume of carbon dioxide is produced? What volume of nitrogen remained unchanged?

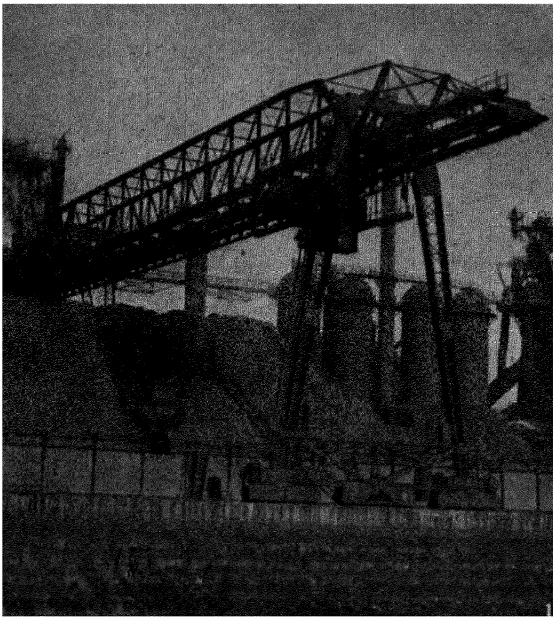
25. When 1800 liters of water gas, $\left\{\begin{matrix}\text{40 per cent}\\\text{42 per cent}\end{matrix}\right.$ carbon monoxide, is burned, what volume of carbon dioxide is formed?

26. What weight of carbon is consumed when $\left\{\begin{matrix}67.2\\44.8\end{matrix}\right.$ liters of carbon dioxide are reduced?

27. When $\left\{\begin{matrix}200\\300\end{matrix}\right.$ grams of calcium carbide, 96 per cent pure, is used with water to make acetylene, what volume of the gas is formed?

28. When $\left\{\begin{matrix}300\\500\end{matrix}\right.$ grams of limestone, 95 per cent pure calcium carbonate, is intensely heated, what weight of lime remains? What volume of gas is driven off?

UNIT
SIX


1

THE METALS

Steel comes from a rusty rock that is mined in huge quantities. The iron and steel industry is big business, dealing in tons and shiploads and using equipment costing millions of dollars. As far as usefulness goes, iron is far more valuable than gold.

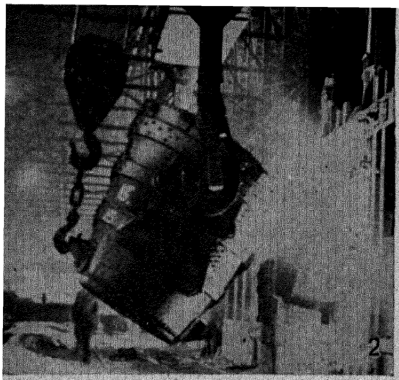
Blast furnaces (1) are surrounded by stock piles of raw materials, which they consume voraciously. Ore is located under the movable bridge. The silolike structures are stoves for preheating air.

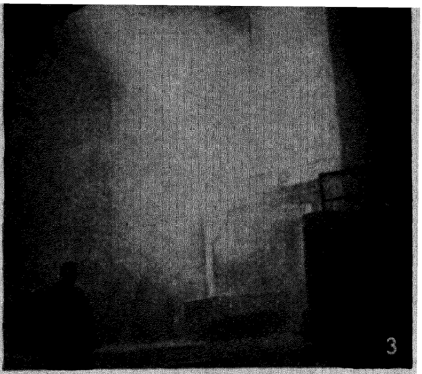
The blast furnace has an inclined track leading to the charging "bell" on top of it. Melted pig iron from the blast furnace is carried in a huge ladle and is poured into the open-hearth furnace (2). This is the start of the process of steelmaking.

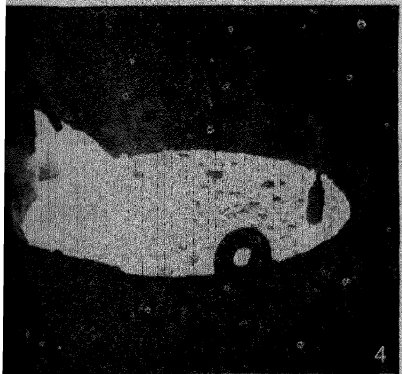
In the Bessemer process, air bubbling through melted pig iron in the converter (3) refines pig iron into steel. The flame blasting from the converter mouth is caused by being burned carbon in the pig iron.

After steel has run from a furnace, the lighter slag (4) follows.

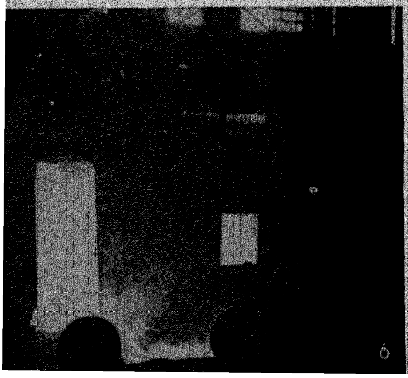
When the rod at the right of (4) is lifted, the liquid steel flows into an ingot mold (5). A deoxidizer is added during the pouring process. Crablike tongs (6) move the partly cooled ingot from the mold to a gas-fired soaking pit of uniform temperature. The ingot is then ready for the rolling mill, which squeezes the ingot to a bloom, billet, and rod in succession. Picture (7) shows the making of wire from rod.

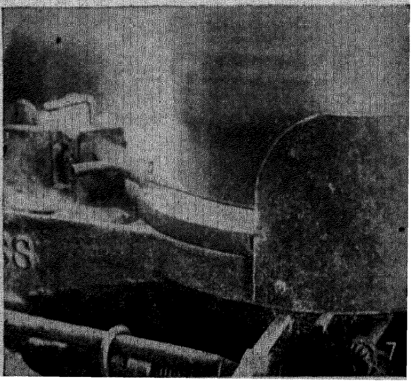

2


3


4


5


6


7

Courtesy of American Iron and Steel Institute

UNIT SIX .... CHAPTER XXV

IRON AND STEEL

Iron ore, coal that makes good coke, and limestone are three essentials of an industrial nation. For economic reasons the sources of these three materials must be located near each other if a country is to compete in the world as a builder of heavy machinery, railroads, or automobiles. We find that the heavy industries, in which iron and steel are made, are located as a rule near the source of coal, for the brittle coke cannot be hauled a great distance successfully.

Three regions in the world are outstanding in respect to these three prime essentials. They are the Chicago-Ohio-Pittsburgh region in the United States, the English Midlands, and the Ruhr Valley. Other regions are of less importance from a standpoint of tonnage produced, but they have possibilities of growth. They include the district around Birmingham, Alabama, and certain localities in the U.S.S.R., France, and possibly China.

Among metals, iron is the giant. Copper, the second most important metal, does not approach the world's tonnage of iron and steel. The entire amount of pig iron, the first step in steelmaking, produced in the world in any given year varies greatly. In 1937, world production of pig iron was about 100 million metric tons of 2205 lb each. The United States produced about two-fifths of this amount. Germany, Great Britain, the U.S.S.R., and France together produced almost all the rest.

The steel in an automobile is manufactured into motor, body, and accessories. The price per pound of the completed car is about the same as the purchaser pays for beefsteak, less than 50 cents a pound. In peacetimes enough automobiles are registered in the United States alone to seat the entire population. Still the automobile industry, the largest single user, consumed in normal years only about one-fifth of the steel produced in this country. Automobile manufacturers have used as much as 7 million tons of steel in a single year.

Other important industries that use immense amounts of steel are

---

New Terms

pyrite
magnetite
limonite
hematite
casehardening
nitriding
blast furnace
reverberatory furnace
converter

railroads, building construction, farm and shop machinery making, container manufacture (tin cans, drums for oil, chemicals, fats, etc.), oil and gas industries. In 1942, during World War II, shipbuilding used the greatest tonnage of steel, 16 per cent.

Iron Ores. Although less abundant in the earth's crust than aluminum, iron is a very common element. It is estimated that 4.7 per cent of the earth's crust is iron. Iron is found in plants, animals, and the human body, especially in the blood. The iron from the iron compounds in a human body, collected together, would be enough to make a common nail. Millions of fragments of celestial dust, iron meteorites, fall on the earth each year.

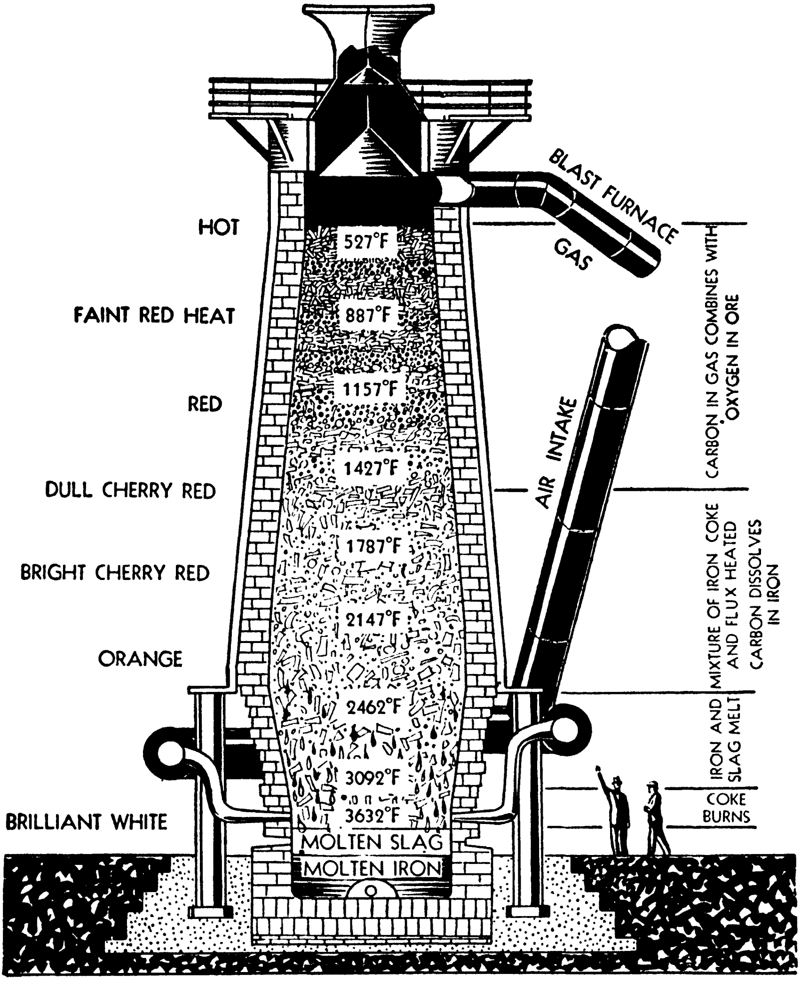
"Fool's gold," or ***pyrite*** (FeS_2), is mined for its sulfur content, and not for iron. One of the iron ores used in England is ***siderite*** ($FeCO_3$). About 5 per cent of all iron ores is the black ***magnetite*** (Fe_3O_4), a magnetic material. ***Limonite*** ($2Fe_2O_3 \cdot 3H_2O$) is a yellow ore of some importance, but by far the greatest amount of iron comes from ***hematite*** (Fe_2O_3), which is similar in composition to ordinary red iron rust. Hematite is found in a range of colors from red to red-brown. It is the coloring matter in many natural rocks, in bricks, in red barn paint, and even in cosmetics. The Indians used it for war paint.

The most important ore deposit in the United States is the hematite deposit a few miles from the western end of Lake Superior in the Mesabi Range. After the overburden of loose earth is removed, the ore is dug out of the open pit by huge power shovels. Here man has made one of the mightiest scars on the face of the earth.

After a short haul by rail to the upper lake ports, Duluth and Superior, the ore is loaded by chute into ore boats. These lake steamers may be completely loaded with 11,000 tons of ore in as short a time as 39 minutes. Once they start in the spring they run continually from mine (upper lake) port to lower lake ports, Cleveland, Buffalo, Ashtabula, and others. Enough ore must be accumulated during the summer months to supply the blast furnaces in the winter when ice locks the boats tightly in the lake.

The Blast Furnace. The blast furnace serves to reduce iron ore to metallic iron. It is built like a huge smokestack, about 90 ft high and 25 ft in diameter at the widest part, and is lined throughout with firebrick. This tubelike furnace flares out a little from the top, tapering downward to provide proper flow of materials; it narrows in diameter near the lower part to prevent slumping of the charge and to concentrate the usable product. (See Fig. 25-1.)

The charges of limestone, coke, and ore are put in the top through the "bell," a double trap-door arrangement that allows solids to enter



Courtesy of General Motors Corporation

FIG. 25-1.—Above is a diagram of a blast furnace in operation showing the bell, the lining, and the ports for jets of hot air.

without much gas escaping. The solids descend slowly through the furnace and meet the rising hot gases. Such an excess of hot carbon monoxide is provided that the ore is reduced to metallic iron.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$
$$2Fe_2O_3 + 8CO \rightarrow 4Fe + 7CO_2 + C$$

If carbon alone is considered to be the reducing agent, the reduction is described by this equation.

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2\uparrow$$

The exact reactions in a blast furnace are more complicated than those given in these equations, but they adequately represent the final result.

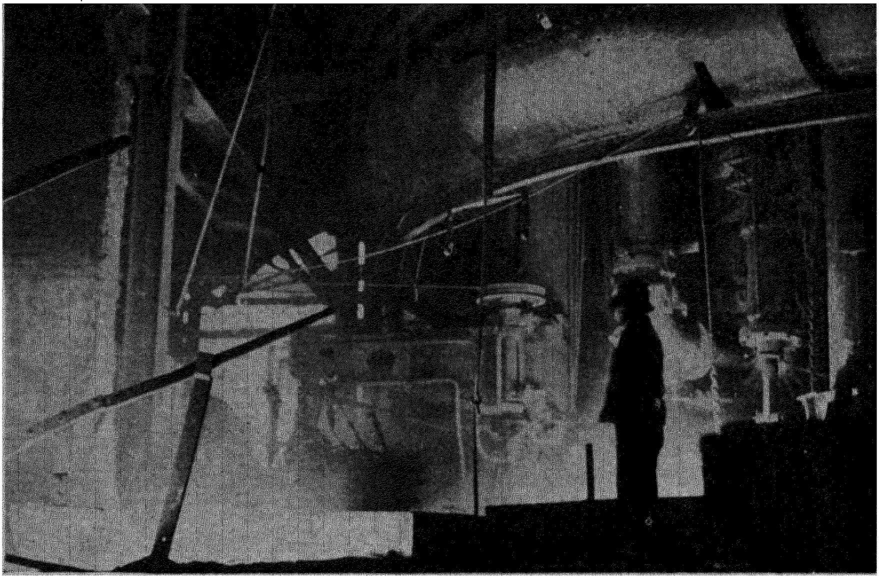
The hot blast of air enters just below the widest part of the furnace. Here coke burns with furious intensity.

$$C + O_2 \rightarrow CO_2$$

The excess hot coke in the upper reaches of the furnace changes almost all the carbon dioxide into carbon monoxide

$$CO_2 + C \rightarrow 2CO$$

Hence, the coke serves as both fuel and reducing agent. The iron, freed from the ore, drops to the bottom of the furnace as a liquid, but not until it has absorbed carbon to saturation and other impurities to a lesser extent.



Courtesy of American Iron and Steel Institute

FIG. 25-2.—The man is watching glowing liquid pig iron flow from a blast furnace. Above him may be seen the hot-air supply pipe that girdles the furnace.

The limestone, added as a flux or scavenger, combines with the unwanted but ever-present silica in the ore, forming a flux.

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2\uparrow$$

This flux also drops to the bottom of the furnace and floats on the molten iron. Both slag and liquid iron are drawn off at their respective levels from time to time. (See Fig. 25-2.)

The hot gases leave the furnace through a big pipe, known as a "downcomer," near the top of the furnace. After going through a dustcatcher, they are used as fuel for engines that move materials into the furnace and also for fuel in open-hearth furnaces. Most of these gases, however, are burned in large stoves to preheat the air used in the blast furnace. Usually four stoves, which are brick-lined towers through which the air takes a tortuous path over white-hot firebrick, are needed with each blast furnace.

Once started, the blast furnace operates continuously until the lining needs repair.

FACTS ABOUT A BLAST FURNACE

Materials put in		Materials taken out	
Coke	C	Iron	Fe
Ore	$Fe_2O_3(SiO_2)$	Slag	$CaSiO_3$
Limestone	$CaCO_3$	Gas	N_2 60% CO 24% CO_2 16%
Air	N_2, O_2		

The *U.S. Bureau of Mines Technical Paper* 442 gives the following facts about a day's operation of a 700-ton blast furnace:

Materials for each charge:

Mixed iron ores	24,500 lb
Limestone	3,900
Coke	9,000
Total	37,400 lb

$$\text{139 charges in 24 hours} = \text{5,200,000 lb of solids}$$

$$\text{Air (at 17.6 lb/sq in. and 1130°F)} = \text{50,000 cu ft/min}$$

or

$$\text{4000 lb/min for 24 hr} = \text{5,800,000 lb of air}$$

QUESTIONS

1. List three essentials for making iron commercially.

2. The Kaiser interests built a blast furnace in southern California in 1942-1943. Point out two reasons why such a project may be considered $\left\{\begin{matrix}\text{sound}\\ \text{unsound}\end{matrix}\right.$ commercially under conditions other than wartime demands.

3. What part of the human body contains considerable amounts of iron? From what source does the body obtain the needed iron?

4. The liver of a newborn calf contains a high percentage of iron. Milk is very low in iron. After about 2 weeks the liver of the calf is low in its iron content. From what source should the calf then begin to get its iron?

5. Considering the facts in the last question, is the higher market price for calf liver over beef liver justified?

6. Why is most soil brown?

7. In 1942, ore to the amount of 92,076,781 tons passed over the Great Lakes. In World War I the tonnage was 65,000,000 for a similar time. Find the percentage of increase.

8. An ore ship holds 15,000 tons; a freight car, 70 tons. How many freight cars are needed to carry the load from an ore ship?

9. A bucket lifts in 65 seconds an average of 15 tons of ore from ship hold to freight car. How much time is required to unload a ship? Compare this answer with the time required to load a ship.

10. Write equations for the reduction of both (1) hematite and (2) magnetite by both (*a*) carbon; (*b*) carbon monoxide.

11. Why is the blast-furnace process a continuous one?

12. Air for the blast furnace is dried by refrigeration. (*a*) What becomes of the moisture? (*b*) What harm would moisture do in a blast furnace?

13. Could a blast furnace operate with pure oxygen instead of air? If so, what advantages or disadvantages would there be?

14. Calculate the amount (tons) of materials that must be stored to supply a 700-ton blast furnace for four winter months.

15. Make a labeled diagram of a blast furnace, indicating (*a*) all substances leaving the furnace; (*b*) all materials supplied to it.

16. What becomes of any aluminum oxide in the gangue of iron ore?

17. What component of the "downcomer" gas is useful for fuel? List three other gases from a blast furnace that are not flammable.

Pig Iron. The liquid iron that runs from a blast furnace is about 92 per cent iron, 3.75 per cent carbon, 2.5 per cent silicon, and 0.05 per cent phosphorus, with some sulfur, manganese, and a few other elements in lesser amounts. It is conducted into a waiting preheated ladle, which may hold 300 tons, mounted on a railroad car. The liquid may be (1) sent to the steel mill for use in open-hearth furnaces or Bessemer converters, (2) cast into bars, called pigs, of 40 to 100 lb each, or (3) made into wrought iron. The pigs of iron look like huge rusty loaves of coarse, dark bread. (See Fig. 25-3.) As a common article of commerce they are shipped to foundries in open freight cars.

Cast Iron. The crude product of the blast furnace is remelted with a flux in foundries as one process in the manufacture of iron castings. The liquid metal is poured into a prepared sand mold of a desired shape. One of the crudest examples of this sort of work is seen in a sash weight, the counterweight for a window. The supports for a pupil's schoolroom desk and seat are usually made of cast iron. Radiators, furnaces, black stoves, engine blocks, sewer pipes, some toy soldiers, and legs and bases for machines in shops are made of cast iron. From these uses it can be seen that cast iron is strong enough to withstand a steady load under compression. It does not resist tension or shocks well, however, and it is quite apt to break if struck sharply. Cast iron rusts very slowly.

Courtesy of American Iron and Steel Institute

FIG. 25-3.—Pig iron, in addition to being used in the molten condition for making steel, may be cast into "pigs." These are bought by foundries, which refine them into cast iron, or by steel plants that do not have their own blast furnaces.

$$\text{Pig iron}\begin{cases} 16\% \begin{cases} \text{Cupola} \rightarrow \text{cast iron} \\ \text{Reverberatory furnace} \rightarrow \text{wrought iron} \\ \text{Bessemer converter} \begin{cases}\text{acid}\end{cases} \rightarrow \text{steel } 66{,}500{,}000 \text{ tons (in 1941)} \end{cases} \\ \qquad\qquad\qquad \text{Electric furnace } 1.5\% \rightarrow \text{refined steel} \\ 84\% \begin{cases} \text{Open-hearth furnace} \begin{cases}\text{acid}\\ \text{basic}\end{cases} \rightarrow \text{steel} \\ \text{Crucible} \rightarrow \text{steel}\end{cases}\end{cases}$$

Types of Iron Castings. When cast iron cools slowly, ordinary gray iron castings form. Photomicrographs of this iron show the carbon separated out in the form of large flakes of graphite. This explains the weakness of cast iron to blows: it is honeycombed throughout with very weak graphite flakes.

If iron castings are suddenly chilled after pouring, a white cast iron results. Such castings are very hard, brittle, and strong. Often the excess metal is removed by grinding to desired dimensions. The carbon in the iron is in the form of the compound, iron carbide (Fe_3C). It appears as shiny, white streaks in photomicrographs. (See page 282.)

When white iron castings are heated to 1600°F, held at that high temperature for several days, and then cooled slowly, malleable iron castings are formed. These castings are not quite as strong as steel, but they are easier to make to size and are cheaper. Like wrought iron they can be bent, for the heat-treatment has decomposed the brittle iron carbide. Malleable castings are used for pipe joints and parts of farm machinery and locomotives. Photomicrographs reveal that most of the carbon in malleable castings exists as fine particles, not as large flakes as in ordinary gray iron castings.

Wrought Iron. When cast iron is heated and worked in a furnace with iron ore and a suitable flux, practically all the impurities are removed. The result is almost pure iron, except for inclusions of slag. The furnace for making wrought iron has a low roof to reflect the heat downward on the molten metal. The heat is supplied by burning fuel outside the furnace and directing the hot products of combustion onto the melt.

Either by hand or by mechanical puddling, slag is stirred into the iron; the resulting wrought iron has thus many fibers of slag running through it. Wrought iron rusts very little because the glasslike slag protects the iron from corrosive influences.

Hardware on docks, anchors, chains, fancy fences, grilles, and ornamental ironwork that is used with the Spanish style of architecture are made of wrought iron. Wrought iron, as the name suggests, was originally wrought, or pounded, into shape, while hot, by the strength of the blacksmith's arm. Mild (low-carbon) steel is used for bridge lamps, plant stands, and brackets today. Formerly they were made of wrought iron. The steel is cheaper and practically equivalent to wrought iron for many purposes.

The Age of Alloys. The importance of steel needs no demonstration in modern times. We use it for ships, baking pans, power shovels, nails, chicken wire, tractors, bridges, kitchen knives, and automobiles. But we do not use the same kind of steel for all purposes. Everyone knows that an automobile contains several kinds of steels—alloy steels, that is, steels with other metals melted into them. These are improved steels, adapting the metals better to the shocks and pulls they will receive in service. So many alloys of steel and of other metals are on the market today that the present era is sometimes called the ***age of alloys.***

The increased cost per ton of steel for some alloying metals is shown in the following table:

Vanadium	For each 0.1%	$8.00
Tungsten	For each 1.0%	24.00
Chromium	For each 1.0%	2.30
Nickel	For each 1.0%	8.00

Obviously a great opportunity awaits workers who can produce these needed alloying metals or the equivalent properties in steel at a lower price, for thousands of tons of each are used every year.

Steel. Steel is essentially an alloy of iron and carbon, the amount of carbon varying from 0.2 to 2.0 per cent. Other alloying elements may be added to impart special properties.

There are two principal ways of making blast-furnace iron into steel: they are the ***Bessemer*** and the ***open-hearth*** processes. The open-hearth process is by far the more important of the two, for it makes a satisfactory steel from pig iron that contains phosphorus.

Changing iron into steel is a process of purifying the iron; the impurities are burned out, forming oxides. The gaseous oxides can be readily driven off, and the steelmaker endeavors to make the solid oxides form into a slag that can be drained off. In the steelmaking process almost all the impurities are removed. For practical purposes it is desirable to have about 0.2 to 0.5 per cent of carbon in the finished steel, as well as small amounts of silicon and manganese. Phosphorus and to a lesser extent sulfur are considered undesirable impurities. The desired elements are added to liquid steel just before it is poured. Manganese, for example, is added as an iron-manganese alloy. Not only does adding manganese to the steel make a better quality steel than one lacking it, but it makes the ingot more sound and improves the pouring and rolling qualities.

Bessemer Steel. In 1847 William Kelly of Kentucky and in 1855 Henry Bessemer in England discovered independently an economical method for changing pig iron into steel. The process today bears the name of Bessemer, and the furnace is called the Bessemer converter. (See Fig. 25-4.) Air is blown through liquid iron until the impurities that act like a fuel are burned. Carbon burns readily and forms gases that disappear in the blast of air. Sulfur is diminished by about 20 per cent, but phosphorus not at all. Silicon and manganese are easily oxidized, uniting to form a slag.

In modern practice a pear-shaped steel vessel is used in the Bessemer process. This converter is mounted so that it may be emptied by tipping. It is lined with silica firebrick (SiO_2—acid Bessemer process) or with dolomite ($CaCO_3 \cdot MgCO_3$—basic Bessemer process), depending on the impurities to be removed. The acid-lined converter is more widely used in the United States.

About 12 tons, but not more than 20 tons, of liquid iron is poured into the open converter. This vessel is then furnished with a blast of air that enters through holes in the bottom. For about 20 minutes, long yellow flames roar from the top of the converter. When the flames change in character, becoming shorter and deeper brown in color, this indicates that the burning is complete. The air is then turned off. The necessary carbon and manganese are added, and the steel is poured out by tipping the converter.

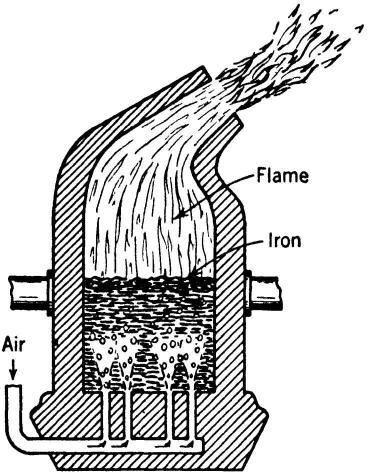
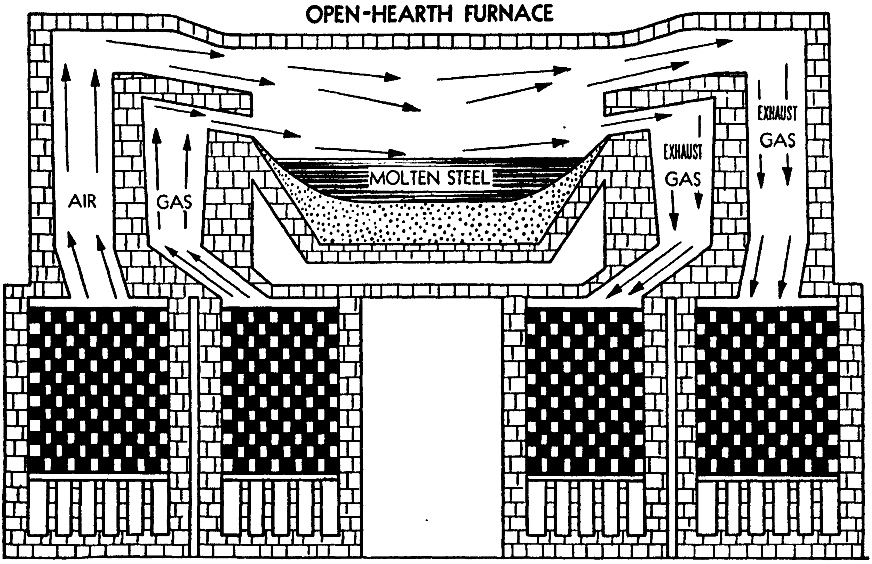


FIG. 25-4.—The Bessemer converter is a device for changing iron into steel by burning out a large part of the carbon. The process is a rapid and spectacular one.

Although the Bessemer converter still makes tremendous amounts of steel, its relative importance decreased before World War II in favor of the slower, more versatile open-hearth process.

Open-hearth Steel. An open-hearth furnace is a firebrick-lined chamber about as large as the first floor of a small one-family dwelling house. (See Fig. 25-5.) The roof is about as high as the ceiling of the rooms. The interior is lined with dolomite in such a way that it forms a large basin on the center of the floor. There are several charging, or loading, doors along one of the long walls. In the lower central part of the opposite wall is the pouring outlet, plugged with clay until used. A large volume of preheated air and fuel gas, fuel oil, tar, or a combination of two or more of these is blown in from one end of the chamber, producing an intensely hot flame as they burn together over the puddle of steel in the furnace. The hot products of combustion are led through other chambers filled with checker-laid bricks before going up the smokestack. These bricks become intensely hot. Every 15 minutes the direction of the flow of gases is reversed, and the heated checker-laid bricks warm the incoming gases.

The open-hearth furnace (see Fig. 25-5) is charged with pig iron (sometimes solid, but more commonly liquid), rusty scrap steel, and a suitable flux. After 11 to 12 hours the steel has formed. Most of the phosphorus and some of the sulfur have been oxidized and passed into the flux to form slag. The 100-ton charge is then tapped. A huge ladle



Courtesy of General Motors Corporation

FIG. 25-5.—The open-hearth furnace has a huge puddle of liquid metal heated from the top. The liquid metal is covered by a slag, which washes off undesirable impurities. The direction of the air flow is reversed frequently.

receives the liquid steel. Other metals that alloy with iron are added if necessary. The slag overflows into another ladle on one side.

The blast of the Bessemer converter and the tapping of an open-hearth furnace are two of the most brilliant sights in modern industry.

Comparison	Bessemer	Open-hearth	Other methods
Steel per charge	15–25 tons	100–200 tons	
Charges per day (24 hr)	30	2–	
Steel per day (24 hr)	600 tons	300 tons	
Lining	Usually silica, infrequently dolomite	Usually dolomite, sometimes silica	
Percentage of steel:			
1900	65.5	34.3	0.8
1935	7.5	90.5	2.0
1941	8.0	83.0	9.0

Crucible Steel. Starting with a good grade of pig iron, high-quality steel can be made by a careful hand process. The pig iron is melted in a small crucible. If carbon is to be removed, selected iron ore is added. If carbon is to be added, charcoal is put into the crucible. Alloying metals may be added as needed. When the desired sort of steel is obtained, the crucible is removed from the furnace. Crucible steel is used for some tools and watch springs. Only 6 tons in all of this steel was ordered in the United States in 1940. It is more expensive than Bessemer steel.

The Electric Furnace. (See Fig. 14-9.) Scrap steel is remelted in an electric-arc furnace. Three graphite electrodes carry an enormous surge of electric current, the source of the heat, making a hot sparking arc, flashing from one electrode to slag to metal to another electrode. From 1 to 25 tons of steel is made at each heat, depending on the size of the furnace. In this controlled process the impurities in the steel are readily converted into slag, for no hot oxidizing flame is present unless desired. The liquid steel is removed from the furnace by tipping the entire vessel. It is cast into strong, useful forms, such as frames for motors, pipe valves, and castings for turbines. Electric-furnace steel may be rolled and forged also. Nearly all steel used in airplanes is produced in this way.

QUESTIONS

18. What is the composition of pig iron?

19. How many 80-pound pigs make a 60-ton carload?

20. Distinguish white from gray cast iron in regard to carbon content.

21. What becomes of a sand mold after the iron has been poured into it?

22. What is a "pattern" (consult a dictionary)? Are patterns for cast iron the same size as the finished casting?

23. Account for wrought iron's very slow rate of rusting.

24. Of what sort of iron should one make (*a*) horseshoes; (*b*) manhole tops (for city streets); (*c*) fireplace andirons; (*d*) fireplace grates; (*e*) marine lanterns?

25. What is the increased cost per ton of steel containing 3 per cent chromium and 2.2 per cent vanadium?

26. List three parts of an automobile for which special alloy steels are used to enable them to withstand special types of forces.

27. Name two important methods of making pig iron into steel.

28. To what sort of pig iron is the Bessemer converter action well adapted?

29. Why is the lining of the Bessemer converter called acid and that of most open-hearth furnaces called basic?

30. When the relatively cool air strikes the liquid iron in a Bessemer converter, why does not the entire mass solidify?

31. Account for the sudden revival of interest in the Bessemer process in the United States during World War II.

32. Explain this sentence: The open-hearth process is more versatile than the Bessemer process.

33. About how many times more steel is made per charge in the open-hearth furnace than in the Bessemer converter? About how many times faster is the Bessemer process than the open-hearth?

34. What two compounds are formed in the slag when phosphorus-bearing pig iron is refined in a basic open-hearth furnace?

35. Just at the time when a furnace is tapped or steel is poured, pieces of aluminum are sometimes added. What useful purpose does the aluminum serve?

36. In the electric furnace, selected iron ore is sometimes added. What effect has the addition of ore on the percentage of carbon in the resulting steel?

37. If scrap steel averaging 0.5 per cent carbon is used for charging an electric furnace, the final product may have higher percentage carbon. From what source does the carbon come?

Processing Steel—Ingots. After steel is made by the open-hearth or the Bessemer process, it is cast into ingots—huge, white-hot masses of solid metal. The liquid metal freezes or solidifies within the ingot mold from the outside in. Obviously the ingot is not uniform and therefore is unsuited to rolling. To take care of this difficulty, it is placed within a large gas-fired furnace, called a ***soaking pit,*** until the temperature is equalized throughout the metal. The ingot is then passed between rollers in a machine, called a ***blooming mill,*** that squeezes and lengthens it. This process is continued through several mills until the steel is rolled into sheets, rods, rails, or beams. Wire is made by drawing a rod or larger wire through a die of hard steel, a carbide, or even a diamond as shown in Fig. 25-6.

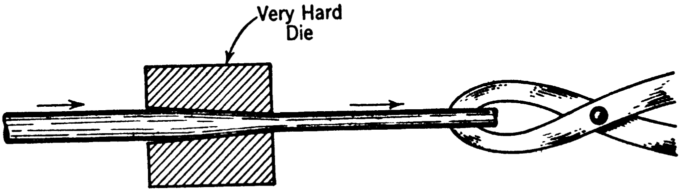


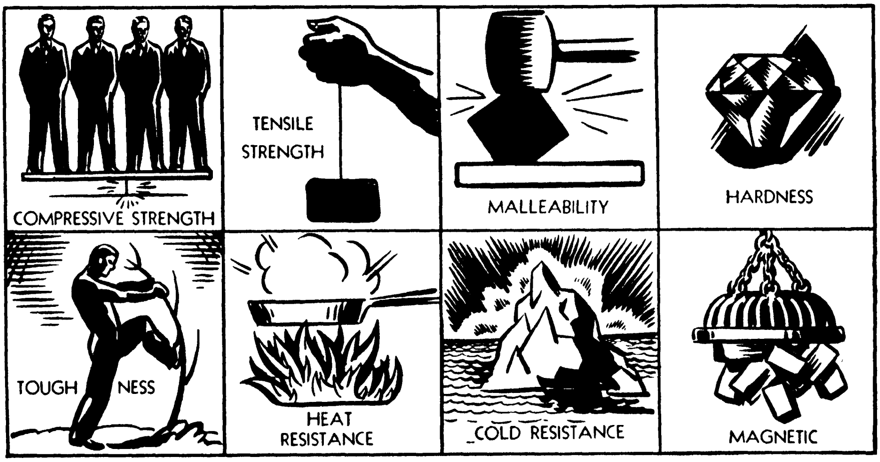
FIG. 25-6.—A wire becomes smaller in diameter and longer when it is drawn through a die. Only ductile metals will undergo this treatment without breaking.

Other methods of forming steel include melting and casting into sand molds, drop-forging heated metal, cold-rolling, and cold-forming.

The Steel Catalogue. In modern shop practice, steel is designated by a number system established by the Society of Automotive Engineers (SAE). The digit that designates the type of steel and other information about the steel are given in the following table:

Principal element	SAE digit	Properties and uses
Carbon:	1	
High 0.75–1.4%		Tools, springs—generally heat-treated
Medium 0.25–0.75%		Automobile axles, rails, car wheels—sometimes heat-treated
Low 0.05–0.25%		Bridge girders, automobiles, ships, buildings, nails
Nickel	2	Rolled structural steel, boiler plates, large castings
Nickel-chromium	3	Stainless steel, cutlery—hard, tough, shock resisting, corrosion resisting
Molybdenum	4	Automobile parts, leaf springs, drive shafts, bolts, gears
Chromium	5	Axles, steering knuckles, gears, files, axes, hammers, ball bearings
Chrome-vanadium	6	Casehardened parts—gears, springs, tools
Tungsten	7	Tools for machining steels—retains hardness when hot
Silicon-manganese	9	Leaf and coil springs

Two examples of steel numbers will illustrate the system. One steel number is 2 3 40. This is a nickel steel (observe the digit 2) with 3 per cent nickel and 0.40 per cent carbon. Steel number 7 13 60 meets the following specifications: tungsten steel (7) with 13 per cent tungsten and 0.60 per cent carbon. It can be seen that the last two or three figures tell the carbon content in hundredths of 1 per cent. The second one or two numbers give the percentage of the most important element in the steel.



Courtesy of General Motors Corporation

FIG. 25-7.—Some of the properties of metals.

The first digit of the number designates the type of steel as listed in the table.

Alloy Steels. Many different elements are introduced into melted steel to improve it for special uses. About 8 per cent of the steel in use today is alloyed with some element in addition to carbon. Manganese steel is considered an alloy only if above 1.65 per cent manganese.

An example of an alloy steel is high-speed tool steel of the following composition:

COMPOSITION OF HIGH-SPEED STEEL

Carbon	C	0.5– 0.8%
Tungsten	W	12.0–20.0%
Chromium	Cr	2.5– 5.0%
Vanadium	V	0.5– 2.5%

Only about 1.5 per cent of all the alloy steel is of this sort.

High-speed steel is very hard after heat-treating. Moreover, it will cut other steel and has the admirable quality of keeping its temper while red-hot. These quick-cutting tools in modern machines are an important factor in today's mass production of automobiles, airplanes, and household appliances.

One type of stainless steel, commonly used as blades for knives and metal for streamlined trains, contains 14 per cent chromium. This steel is also used for making kitchen pots and pans, food machinery, laundry machinery, and other objects that require strength, hardness, and rust resistance. The most common stainless steel contains 18 per cent chromium and 8 per cent nickel. It is nonmagnetic.

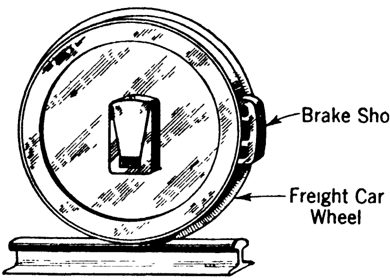


Fig. 25-8.—Tough manganese steel is used in the brake shoes that press against the steel rim of each rotating wheel to stop a train.

Armor plate is the 12 to 14 in.-thick metal wall, like a blister, about the hull of a battleship. It contains 3.3 per cent nickel and 1 per cent chromium, casehardened.

The brake shoes that rub on a train wheel to stop it (see Fig. 25-8) must be made of tough steel. Manganese (14 per cent) gives the required characteristics to this steel. Other uses for tough steel are the entering prongs of a power shovel (manganese-nickel steel), the steel jaws of rock crushers, and safes.

Almost every metal part of a modern automobile is made of a special steel. The axles contain chromium, the springs chromium and vanadium, the engine block nickel, and the drive shaft molybdenum. Strong, light wrenches used by mechanics are made of vanadium steel.

The one obstacle in the path of the wider use of alloy steels is their cost. Nickel costs about $700 a ton; tungsten, $3,500. Of course, only a relatively small amount of the alloying elements is present in a ton of alloy steel, but alloy steels cost more than plain carbon steel (see page 437).

Heat-treating. Take a girl's hair clip, or "bobby pin," and straighten it. Notice the springiness, or elasticity, of the wire. Now hold one end in a pair of forceps, and heat the metal to redness. Let the wire cool slowly until room temperature is reached again. Now, when the wire is bent, notice that the metal is inelastic, lifeless. We say that it has lost its temper.

Again, let us heat a hair clip to redness and while it is still hot plunge it into a jar of cold water. Now let us try to bend the steel. It snaps readily. In fact, a piece ½ in. long can be broken in the fingers. It is as brittle as a clay pipestem.

If we wish to make steel suitable for a woodcutting chisel, we harden the steel, containing 1.3 to 1.5 per cent carbon, preferably in the upper part of the range 700 to 770°C, just as in the experiment with the hair clip. Then we reheat it to a mild temperature and let it cool slowly. Some hardness is subtracted and greater toughness imparted, and the steel is said to be tempered. Heating to a higher temperature in the tempering process subtracts more of the hardness, leaving the steel less brittle and tougher.

To make a wood saw in which the steel is both tougher and more flexible than that in the chisel, we select a steel of a lower percentage carbon. It is hardened and then tempered at a higher temperature than the chisel.

Heat-treating may increase the strength of steel as much as threefold, besides having a marked effect on the hardness of the steel. The International Nickel Company reports that steel SAE 3140 (1 per cent Ni, 0.40 per cent C) has tensile strength of almost 250,000 lb per sq in. when tempered at 400°F but only 105,000 lb per sq in. when tempered at 1300°F. An ordinary structural girder has tensile strength of 75,000 lb per sq in.

Surface-treating Steel. When steel is packed in a carbonaceous material (see page 510) and heated, carbon penetrates the steel a short distance. The higher carbon alloy formed on the exterior of the piece gives the steel a hard-wearing surface. A similar effect may be produced by heating the steel in melted cyanide (KCN, for example). Steel so treated is ideal for gears (see Fig. 25-9) and files that need a hard-wearing surface and a tough interior. Steel treated in this way is said to be ***casehardened.***

Special alloy steels may be hardened by heating them in an atmosphere of ammonia. This process is called ***nitriding.*** The ammonia decomposes to form nitrogen and hydrogen.

$$2NH_3 \rightarrow 2[N] + 3H_2$$

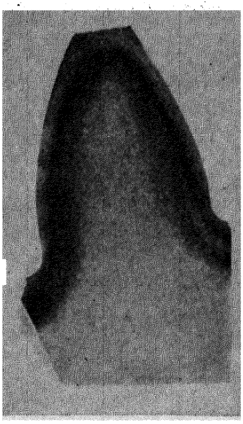
The nitrogen unites with elements other than iron, chiefly aluminum or vanadium in the steel, forming nitrides. These compounds give the steel a corrosion-resistant surface, as well as a hard one.

SUMMARY

Iron is the most important metal. The economical commercial production of iron depends on the nearness of coal, limestone, and ore to each other and to markets.

Iron is widely distributed; it is found in most soils, plants, and animal bodies. The principal ores are Fe_2O_3, hematite; $2Fe_2O_3 \cdot 3H_2O$, limonite; $FeCO_3$, siderite; Fe_3O_4, magnetite.

Commercial iron is produced in a blast furnace. It contains about 5 to 8 per cent impurities, including carbon, manganese, sulfur, phosphorus, and silicon. The blast furnace input is coke, ore, limestone, and preheated air; the blast furnace output is pig iron, slag, and gases. Iron oxides are reduced by hot carbon monoxide or hot carbon in a blast furnace, and slag is formed by the reaction between limestone and silica or silicates in ore.



Courtesy of General Motors Corporation

FIG. 25-9.—This cut section of a case-hardened gear tooth shows the extent of penetration of carbon in the hard-wearing exterior or case. Case-hardened gears are used in automobiles.

Remelted pig iron is called cast iron; it may be gray, white, or malleable. Iron is easily cast, has great strength to withstand steady force, but is brittle to shocks. It is used for machine bases and some water pipes and for stove grates.

Wrought iron is pig iron heated on a bed of ore while the slag is puddled into the mixture. Wrought iron is tough and malleable and rusts very slowly. It is used for marine and ornamental hardware, some water pipes, and chains.

Steel is commercial iron purified by oxidizing the impurities. Steel is strong and elastic; many alloys of steel are formed. It has a wide range of properties available by alloying with various metals. Steel is used for automobiles, ships, military purposes, railroads, and building construction.

In the Bessemer process heated air is blown through liquid iron in a pear-shaped converter that has a perforated false bottom. Impurities are oxidized. This is a rapid process of making steel, one that is good for iron low in sulfur and phosphorus.

In the open-hearth process, fuel gases are burned over a puddle of steel and slag. The impurities, including phosphorus, are burned out or go into slag. This is a relatively slow process, but one carefully controlled and easily adapted to special needs. An electric furnace refines steel. It has controlled conditions, it removes sulfur, and it is adapted to making alloy steels.

The fabrication of steel is a big business. The steps are as follows: ingots cast; equalized in temperature; rolled into sheets, rods, or rails; or cast into molds; or forged by powerful hammers.

Steel is designated by an SAE number classification system in which the last two (or three) digits represent the percentage of carbon.

Alloy steels develop special properties, such as toughness, hardness, resistance to corrosion, and resistance to fatigue. Examples are stainless steel, 18 per cent Cr, 8 per cent Ni; manganese steel, 14 per cent Mn for very tough steel; light strong tools of steel may contain vanadium.

The properties of steel are controlled to a large measure by heat-treatment, which regulates the relationship of the carbon to the iron, influences grain size and structure, and controls other factors. Hardening is accomplished by sudden cooling of hot steel. Tempering is done by reheating, but not to as high a temperature as when hardened, and cooling slowly.

Surface treatment of steel may give a hard, wear-resisting surface. Case-hardening, in effect, adds carbon to the outside portion of a steel object. Nitriding converts the surface in part to metallic nitrides.

QUESTIONS

38. When white-hot steel is rolled between steel rollers in a mill, what prevents the mill rolls from melting and sticking to the steel being processed?

39. Describe the steps needed to change open-hearth steel into plates for battleship armor.

40. Describe the steps needed to change Bessemer steel into railroad rails.

41. A certain steel used for propeller shafts contains 3 per cent nickel and 0.4 per cent carbon. What is its SAE number?

42. Tell the composition of Bessemer screwstock, 1112; fatigue-resisting steel, 3335; rear-axle stock, 4140; stainless steel, 30905.

43. A modern battleship displaces 35,000 tons. Let us assume that 5 per cent of its weight is armor plate. What weight of nickel is needed for this purpose alone in constructing a battleship?

44. A hoe was used to tend a bonfire. It became red-hot in the fire, and afterward it did not cut weeds as well. Explain.

45. Can nails that are collected from waste wood ashes be straightened and used again successfully?

MORE CHALLENGING QUESTIONS

46. In manufacturing steel files, what treatment is given them so that they will cut well?

47. An electric furnace operates about one-half the time during a 2-hour heat. If 4000 amperes at 110 volts is drawn from the transformer, how many calories (Cal) of heat are supplied by the current? (See top of next page.)

$$H\ (\text{Cal}) = \frac{0.239\ I^2\ (\text{amperes})\ R\ (\text{ohms})\ t\ (\text{sec})}{1000} \qquad R = \frac{E\ (\text{volts})}{I}$$

48. A furnace contains 10 tons of steel containing 5 per cent manganese. What weight of steel, 50 per cent manganese, should be added so that the final mixture will contain 14 per cent manganese?

49. What alloy is used for (*a*) hacksaw blades; (*b*) high-speed cutting tools; (*c*) leaf springs for trucks; (*d*) sewing needles?

50. Make a miniature of either a Bessemer converter or an open-hearth furnace.

51. Report on the advertising of steel manufacturing companies in popular magazines. Since these companies sell nothing directly to retail trade, often these advertisements are sources of general information. Point out the messages from several of the advertisements.

52. Investigate and report on "sponge iron."

UNIT SIX - - - - - - - - - - - - - - CHAPTER XXVI

THE LIGHT METALS

When Napoleon III (1808–1873), nephew of Napoleon Bonaparte, dined in state, his guests had to be content to use gold forks. Napoleon himself used an aluminum fork; only the great were privileged to use such an expensive and light metal as aluminum.

The price of aluminum was $545 per pound in 1852. In 1862 one of its first uses is recorded: the baby's rattle for the Princess Imperial of France was made of aluminum. By that time the price of aluminum had dropped to $16 per pound. A few years later the quantity of the metal produced increased very markedly, and the price dropped continuously. Today aluminum costs only about 15 cents per pound.

Public attention was drawn to aluminum in 1876 when the Washington Monument was capped with this metal. Recent inspection of the cap showed the metal to be in good condition after more than 60 years of exposure to the weather.

Napoleon's interest in aluminum was not mainly for eating utensils. After dragging heavy iron military equipment over a great part of Europe, the possibility of using a light but strong metal instead of iron for military purposes was a welcome idea. Steel is 2.8 times denser than aluminum.

In the development of the dirigible type of aircraft, Count Zeppelin needed a strong light alloy. To meet this and other demands, an alloy called ***duralumin,*** or dural, was developed in Germany. It contained 4.0 per cent copper, 0.5 per cent magnesium, 0.5 per cent manganese, and the remaining 95 per cent commercial aluminum. The superior strength of the alloy is attained by a novel method of heat-treatment. The finished metal has approximately the strength of boiler steel, tensile (pull-apart) strength 62,000 lb per sq in., and about one-third its weight.

The making of duralumin increased the demand for magnesium. Then, in an effort to make lighter, and yet strong, metals, experiments were

---

New Terms

duralumin
Hall process
Thermit
bauxite
alumina
cryolite
magnesia

performed to find out the properties of magnesium and its alloys. The aluminum alloys are about 1.6 times denser than magnesium alloys. Alloys of both aluminum and magnesium are used extensively in the manufacture of airplanes. The demand for them is extending to other fields, also, where both lightness and moderate strength are required.

Thus a scientific and a military motive prompted the investigation of the lighter metals. Both aluminum and magnesium are abundant; in fact, aluminum is the most abundant of all the metals. No shortage of raw materials for the production of magnesium is foreseen, for today they are being extracted from sea water. It is interesting to note that a period of over 50 years elapsed between the first isolation and the commercial production of both aluminum and magnesium.

Aluminum

Aluminum's Infancy. The isolation of metallic aluminum was first announced in 1825 by Hans Christian Oersted (1777–1851), a Danish physicist and chemist. He replaced aluminum from its fused chloride by the active metal potassium in the form of an amalgam.

$$AlCl_3 + 3K \rightarrow 3KCl + Al$$

The arrival of the new metal created no more interest than the arrival of a new baby in a distant city. It was interesting only to those interested in it.

Thirty years later (for new metals mature slowly) the supply of the metal was large enough for it to venture into the Paris Exposition. There, in 1855, was displayed a bar of the silvery metal made by chemical reduction, but by using sodium instead of potassium to act on the aluminum chloride.

At Oberlin, Ohio. When Prof. Frank F. Jewett of Oberlin College remarked in one of his lectures that the discoverer of a cheap method of extracting aluminum from its ore would be a great benefactor to mankind as well as the gainer of a fortune for himself, the thought captured the imagination of his pupil, Charles Martin Hall (1863–1914). After graduation, Hall went to work in the family woodshed with a homemade apparatus, experimenting to meet the challenge. When he was only twenty-two years old, after many discouragements he found a method for extracting aluminum by using electricity.

Hall's successful method was the electrolysis of aluminum oxide dissolved in a bath of molten cryolite. He also discovered that the cathode of the apparatus should be a carbon-lined container.

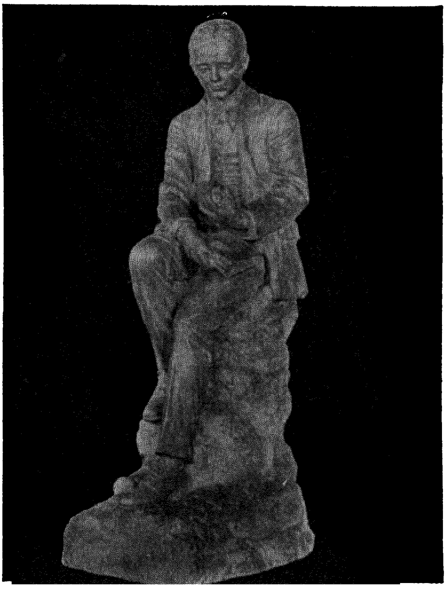
At almost the same time, in 1886, a young man in France, Paul Louis Toussaint Héroult (1863–1914), discovered a method of making aluminum. (See Fig. 26-1.) He applied for a United States patent on his process. Imagine his surprise to learn that Hall had worked out the identical process independently in the United States just before him. These coincidence twins, Hall and Héroult, born the same year, might have become bitter rivals. Instead, they cooperated. Incidentally, they died in the same year.

Today a life-sized statue of Charles Martin Hall, appropriately enough cast in aluminum, is located in the chemistry laboratory of Oberlin College. (See Fig. 26-2.) The young inventor never forgot the college from which his inspiration came. After Prof. Jewett's prediction had been fulfilled and fame and fortune had come to him, he gave generously to the college.

Also Ran. A third competitor in the race to make cheap aluminum deserves notice. He was an American named Hamilton Y. Castner. He reasoned that cheaper sodium would make cheaper aluminum. He was correct. Moreover, in 1886 he developed a process for making sodium cheaply by electrolysis. Making aluminum by the use of sodium is, however, costlier than by the Hall-Héroult process, and therefore the method of Castner was abandoned. Castner's experience was put to good account, nevertheless, and soon he was producing cheap metallic sodium by the electrolysis of melted sodium hydroxide.

Courtesy of Aluminum Company of America

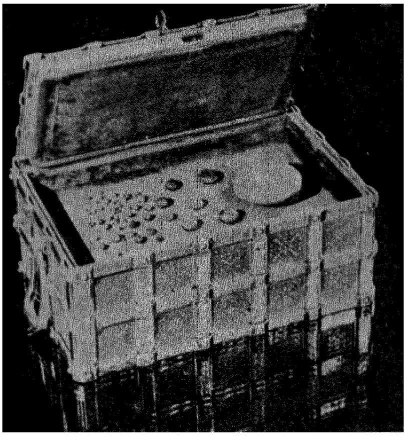
FIG. 26-1.—Paul Louis Toussaint Héroult (1863–1914) discovered the same commercial method for extracting aluminum as did Charles Hall. Compare Hall's and Héroult's dates of birth and death.



Courtesy of Aluminum Company of America

FIG. 26-2.—Charles Martin Hall (1863–1914) was the discoverer of a commercial method for the extraction of aluminum. His life-size statue in cast aluminum now stands in the Severance Chemical Laboratory, Oberlin College, Oberlin, Ohio.

Where Aluminum is Found. Aluminum is never found free in nature. Consequently it was unknown to peoples in ancient civilizations. It is a metal associated with twentieth century life. Its compounds, chiefly oxides and silicates, are abundant. Common clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), bauxite ($Al_2O_3 \cdot 3H_2O$), alunite ($K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$), and corundum ($Al_2O_3$) are well-known aluminum compounds. Cryolite (Na_3AlF_6), the "ice stone," found in Greenland, is important in the making of aluminum.

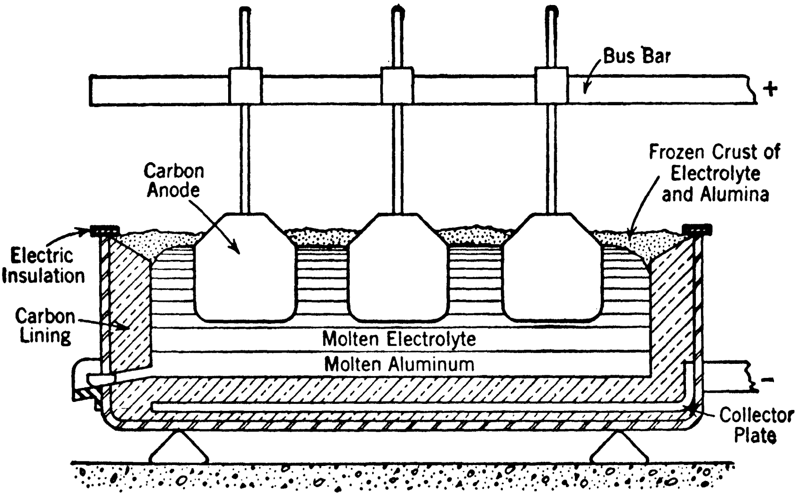


Courtesy of Aluminum Company of America

FIG. 26-3.—The original globules of aluminum obtained by experimenter Hall in his first successful electrolysis.

Bauxite, the chief ore of aluminum, is produced in the United States in Alabama, Arkansas, and several other states. France, Hungary, British and Dutch Guiana, and many other regions have good supplies of bauxite. The mineral is mined both by the underground tunneling and by the open-pit method.

Preparing Aluminum Ore. Crude bauxite is crushed, dried, and treated with sodium hydroxide solution in a chemical purification process.



Courtesy of Aluminum Company of America

FIG. 26-4.—The electrolysis of alumina dissolved in fused cryolite takes place in a carbon-lined steel cell. Carbon anodes hang into the cell. The metal is withdrawn from the bottom at intervals.

It is necessary to change the mineral into almost pure ***alumina*** (Al_2O_3) before using it in the production of aluminum. The chief reactions in the process are as follows: (1) Dissolving crude bauxite in caustic soda.

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

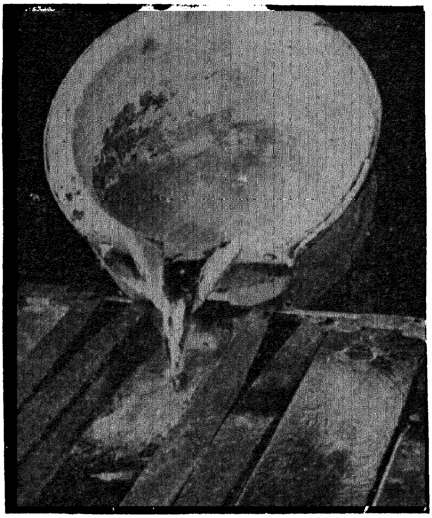
(2) Precipitating aluminum hydroxide from the sodium aluminate solution by slow cooling.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 \downarrow + NaOH$$

(3) Dehydrating the precipitate by intense heat.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

Making Aluminum. The furnace for making aluminum (see Fig. 26-4) is a rectangular steel box or pot, lined with carbon, that serves as the cathode. Molten cryolite (Na_3AlF_6) with a little fluorspar (CaF_2) is the electrolyte; aluminum oxide (Al_2O_3) is added from time to time as needed. Anode rods of graphite are suspended in the electrolyte. When current is passed through the electrolyte, liquid aluminum (m.p. 660°C) collects at the bottom of the furnace. The furnace is tapped daily for this metal. Oxygen is deposited on the anodes, causing them to burn.



Courtesy of Aluminum Company of America

FIG. 26-5.—Molten aluminum from the Hall cell is poured into ingot molds to harden for shipment.

4 lb bauxite	($Al_2O_3 \cdot 3H_2O$) makes
2 lb alumina	(Al_2O_3), which produces
1 lb aluminum	(Al)

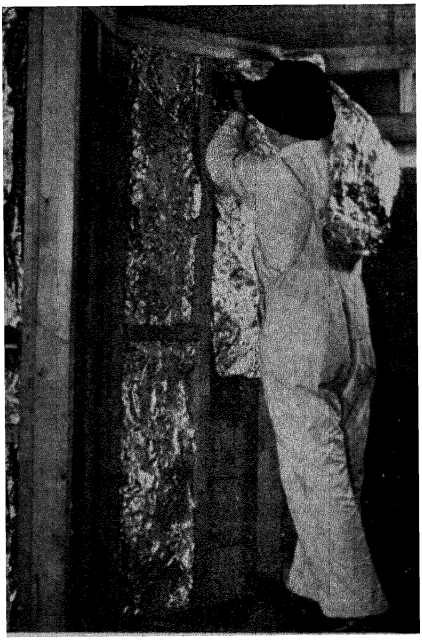
Three-fourths of a pound of carbon electrode is also used up in the process, and 12 kilowatt-hours (kw-hr) of electricity. Total production of aluminum in the world in 1939 was about 650,000 metric tons of 2205 lb each. In 1943 the production of the metal in the United States alone was over 2 billion pounds as a result of military demands.

The industry is one of the largest consumers of electricity. Aluminum-extraction plants are usually located near a source of electricity from water power.

Physical Properties of Aluminum. Aluminum is a silvery metal that is light, ductile, and malleable. It can be hardened and strengthened

Courtesy of Aluminum Company of America

FIG. 26-6.—Forging an aluminum-alloy propeller blade is a convenient way of rough-shaping the metal.



Courtesy of Aluminum Company of America

FIG. 26-7.—This workman is applying metallic aluminum-foil insulation in a home. Aluminum is a good reflector of radiant heat; hence it acts as an insulator. Aluminum is also a good conductor of heat.

by alloying with other metals. It can be fabricated by rolling, drawing, extruding, casting, forging (see Fig. 26-6), and machine cutting—in fact, by all known methods of metal working. It can be welded electrically and by the torch. It is an excellent conductor of both heat and electricity. Aluminum exceeds copper, weight for weight, as a conductor of electricity, but copper is a better conductor size for size.

The density of aluminum is 168 lb per cu ft. A cubic foot of water weighs 62.4 lb. We say that the specific gravity of aluminum is $\frac{168}{62.4}$, or 2.7, its weight relative to the weight of an equal volume of water.

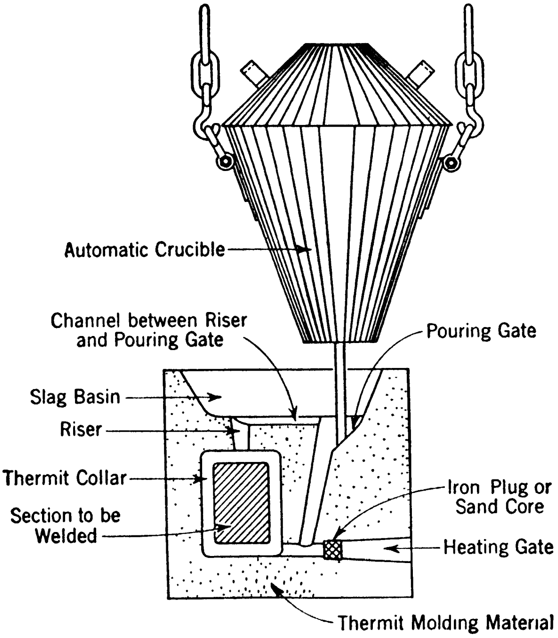
Pure aluminum melts at 660°C. Its shiny surface is a good reflector of radiant heat. Hence aluminum foil is used in insulating homes and mechanical refrigerators. (See Fig. 26-7.) Aluminum is nontoxic; and this fact, together with its strength, lightness, and durability, makes it an excellent material for the construction of cooking utensils.

Chemical Activity of Aluminum. Aluminum, when freed of its oxide film, acts readily on hot water, liberating hydrogen.

$$2Al + 6H_2O \rightarrow 3H_2\uparrow + 2Al(OH)_3$$

To observe this action, scratch aluminum with sandpaper while it is under mercury. Keep the surface of the aluminum away from air until the hot air is added above the mercury.

Everyone knows, of course, that an aluminum kettle does not act chemically on water boiling in it; that is, hot water does not seem to attack aluminum. The explanation of the difference between this case and the one above is that aluminum is protected from the corrosive action of the water by a hard, tightly adhering skin, a film of aluminum oxide (Al_2O_3).



Courtesy of Metal and Thermit Corporation

FIG. 26-8.—The arrangement of mold and crucible when a Thermit weld is being made.

Aluminum powder burns with a bright flash when it is tossed into a flame.

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

A dilute acid dissolves the oxide film on aluminum and readily attacks the metal beneath. The action of hydrochloric acid on aluminum, liberating hydrogen, may be considered typical.

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow$$

Sodium or potassium hydroxide solution, each a strong alkali, acts vigorously with aluminum to produce hydrogen. The action is represented by the following equation:

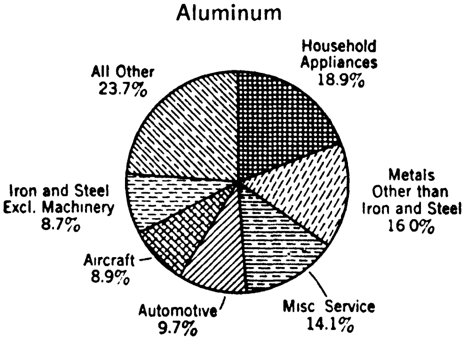
$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2\uparrow$$

The Goldschmidt Process. The strong affinity of aluminum for oxygen is spectacularly illustrated by the vigorous reducing action of the metal. A mixture of powdered aluminum and iron oxide (Fe_2O_3 or Fe_3O_4) is sold under the name of ***Thermit.*** When brought to a high enough temperature, the mixture reacts violently, liberating so much heat in such a short period of time that the iron formed is in a liquid state. (See Fig. 26-8.)

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \text{ (at 1650°C)}$$

The liquid iron formed by this reaction can be run into properly prepared molds to weld breaks in steel that are difficult to repair by any other method. By adding other substances, an iron alloy of the correct composition for the weld can be made.

Chromium and managanese are produced from their oxides by the use of aluminum as a reducing agent. This process was discovered and developed by the experimenter, Hans Goldschmidt (1861–1923).



Courtesy of Dun and Bradstreet, Inc.

FIG. 26-9.—Character of normal aluminum consumption.

Aluminum Alloys. Aluminum is alloyed with such metals as copper, magnesium, silicon, zinc, manganese, and chromium. More than 30 different alloys are now in extensive commercial use. Duralumin (composition already given, page 449) is a strong aluminum alloy that obtains its maximum strength by heat-treating. An even stronger alloy, developed in the United States and known as alloy No. 24S, is used extensively in airplane construction.

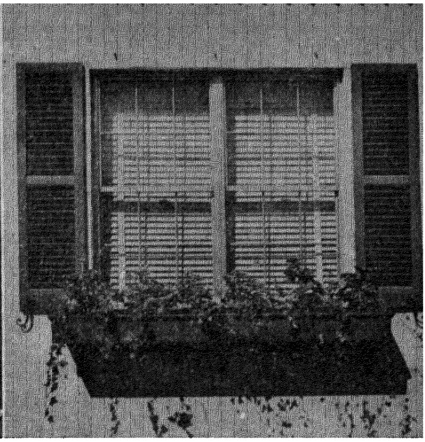
Cooking utensils are commonly made from an alloy containing 1.25 per cent manganese and 98.75 per cent commercial aluminum.

Uses of Aluminum. In addition to cooking utensils and household equipment such as vacuum cleaners, aluminum is extensively used in transportation vehicles, such as aircraft, automobiles, trucks, and railway cars; in architectural applications; and in thousands of manufactured products.

Flake aluminum makes a good paint pigment either alone or mixed with other pigments. Aluminum foil is used for candy wrapping, insula-

Courtesy of Aluminum Company of America

FIG. 26-10.—Air transportation depends upon light, strong metals.



Courtesy of Aluminum Company of America

FIG. 26-11.—Window frames and sash made of aluminum alloy permit wide vision.

tion in homes, boilers, and naval vessels. Aluminum wire and bus bars are widely used in electrical work. Enough steel-cored aluminum cable is used to girdle the globe at the equator twenty-four times.

QUESTIONS

1. What percentage of the earth's crust is estimated to be composed of aluminum?

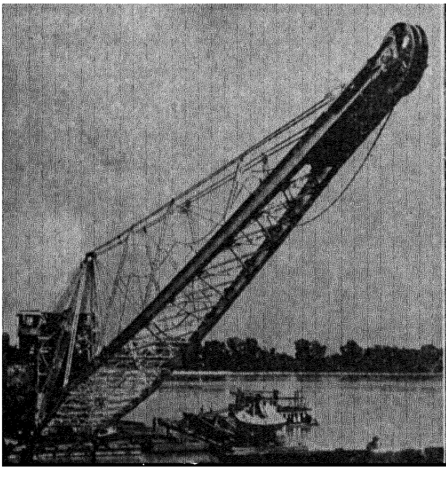


FIG. 26-12.—The 240-foot dredge boom is made of structural aluminum alloy.

Courtesy of Aluminum Company of America

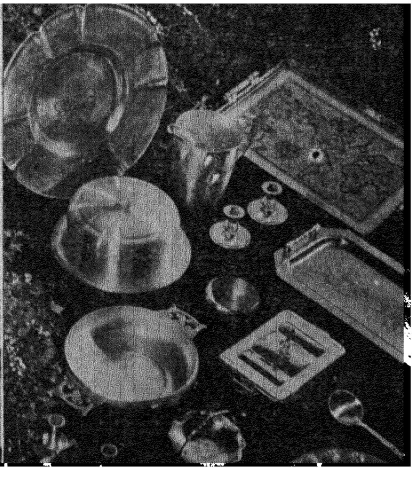


FIG. 26-13.—This attractive giftware is made of aluminum alloy.

Courtesy of Aluminum Company of America

2. Why are many aluminum-producing factories located near river dams?

3. Aluminum, an abundant metal, was unknown to ancient peoples, while gold, a rare metal, was well known. Explain this apparent contradiction.

4. Make a labeled diagram of the Hall electrolysis furnace for producing aluminum.

5. In the preparation of aluminum by the Hall process, what purpose is served by (*a*) alumina; (*b*) cryolite; (*c*) carbon?

6. Write equations for Castner's process: (*a*) electrolysis of fused sodium hydroxide to form metallic sodium; (*b*) replacement of aluminum in aluminum chloride by metallic sodium.

7. Why does the Hall process produce relatively pure aluminum?

8. Write formula equations for the action of aluminum hydroxide (*a*) with sodium hydroxide solution; (*b*) when heated strongly; (*c*) when mixed with sulfuric acid.

9. Four pounds of bauxite ($Al_2O_3 \cdot 3H_2O$) eventually produces 1 pound of metallic aluminum, indicating that aluminum is 25 per cent of bauxite. (*a*) What is the actual percentage of aluminum in bauxite? (*b*) What is the percentage effectiveness of the recovery of the metal from the ore?

10. What properties of aluminum account for its popularity for kitchen utensils?

11. What properties of aluminum foil account for its effectiveness for insulation?

12. A camper placed a bright, shiny aluminum frying pan over a charcoal fire but could not get the pan warm enough to fry an egg. Then he dirtied the bottom of the frying pan and had no more trouble in cooking. Explain.

13. How many kilowatt-hours of electricity are needed to produce 2 billion pounds of aluminum?

14. How many times the specific gravity of aluminum is (*a*) mercury (13.6); (*b*) iron (7.2)?

15. Write equations for the reactions of aluminum with (*a*) hydrochloric acid; (*b*) dilute sulfuric acid; (*c*) sodium hydroxide solution; (*d*) oxygen; (*e*) chlorine.

16. Write equations for the reactions of aluminum as a reducing agent on (*a*) vanadium oxide (V_2O_5); (*b*) titanium dioxide (TiO_2); (*c*) nickel oxide (NiO): (*d*) molybdenum oxide (MoO_3); (*e*) silica (SiO_2).

17. List two important aluminum alloys, and give their composition.

18. What weight of aluminum can be made from $\left\{\begin{matrix}204\\408\end{matrix}\right.$ pounds of alumina, assuming that all the metal is recovered?

19. What weight of pure alumina must be supplied to a Hall cell that produces $\begin{cases}240\\270\end{cases}$ pounds of aluminum daily?

20. An aluminum pig weighs $\begin{cases}48\\50\end{cases}$ pounds. How many pounds of carbon were consumed in its manufacture?

21. What increase in weight is noted when $\begin{cases}9\\27\end{cases}$ grams of aluminum is converted to aluminum nitride (AlN)?

22. What volume of ammonia must be decomposed in order to provide the nitrogen needed for the preceding problem?

Magnesium

The Story of Magnesium. In 1808, Sir Humphry Davy first prepared impure magnesium by electrolysis. In 1830 it was produced in a purer form by replacing the metal from its chloride by the use of potassium. For many years it remained a laboratory curiosity. Commercial production of the metal developed first in Germany, then later in the United States. For many years its chief use was in flash powders for photographers.

Where Magnesium Is Found. Magnesium is the third most abundant metal. Because, like aluminum, it is never found free in nature, it is a metal associated with modern times.

Its compounds are very abundant. Perhaps the best-known compound of magnesium is Epsom salts ($MgSO_4 \cdot 7H_2O$), which is found in solution in the waters of many mineral springs and even as the solid crystals in salt deposits. The mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) is obtained from the famous Stassfurt mines in Germany. This compound is used as a source of magnesium. Magnesium compounds in sea water are used today as a starting material in making magnesium metal.

Magnesite ($MgCO_3$) and dolomite, or dolomitic limestone ($MgCO_3 \cdot CaCO_3$), are found as huge mountain masses of rocks in the Alps and elsewhere. Complex magnesium silicates include asbestos, a fibrous rock used in insulation, and soapstone and talc, used for sinks and, when ground, for talcum powder.

Preparation of Magnesium. Like aluminum, magnesium is prepared commercially by electrolysis of a fused compound in the absence of water. Anhydrous magnesium chloride from carnallite or from brine is melted, and this liquid salt (m.p. 708°C) is the electrolyte. The metal gathers at the cathode, where, while hot, it must be protected from contact with the air. (See Fig. 26-14.) The change brought about by the electrolysis is

$$MgCl_2 \rightarrow Mg + Cl_2\uparrow$$

In another modern process, magnesite is heated to form magnesia.

$$\underset{\text{magnesite}}{MgCO_3} \rightarrow \underset{\text{magnesia}}{MgO} + CO_2\uparrow$$

The magnesia, mixed with carbon, is now heated to 2000°C in an electric-arc furnace.

$$MgO + C \rightleftarrows Mg\uparrow + CO\uparrow$$

The hot vapors containing magnesium and carbon monoxide are chilled rapidly to 200°C in a blast of hydrogen or natural gas. The result is magnesium dust, which can be purified by distillation at 750 to 950°C under reduced pressure. The method is not without dangers, however, and explosions have occurred.

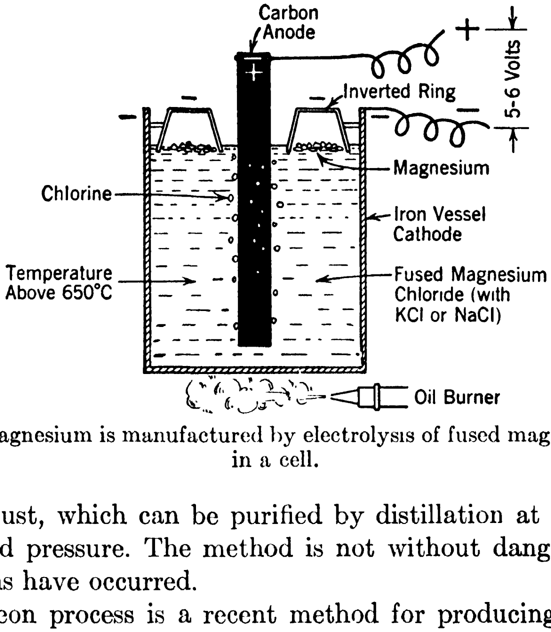


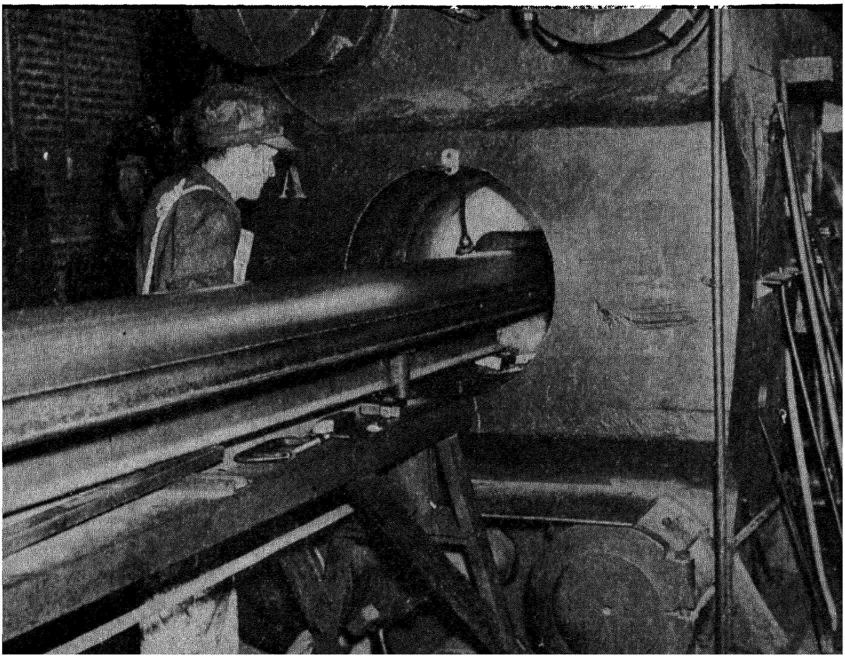
FIG. 26-14.—Magnesium is manufactured by electrolysis of fused magnesium chloride in a cell.

The Pidgeon process is a recent method for producing magnesium. A mixture of ferro-silicon alloy (75 per cent silicon) and dolomitic lime (MgO and CaO) is heated to 1150°C *in vacuo*. The magnesium vapor, liberated by the chemical reduction of the magnesium oxide, condenses in stainless-steel condensers. While this process at present is more expensive to operate than the electrolytic process, it has the advantage of requiring only small installations.

The total production of magnesium was 2120 tons in 1935, 6250 tons in 1940, 50,000 tons in 1941, and 290,000 tons in 1944.

Description of Magnesium. Magnesium is a remarkably light, silvery metal; its density is only 1.74 times that of water at 20°C. It melts at 650°C.

The Strongest Light Alloy. In the United States, the principal magnesium alloys in use contain aluminum, zinc, and manganese. For example, an alloy commonly used for extruded angles, I-beam sections, and the like, has 6.5 per cent aluminum, 0.8 per cent zinc, and 0.2 per cent manganese. When worked and heat-treated, it has a tensile strength of 44,000 lb per sq in. An alloy used for sand castings contains 6 per cent aluminum, 3 per cent zinc, and 0.2 per cent manganese; its strength is 35,000 lb per sq in.



Courtesy of The Dow Chemical Company

FIG. 26-15.—In the same manner that toothpaste is squirted from a tube, magnesium alloy (Dowmetal) is extruded from the opening of this powerful machine.

Light magnesium alloys are used for typewriter and camera parts; airplane parts; wheelbarrow, truck and bus bodies; and even for the stratosphere flight gondola of the National Geographic Society–United States Army Air Corps (1935). (See Fig. 26-16.)

Chemistry of Magnesium. Piles of magnesium chips or turnings from a machine on which magnesium is being cut constitute a fire hazard, for they may catch fire from the heat developed by friction at the cutting tool in the machine. Such chips burn with a brilliant flash and intense heat, forming a white powder. Magnesium confined in oxygen makes a good photo-flash.

Courtesy of the Dow Chemical Company

FIG. 26-16.—A gondola fabricated from magnesium alloy (Dowmetal) was used in a famous stratosphere exploration ascension.

The white powder formed when magnesium burns is chiefly magnesium oxide (MgO), magnesia, but some magnesium nitride (Mg_3N_2) is also produced, for the hot metal combines with nitrogen as well as with oxygen.

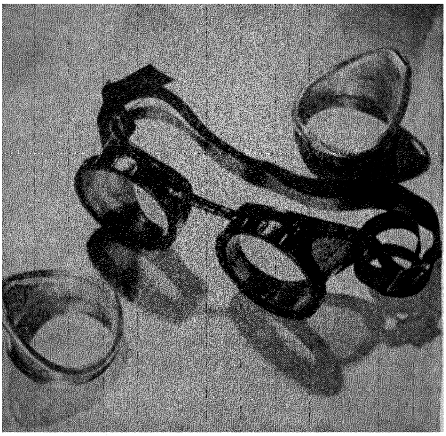
$$2Mg + O_2 \rightarrow 2MgO$$
$$3Mg + N_2 \rightarrow Mg_3N_2$$

An ordinary carbon dioxide type of fire extinguisher does not put out a magnesium fire readily, for hot magnesium burns in carbon dioxide.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

or possibly

$$Mg + CO_2 \rightarrow MgO + CO$$



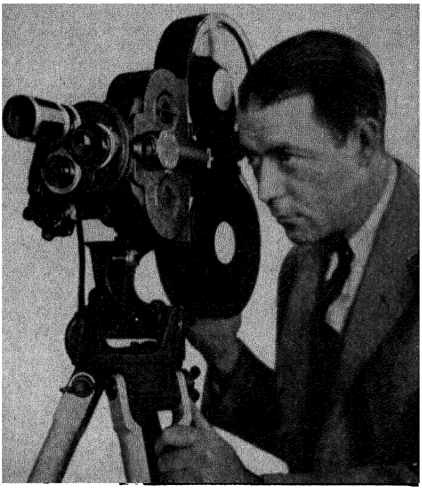
Courtesy of The Dow Chemical Company

FIG. 26-17.—Light, strong magnesium alloy (Dowmetal) is an ideal metal for constructing featherweight safety goggles.

Nor will water in relatively small amounts put out the fire; for steam acts on the metal, or the metal will act slowly on hot water.

$$Mg + H_2O \rightarrow MgO + H_2\uparrow$$
$$MgO + H_2O \rightarrow Mg(OH)_2$$

The surface of this active metal tarnishes slowly in air to form a white covering. Salt water is a corroding agent, and most acids, even weak ones, act on magnesium with rapid evolution of hydrogen gas. Often enough heat is produced to cause steam if the acid has water with it.



Courtesy of The Dow Chemical Company

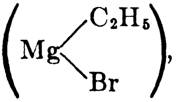
FIG. 26-18.—In fine motion picture cameras and projectors, a light, strong magnesium alloy (Dowmetal) is used.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow$$

Treatments with hot solutions containing chromates produce coatings on the metal that help resist corrosion.

The Incendiary Bomb. Much attention has been drawn to the metallic incendiary bomb used in warfare. A common type is the 1-kilogram (kg) (2.2-lb) magnesium bomb. (See Fig. 26-19.) This bomb is detonated by a fuse (striking head) that explodes when the bomb lands. This, in turn, ignites a small charge of Thermit, which sets the magnesium on fire. Incendiary bombs of this sort have caused extensive damage, especially if dropped from airplanes on buildings already damaged.

The simplest manner of controlling metallic incendiary bombs that have been ignited is to let them burn out without setting other fires. In general, either a spray or a stream of water hastens the burning of the magnesium. At the same time the surroundings are kept wet, preventing spreading of the fire.

Uses of Magnesium. In addition to uses already mentioned, metallic magnesium is used extensively as an agent in chemical synthesis. Organic compounds of magnesium, such as magnesium ethyl bromide  $\left(Mg\begin{matrix}C_2H_5\\Br\end{matrix}\right)$, are easily made, and they are reactive. By using these so-called Grignard compounds, chemists have produced superior drugs, dyes, and perfumes—some of the triumphs of modern chemical research.

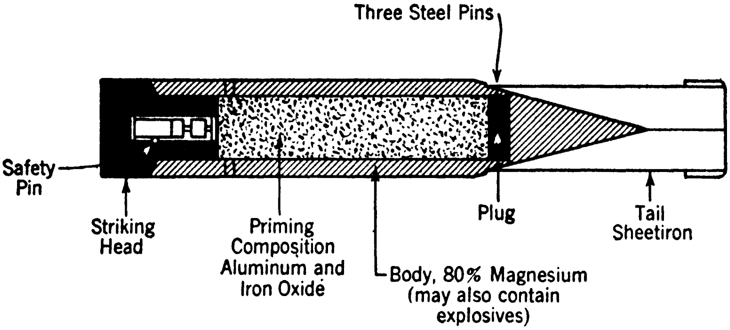


FIG. 26-19.—The magnesium incendiary bomb is used in military operations for setting fires.

QUESTIONS

23. What properties of magnesium account for its never being found free in nature?

24. What is the percentage of magnesium in (*a*) magnesite; (*b*) dolomite; (*c*) magnesia?

25. Give a use for each of the following: (*a*) asbestos; (*b*) magnesia; (*c*) dolomite; (*d*) Epsom salts; (*e*) talc.

26. In the process of preparing magnesium from sea water (*a*) oyster shells are heated in a kiln; (*b*) the resulting lime is slaked; (*c*) the slaked lime is added to sea water containing magnesium chloride, precipitating magnesium hydroxide; (*d*) the precipitate is treated with hydrochloric acid; (*e*) the resulting magnesium chloride (after dehydration) is decomposed by electrolysis. Write equations for the five chemical changes in the process.

27. In the ferro-silicon process for making magnesium, announced through the Canadian National Research Council (*a*) dolomite is roasted; (*b*) the resulting magnesia is treated with silicon (by means of ferro-silicon) and then distilled from the mixture *in vacuo*. Write equations for the two chemical changes in this process.

28. Write equations for the action of magnesium on (*a*) hydrochloric acid; (*b*) dilute sulfuric acid; (*c*) oxygen; (*d*) carbon dioxide; (*e*) water; (*f*) nitrogen; (*g*) chlorine.

29. Give four examples of uses for magnesium alloys.

30. (*a*) Why are magnesium fires so hard to extinguish? (*b*) What materials are used to smother magnesium fires?

31. When magnesium chips are burning around a machine, which is the more satisfactory fire extinguisher, sand or graphite?

32. What weight of metallic magnesium can be made from $\begin{cases}380\\475\end{cases}$ grams of anhydrous magnesium chloride?

33. What is the most satisfactory method of extinguishing a magnesium incendiary bomb, assuming that it contains no further explosive?

34. What is the percentage composition of magnesium ethyl bromide?

35. Write the formulas for (*a*) magnesium methyl bromide; (*b*) magnesium ethyl chloride.

Beryllium

Properties of Beryllium. Any list of modern light metals should include beryllium. This metal is found in the mineral beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$). The metal, silver-gray, is 1.8 times as dense as water, melts at 1285°C, and is harder than glass. Its present high price, $15 a pound in alloys, is due to two factors: (1) It is difficult to produce. (2) Only a small percentage of this light element is found in its ores.

Uses of Beryllium. The chief use of beryllium is as an alloying element. Springs made of copper alloyed with a little beryllium and nickel may fail only after 20 billion flexings. This record is 10,000 times better than that for a steel spring of equal size. Copper-beryllium alloy tools are hard and never make a spark when dropped on stone or concrete. Wrenches and other tools made of this alloy may be used safely in gasoline fumes and in the vapors of other flammable liquids, for no sparks are produced when the metal is scratched or dropped.

Beryllium has uses in connection with the atomic bomb project.

SUMMARY

Aluminum is never found free in nature. Its compounds, including clay, are abundant in the earth's crust. The chief commercial source is bauxite, a hydrated oxide.

Aluminum is prepared from alumina by the Hall method. This consists of electrolysis of purified alumina in molten cryolite. Carbon anodes and a carbon-lined steel box as cathode are needed. The physical properties of aluminum are that it is light, silvery, ductile, malleable, easily alloyed, and a good conductor of heat and electricity.

The chemical properties of aluminum are as follows: Pure aluminum is attacked by water, but a protecting coating of aluminum oxide forms on the surface. Aluminum burns, forming aluminum oxide. Aluminum is attacked by both acids and alkalies. It is a powerful reducing agent, as in the Goldschmidt process.

Aluminum is used in light alloys for airplane, truck, train, and household equipment. It is a pigment in some paints, and a reducing agent.

Magnesium was discovered by Sir Humphry Davy. It is never found free in nature. Examples of compounds of magnesium are Epsom salts ($MgSO_4 \cdot 7H_2O$) and magnesium chloride ($MgCl_2$) in the Stassfurt deposits and in sea water. Magnesite ($MgCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$) are abundant. Magnesium silicates include talc, asbestos, and soapstone.

Magnesium is prepared by electrolysis of molten magnesium chloride. Some is made by reduction of magnesium oxide with carbon and rapid chilling and also by reduction of magnesium oxide with ferro-silicon and distilling magnesium *in vacuo*. The physical properties of magnesium are as follows: (1) It is a light, silvery metal and alloys well, forming light alloys of moderate strength. Its chemical properties are that it tarnishes in air; burns readily in air, forming magnesium oxide and a little nitride; reduces carbon dioxide when hot; joins nonmetals directly; and is readily attacked by acids.

Metallic incendiary bombs may contain magnesium ignited by Thermit. This metal is contained in light alloys manufactured today. It is present in organic magnesium compounds that are used in chemical synthesis.

Beryllium, a very light metal, has less than twice the density of water. It is a silvery, hard metallic element, similar to magnesium chemically, and rather expensive at present. It is useful in alloys that do not produce sparks and for specialties such as springs.

QUESTIONS

36. What is the percentage of beryllium in beryl?

37. One of the richest sources of beryllium is bromellite (BeO). What weight of beryllium metal can be obtained from $\left\{\begin{matrix}50\\20\end{matrix}\right.$ grams of this ore? Assume that all the metal is recovered and that the ore is 100 per cent beryllium oxide.

38. What volume of carbon dioxide can be obtained at standard conditions when an acid is added to $\left\{\begin{matrix}336\\420\end{matrix}\right.$ grams of magnesium carbonate?

UNIT SIX - - - - - - - - - - - - - - - - CHAPTER XXVII

THE DENSER METALS

Lead

The symbol for lead, Pb, is taken from the Latin word *plumbum*. Evidently, then, the plumber of today follows the trade of a long line of leadworkers. Lead pipes were discovered in the ruins of Pompeii, and some of the famous Roman baths were supplied with water through lead pipes, joined end to end by wiped joints. (See Fig. 27-1.)

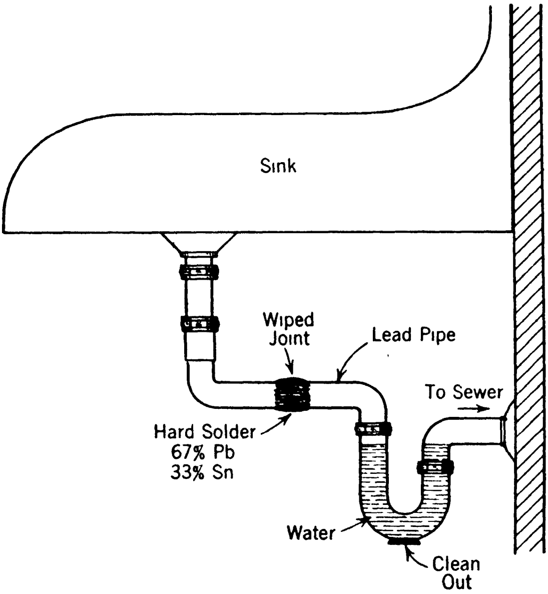


FIG. 27-1.—Using pads to protect his hands, a metal worker pours lead or solder onto the pipe joint. As the metal cools, he fashions a bulgelike joint.

The only important ore of lead is galena (PbS). This dense material

---

New Terms

bronze
matte
blister copper
Monel metal
cassiterite
galena
galvanized iron
powder metallurgy

is often found in well-crystallized cubes that have purplish-gray shiny surfaces and a metallic luster. Zinc sulfide (ZnS) and silver sulfide (Ag_2S) are at times associated with this ore.

The preliminary treatment of lead ore depends, of course, upon the nature of the impurities present and their amount, but, in general, gravity methods of concentration are used.

Production of Lead. About 2 million tons of lead is produced each year in the world. Of this, one-fourth is made into paint pigments and other compounds from which the lead is not recovered after use. The United States leads the world by producing one-fourth of all the lead mined; of this amount, one-third is produced in the state of Missouri.

The ore is concentrated, roasted, and blasted with air to remove sulfur and then reduced by heating with carbon.

The equations that follow summarize the chemical changes in the process:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$2PbO + C \rightarrow 2Pb + CO_2\uparrow$$

Properties of Lead. Lead as ordinarily seen is a dull-gray metal. A piece freshly cut with a knife shines with a silvery, metallic luster, which darkens after a short time, owing to the formation of a tarnish. Lead melts at 327.5°C and is 11.4 times as dense as water. Its tensile strength is very low; in fact, under a strong pull it slowly "creeps." Also, its ductility (ability to be drawn out into a wire) is poor.

Since lead linings are used in the chamber method of making sulfuric acid (see page 351), it is obvious that lead withstands the attack of this acid at the concentration (60 per cent) and temperature found in the chambers. A protective coating of lead sulfate ($PbSO_4$) forms over the lead. With higher concentration of sulfuric acid, this coating dissolves and therefore offers no protection against further corrosion. Weak acids, even carbonic acid (H_2CO_3), corrode lead. For this reason, lead is not suitable for pipes for distilled water. When enough carbonic acid is present, slow corrosion of the lead is produced. Lead pipes carrying slightly alkaline drinking water are protected by a coating of lead carbonate, which is not soluble in mild alkali.

Lead Poisoning. The use of lead pipes for carrying slightly acid drinking water is questionable, for lead compounds are poisonous. Lead compounds are eliminated from the body so slowly that small amounts taken internally accumulate until poisonous concentrations are reached. This trouble may overtake painters and workers who handle tetraethyl-leaded gasoline carelessly. The U.S. Public Health Service considers 0.36 part of lead per million parts of water definitely poisonous.

Chemical Actions of Lead. Molten lead gathers dross or scum on its surface. By careful heating below 585°C, a red powder [red lead, or minium (Pb_3O_4)] is formed.

$$3Pb + 2O_2 \rightarrow Pb_3O_4$$

This dense orange-red compound is the pigment used extensively for the priming coat of paint over structural steel, as it offers good protection against corrosion. In the laboratory it is a good oxidizing agent.

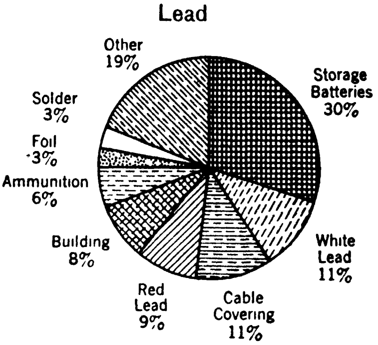
Above 585°C, yellow-brown litharge (PbO) is formed from lead or from minium.

$$2Pb + O_2 \rightarrow 2PbO$$
$$2Pb_3O_4 \rightarrow 6PbO + O_2$$

Some dilute weak acids, such as acetic acid, corrode lead, but hydrochloric and sulfuric acids do this very slowly. Lead chloride ($PbCl_2$) and lead sulfate ($PbSO_4$) are compounds insoluble in cold water. A coating of either of these substances on lead protects the metal from further action.

Nitric acid (HNO_3), a strong oxidizing agent, attacks lead vigorously, forming lead dioxide (PbO_2), a chocolate-brown compound that is used in storage batteries as the positive (+) plate.

Uses of Lead. In disk or cylindrical form, lead is used for weighting dresses and fishing nets. Lead is also used to make shot. For this purpose the metal is alloyed with 0.5 per cent of arsenic to lower the melting point and produce a harder shot.



Courtesy of Dun & Bradstreet, Inc.

FIG. 27-2.—Character of normal lead consumption.

Lead sheets line apparatus that must resist sulfuric acid. Some skyscrapers rest on lead blankets to help cushion shocks. Ornamental windows are set in lead. Lead pipes are easy to install and are, as a rule, satisfactory for drain pipes. The covering sheaths of underground electric wires or of cables are made of lead, sometimes alloyed with 1 per cent of calcium or with other elements to harden them. Spongy, gray lead is used for the negative (−) plate in storage batteries. "Leaded gasoline" contains a lead compound, tetraethyl lead [$(C_2H_5)_4Pb$], added to increase the octane number (see page 538).

Lead alloys have many familiar uses, some of which are listed in the table that follows.

Name of alloy	Composition	Use
Solder (soft)	50 % Pb, 50 % Sn	Joining copper, brass, and other metals together
Type metal	80 % Pb, 20 % Sb	Linotype slugs
Bearing metal (Frary metal)	98 % Pb, 2 % Ba	Antifriction bearings

QUESTIONS

1. What are the name and formula of the chief lead ore?

2. Under what conditions are lead pipes (*a*) satisfactory for plumbing; (*b*) unsatisfactory?

3. What is the percentage of lead in pure lead sulfide?

4. For what purpose is lead or a lead alloy used in each of the following: (*a*) an automobile; (*b*) an airplane; (*c*) an electric motor; (*d*) a fish net; (*e*) draperies?

5. Account for the fact that satisfactory copper wires can be made finer than a human hair but that lead wires as small as this cannot be drawn.

6. The use of lead pipes for conducting well water into a house, for drinking purposes, should be questioned. Under what conditions are such pipes (*a*) safe; (*b*) unsafe?

7. From what source do painters acquire the industrial disease called "painter's colic"? Workers in what other industries may acquire the same disease?

8. What useful property does antimony contribute to type metal?

9. Write formula equations for the chemical actions that take place under the following conditions: (*a*) heating lead in air at a low temperature; (*b*) heating lead in air at a high temperature; (*c*) and (*d*) reducing each of the oxides formed in (*a*) and (*b*) by carbon.

10. What weight of lead must be purchased if a manufacturer is to produce 10 tons of minium?

11. Which of the three oxides of lead contains the highest percentage of the metal?

12. What weight of lead chromate precipitates when a solution containing $\left\{\begin{matrix}993\\662\end{matrix}\right.$ grams of lead nitrate is added to a sufficient amount of potassium chromate solution (K_2CrO_4)? (Cr = 52.)

13. How much lead acetate was present when $\left\{\begin{matrix}323.0\\161.5\end{matrix}\right.$ grams of lead chromate precipitated according to the equation,

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O \rightarrow 2PbCrO_4\downarrow + 2KC_2H_3O_2 + 2HC_2H_3O_2?$$

Tin

Tin is a bright, shiny metal familiar to all as the coating metal of tin cans. Its symbol, Sn, comes from the Latin word *stannum.* This metal has been known since ancient times; in fact, it is reported that one of Caesar's reasons for invading the British Isles was to secure tin from the mines of Cornwall. Tin was an article of commerce carried in ships through the Mediterranean Sea and around the west coast of Europe by ancient Phoenician traders.

The chief location of tin mines today is in the Malay States and the East Indies. Metallic tin ingots are exported through the port of Singapore. Other important deposits are found in Bolivia, South America, and a plant to smelt Bolivian ore has been erected in Texas. Relatively unimportant amounts of tin are produced in this country, although half the world's supply of 200,000 tons annually is consumed here.

Tin Ore. Cassiterite (SnO_2), or tinstone, is found in nature concentrated by the running water of streams, although sometimes it is mined from veins in rocks. It is the chief tin ore. It is further concentrated by flotation of the gangue, heated, and reduced with carbon.

$$SnO_2 + C \rightarrow Sn + CO_2\uparrow$$

The tin is then purified from other metals by applying heat. Tin melts at 232°C, a temperature lower than the melting point of lead (327.5°C), and flows away from the impurities, which have a higher melting point. Further purification can be made by electrolysis.

Properties of Tin. Although relatively soft, tin is harder than lead; it is bright and shiny, but not ductile. Its melting point is lower than that of most common metals. Its specific gravity is 7.3. Below 13°C tin may be converted into an allotropic form, a gray powder. Some museum specimens of tin, for example, break out with spots of this "tin disease" when, as during a Russian winter, they are exposed to low temperatures for a long time.

Tin at 100°C can be rolled into thin sheets, which in turn can be rolled onto previously cleaned sheet steel. Tin may also be deposited electrolytically on sheet iron. From this coated metal, called tin plate, 20 million blanks for tin cans are cut in a year. This use accounts for 40 per cent of the tin imported into the United States. Tin costs more than ten times as much per pound as lead, with recent tendencies upward from that figure.

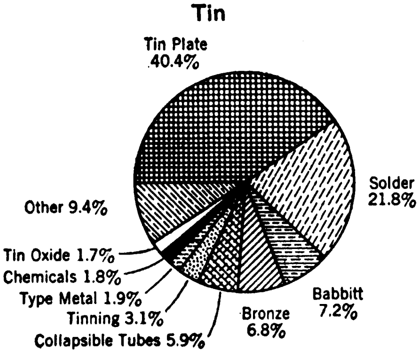
Chemical Actions of Tin. Tin acts slowly with acids. This metal is in fact generally inactive, even less active than lead. Hot hydrochloric acids acts on it steadily, liberating hydrogen.

$$Sn + 2HCl \rightarrow \underset{\text{stannous chloride}}{SnCl_2} + H_2\uparrow$$

Free chlorine will change both tin and stannous chloride to stannic chloride, a compound in which tin is considered to have a combining number of 4. The bond is covalent. This action is one method by which tin is recovered from scrap tin plate, for chlorine attacks tin even more readily than it does iron, the product being so much more volatile.

$$SnCl_2 + Cl_2 \rightarrow SnCl_4$$

Nitric acid and hot concentrated sulfuric acid both act on tin; with nitric acid, however, insoluble metastannic acid (H_2SnO_2) forms. Ordinary moist air and most fruit and vegetable juices do not attack tin.



Courtesy of Dun & Bradstreet, Inc.

FIG. 27-3.—Character of normal tin consumption.

Tin-can Chemistry. The protection of iron by a covering of sheet tin is effective while the tin covering is complete. Practically, it is very difficult to apply a coating of tin to iron, previously pickled free from scale, without pinholes through the tin. When exposed to the weather,

Courtesy of Anaconda Copper Mining Company

FIG. 27-4.—Liquid zinc is poured from a ladle into flat molds. Most of this metal will be used to protect iron.

iron is attacked more readily than tin. A little electric cell is formed in which the iron is the negative (−) pole and tin is the positive (+) pole. Iron dissolves in the action and forms, finally, red iron oxide (Fe_2O_3). That is, tin, being less active then iron, is a good protection for iron while the coating is unbroken. Once broken, as in the case of an old tin can in a dump, the can quickly disintegrates. Notice that tin is below iron in the replacement list (see page 89).

Uses of Tin. Pure "block tin" is used for making pipes to carry distilled water and slightly acid liquids (soda water for fountains in drugstores), for it resists their corrosive action. Long spans of tin pipe must be supported by a trough of stronger material. Some collapsible tubes are made of tin.

Tin is a component of some alloys. Solder has already been mentioned. Pewter used for ornamental tableware, contains 75 per cent or more of tin and the remainder lead. Commercial bronze has less than 19 per cent tin and the rest copper. Sometimes zinc is put in bronze. The metal used for bronze statuary and bells has about 10 per cent tin and the rest copper. Tin foil, once used extensively for candy wrappers, is now replaced in part by aluminum foil, waxed paper, or transparent sheet plastic material because of the high expense of tin.

QUESTIONS

14. What is the chief ore of tin?

15. How is tin obtained from its ore?

16. The concentration of tin ore is sometimes called "reverse flotation." Explain this term.

17. Give the composition of each of the following: (*a*) block tin; (*b*) solder; (*c*) pewter; (*d*) shot; (*e*) bronze; (*f*) red lead; (*g*) a tin can; (*h*) tin foil; (*i*) litharge; (*j*) galena.

18. Explain the theory of protecting sheet steel from corrosion by coating it with tin. How does this work out practically?

19. A manufacturer of bronze tablets estimates that a memorial tablet will weigh $\begin{cases}240\\275\end{cases}$ pounds. What is the cost of the metals alone, assuming that copper costs 12 cents and tin 52 cents per pound?

20. Soldered gasoline cans were cached in the Arctic. Later the cans were found open at the seams with the fuel gone. (*a*) Suggest a possible cause of this disaster. (*b*) Tell how it could have been avoided.

21. Write formula equations for the actions of (*a*) tin with hydrochloric acid; (*b*) tin with chlorine; (*c*) tin hydroxide with hydrochloric acid.

22. Balance this equation (*do not write in this book*):

$$SnCl_2 + I_2 + HCl \rightarrow SnCl_4 + HI$$

23. What weight of tin can be recovered from $\begin{cases}400\\300\end{cases}$ pounds of cassiterite that is 60 per cent tin oxide?

24. By the action of tin and hydrochloric acid, nitrobenzene ($C_6H_5NO_2$) is reduced to aniline ($C_6H_5NH_2$). Write and balance the equation to represent this change.

Zinc

Zinc is another metal that has been known since antiquity. In ancient descriptions and uses it was sometimes confused with tin. A zinc-filled bracelet has been discovered in the ruins of a city that was destroyed about 500 B.C. Zinc, alloyed with copper, was also a component of brass or bronze for weapons and tools in ancient times. Today everyone is familiar with zinc as the blue-gray metal on the outside part of flashlight cells. When free of tarnish, it has a bright luster.

Ores of Zinc. The most important ore of zinc is the sulfide ore (ZnS) that is called zinc blende, sphalerite, or blackjack. It is shiny and dark and a very attractive mineral when well crystallized. Smithsonite ($ZnCO_3$) is also found, and some zincite (ZnO). In New Jersey an ore called franklinite ($ZnO{\cdot}Fe_2O_3$) is mined.

About 1.75 million tons of zinc was produced in 1939. Of this amount the United States produced 28 per cent and Germany 13 per cent. Canada and Poland were important producers, also. Half of the United States supply came from the Joplin region of Missouri and adjacent states.

Obtaining Zinc. Today about three-fourths of the zinc is smelted by the method already described (see page 279). The ore is concentrated from the accompanying valuable lead sulfide (PbS) by froth flotation. The sulfide or carbonate is roasted in air to form the oxide.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$ZnCO_3 \rightarrow ZnO + CO_2\uparrow$$

The oxide is then reduced to metallic zinc. This can be done by mixing it with powdered coal and then heating.

$$ZnO + C \rightarrow Zn\uparrow + CO\uparrow$$

The zinc vaporizes in the operation and is condensed to recover the metal.

In the Maier process, the impure zinc oxide is heated to 1000°C in a tube in a reducing atmosphere of natural gas. The zinc distills over to the condenser, where it deposits out 99.99 per cent pure. This process is continuous and economical as well as producing a high-purity product.

Another way to get zinc from its oxide is to leach the oxide with dilute sulfuric acid.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

The solution of zinc sulfate is then electrolyzed, and the zinc ions (Zn^{++}) plate out as zinc on the cathode (−). Electrolytic zinc has a purity of 99.999 per cent. It is better adapted than spelter (commercial zinc) for making alloys and for certain other purposes. It costs about 4 cents more per pound than spelter. Zinc may be refined by distillation or by electrolysis.

Properties of Zinc. Zinc can be melted easily in the flame of a Bunsen burner, for its melting point is 419.4°C. If liquid zinc is poured slowly into a pail of water, mossy zinc results. The steam formed by the contact of the hot drop of metal with the water expands the drop into an irregular bubblelike shape. Mossy zinc is frequently used in the laboratory to liberate hydrogen.

When heated between 120 and 150°C, zinc is malleable and easily worked but between 200 and 300°C it becomes brittle. The density of zinc, 7.14 g per ml, is about the same as that of iron. Its tensile strength varies with treatment. Cast zinc has a tensile strength of 8000 to 14,000 lb per sq in., while the tensile strength of drawn zinc varies between 22,000 and 40,000 lb per sq in.

Chemistry of Zinc. Zinc resists corrosion well in the temperate zone but not in the tropics. In moist air a coating of zinc basic carbonate [$ZnCO_3 \cdot 3Zn(OH)_2$] forms slowly. Acids, even dilute ones, attack zinc readily, liberating hydrogen.

Impure zinc or zinc wrapped with a piece of copper wire reacts more readily than pure zinc because the action is electrochemical, the action being similar to that of an electric cell.

Zinc dissolves in alkaline solutions, but not as readily as aluminum. It reacts with water in the presence of sodium hydroxide as follows:

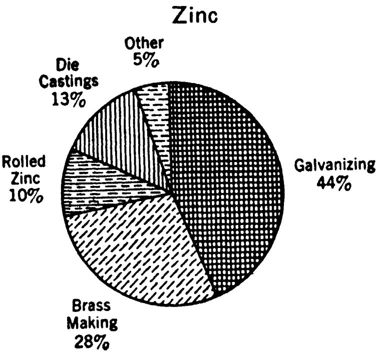
$$Zn + \text{(hot) } NaOH + H_2O \rightarrow \underset{\text{sodium hydrogen zincate}}{NaHZnO_2} + H_2\uparrow$$

It will replace all of the precious metals from their solutions and is used to some extent for this purpose.

$$2AgNO_3 + Zn \rightarrow Zn(NO_3)_2 + 2Ag\downarrow$$

Uses of Zinc. Sheet zinc is used for roofing, valleys in roofs, weatherstripping and, in general, for coverings that must resist weathering. Dry cells use zinc for the outside can, which serves as a cathode (−). Cleaned nails, hardware, sheet iron, and other iron articles are galvanized by dipping them into molten zinc. This gives them a protective coating that resists wear and rusting well. The ordinary galvanized water pail is a good example of a sheet-iron utensil so protected. When it is new, the crystals of zinc can usually be seen on its surface. Zinc is applied to iron in several other ways. One of them, Sherardizing, covers the articles with powdered zinc and then melts the zinc onto the metal by the application of heat.

Zinc is used in the Parkes process for separating silver or gold from lead (see page 666); it dissolves the silver or gold but not the lead. Photoengravers use zinc for reproducing line drawings. Figure 27-1 in this book and the cartoons in a school classbook are printed from an original zinc plate. The tops of many glass preserving jars are made of zinc, a use that requires over 15,000 tons a year.



Courtesy of Dun & Bradstreet, Inc.

FIG. 27-5.—Character of normal zinc consumption.

Brass, an alloy of copper 60 to 90 per cent and zinc 40 to 10 per cent, is much used for pipes, hardware, cartridge casings, and other purposes familiar to all. Zinc-base-alloy, die-cast metal, contains 2.5 to 3.5 per cent copper, 3.5 to 4.5 per cent aluminum, and the rest zinc. This alloy when liquid can be cast in permanent molds and gives castings with fine details. Many automobile parts are made in this way. An ordinary computing gasoline pump, such as is seen at filling stations, may contain over 70 different parts made of zinc die-cast alloy. No sparks are produced if the metal is accidentally hit.

QUESTIONS

25. Zinc occurs in what three sorts of ores?

26. Why is zinc not found free in nature, while copper is?

27. Show by a series of equations how zinc may be obtained (*a*) from zincite; (*b*) from zinc blende; (*c*) from smithsonite.

28. What four metals are obtained from the Joplin, Missouri, region?

29. Make a labeled diagram of a cell in which zinc may be refined by electrolysis.

30. What volume of sulfur dioxide is produced when $\begin{cases}200\\500\end{cases}$ grams of zinc blende, 60 per cent zinc sulfide, is roasted in air?

31. What weight of zincite, 80 per cent zinc oxide, is needed to form $\begin{cases}390\\325\end{cases}$ pounds of zinc?

32. When brass is melted, a white smoke arises from the crucible. What is the chief component of this white smoke?

33. A demonstrator was showing the violent reaction of zinc with sulfur. He mixed the powdered elements and set them afire. A portion of the reacting mixture flew into unprotected supplies of zinc and of sulfur and set them afire, also. Write equations for all three burnings.

34. In what weight proportions should zinc and sulfur be mixed for maximum violence of reaction?

35. What is the composition of (*a*) galvanized iron; (*b*) spelter; (*c*) zinc white; (*d*) zinc ointment; (*e*) zinc stearate? [(*d*) and (*e*) are reference questions.]

36. State a use for each of the substances mentioned in the previous question.

37. What metals are present in each of these alloys: (*a*) brass; (*b*) bronze; (*c*) nickel silver; (*d*) pewter; (*e*) type metal?

38. A cheap ladle made of zinc is placed in punch slightly acid with fruit juice. What happens?

39. Balance this equation (*do not write in this book*):

$$Zn(OH)_2 + NH_4Cl + NH_3 \rightarrow Zn(NH_3)_4Cl_2 + H_2O$$

40. (*a*) When $\left\{\begin{matrix}130\\195\end{matrix}\right.$ grams of zinc is put into dilute hydrochloric acid, what volume of hydrogen is liberated at STP? (*b*) What volume of hydrogen is generated if the pressure is $\left\{\begin{matrix}750\\740\end{matrix}\right.$ millimeters and the temperature $\left\{\begin{matrix}17\\20\end{matrix}\right.$°C?

Cadmium

Properties and Uses. When zinc is distilled, an impurity, cadmium, distills over at a boiling point lower than that of zinc. Cadmium is a metal that melts at 321°C and boils at 778°C. It is a little harder than zinc and less active chemically.

Cadmium is applied by electroplating; we often see it on household hardware, automobile wheel rims, and parts of typewriters. When thus applied to steel, it gives a dense, silver-white, fibrous appearance.Its most important use, however, is in alloys. These include a cadmium-copper alloy for power and telephone wires and a low-melting alloy (Wood's metal—parts by weight: bismuth 5, lead 2.5, tin 1.25, and cadium 1.25; m.p. 65.5°C).

Cadmium is an important alternate metal for zinc. It resists corrosion better than zinc. It will burn to form a brown oxide (CdO). Cadmium sulfide (CdS) is widely used as a yellow pigment.

QUESTIONS

41. Distinguish cadmium from zinc in respect to (*a*) color; (*b*) boiling point; (*c*) chemical activity.

42. Write equations for (*a*) burning cadmium in air; (*b*) passing hydrogen sulfide through cadmium nitrate solution.

43. What properties of cadmium make it a suitable metal for electroplating over other metals?

44. Balance this equation (*do not write in this book*):

$$K_2Cd(CN)_4 + H_2S \rightarrow KCN + HCN + CdS\downarrow$$

Copper

Early History of Copper. The Mediterranean island of Cyprus, off the Greek coast, was a source of copper for the early peoples of that region. They called copper the Cyprian metal. Eventually the same name has reached us today through the Latin word *cuprum*. In China, Peru, and Asia Minor and in North America among the Indians, copper was used by primitive man. Some articles preserved to us are copper utensils, ornaments, weapons, and sacred figures.

The use of copper was so widespread that historians refer to the period of the rise of mankind from savagery to a tool-using animal as the ***bronze age***—bronze age, rather than copper age, because copper was often found naturally alloyed with other metals.

At Thebes in Egypt, on the walls of Rekh-y-Re's tomb, were found scenes of the casting of the metal for the large bronze doors for the temple at Karnak.

In Italy, Benvenuto Cellini (1500–1571), an artist, cast in bronze a heroic statue of Perseus, son of the Greek god Zeus.

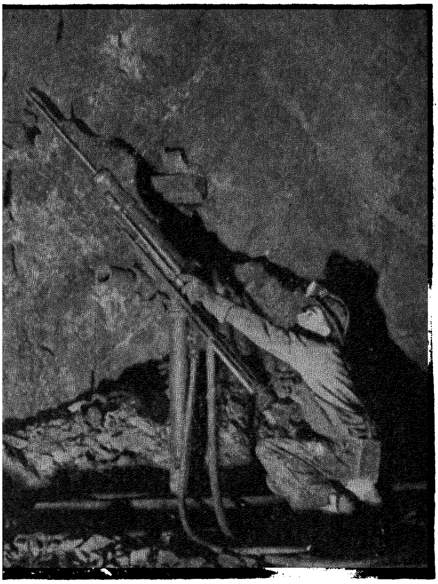
After this extensive use in the early arts and crude industries, modern science stepped into the picture. Scientific investigations show that not only native copper, but also many low-grade sulfide ores are valuable as sources of copper. An ore containing as little as 1 per cent of the metal can be concentrated by froth flotation.

The properties of copper have been studied with care. This metal is found to be the best practical conductor of electricity, ranking second to silver. In 1882, when the world's first electrical power plant was opened in New York, Thomas Alva Edison used about 125,000 lb of copper in its equipment. It supplied power for 5000 electric lamps in 1883 and a year later for 11,000.

The spread of the use of copper for electrical purposes has been rapid. Today this country, both above and below the surface, is enmeshed with copper strands carrying power and messages, as if a million Lilliputian wires were binding the giant Gulliver, the United States.

Where Copper is Found. The chief copper-producing region, accounting for about one-half the world's supply, is the United States, with Chile, Canada, and Rhodesia in South Africa also important. In this country the leading copper-producing states are Arizona, Utah (famous for the large open-pit mine in Bingham Canyon), Montana, Nevada, and Michigan, where on the Keweenaw Peninsula free copper has been secured from the time of the early Indians and ever since.

Copper Ores. About one half of all the ores mined is chalcopyrite ($CuFeS_2$), and one fourth is chalcocite (Cu_2S). All copper deposits contain cuprite (Cu_2O). The remaining fourth of the copper ores is chiefly native copper with deep-green malachite [$CuCO_3 \cdot Cu(OH)_2$] and blue azurite [$2(CuCO_3) \cdot Cu(OH)_2$].



Courtesy of Anaconda Copper Mining Company

FIG. 27–6.—A miner prepares to attack a vein of copper ore with a compressed-air gun.

Copper Metallurgy. 1. Low-grade ore, usually sulfide, is concentrated by several methods, including froth flotation.

2. The ore is then roasted with air available so that part of the sulfide is changed to the oxide.

$$Cu_2S + 2O_2 \rightarrow 2CuO + SO_2$$

3. The roasted ore is heated again in a large reverberatory furnace to remove iron as a slag. The resulting ***matte*** (Spanish for "dull") is about 50 per cent copper.

4. The matte is now placed in a converter that resembles a Bessemer converter. Here an air blast completes the oxidation of the sulfur and forms copper 98 per cent pure, which, because of the gas bubbles that it contains, is called ***blister copper.***

When certain types of ores are used, these last two steps (3 and 4) can be more or less combined in a large reverberatory furnace. In this case the ore contains both sulfides and oxides, which act on each other.

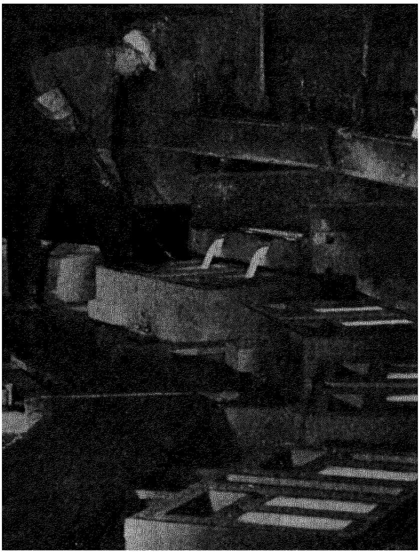
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2\uparrow$$

Gold and silver are retained in the blister copper. The metal in this form is cast into anode slabs, ready for electrolytic refining.

In the famous Minas de Rio Tinto, in Spain, which have produced copper ever since the dawn of history, as well as in some United States and South Africa locations, the copper is mined by leaching. The air slowly oxidizes the ore to copper oxide. A liquid, sometimes sulfuric acid (H_2SO_4), trickles slowly through the pile of ore. Copper dissolves, and copper ions (Cu^{++}) are formed. These are recovered as copper either by electroplating or by replacement when scrap iron is added.

$$Cu^{++} + Fe \rightarrow Cu + Fe^{++}$$

Refining Copper. Slabs of blister copper as large as the top of an office desk are hung in a tank of copper sulfate ($CuSO_4$) solution containing some sulfuric acid. These are anodes (+) that are to be refined. Suspended between these slabs are sheets of pure copper cathodes (−). A regulated current surges between them and through the solution. The Cu^{++} ions are deposited from the solution onto the cathode. The solution is in turn resupplied by copper dissolved from the anode. This process continues until the anode is quite thin. Zinc, iron, and lead impurities go into the electrolyte. Gold and silver drop out of the anode and collect as a slime in the bottom of the tank. This sludge, an important source of precious metals, is sometimes of sufficient value to pay cost of the refining process. The expense for the electrical energy is important in this process. Copper deposits at the rate of 0.3294 milligram (mg) per ampere per sec. Electrolytically deposited copper may be 99.98 per cent pure. Copper conducts electricity without much loss from energy changed to heat, but as little as 0.3 per cent arsenic lowers the conductivity 14 per cent. If the electrical resistance of a strand of silver wire is taken as standard at 1.0 for a given size and temperature, then that of copper is 1.05.



Courtesy of Anaconda Copper Mining Company

FIG. 27-7.—Refined copper is cast into cakes before being sent to market.

Physical Properties. Copper is the only red-colored metal. It is soft, ductile, and malleable under most conditions. Cold-working the metal increases its hardness. This process of increasing the hardness of copper by working the metal when cold has given rise to the story that the ancients were able to temper copper and that the art has since become lost. White[1] states, "Copper tools and weapons used by the American Indians were hardened by cold work and not by any lost or secret process."

Modern workers have copper tools, made of an alloy of copper and beryllium, that not only give no sparks, as iron alloys do, but also are harder than any copper tool known to antiquity.

---

[1] A. H. WHITE, *Engineering Materials*, p. 228, McGraw-Hill Book Company, Inc., New York, 1939.

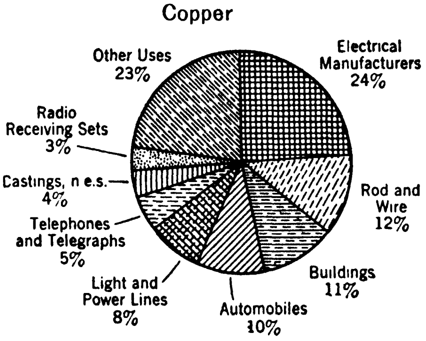
Copper is 8.9 times as dense as water. It melts at 1083°C. Its ductility is so great that copper wires can be made that are finer than a human hair. The tensile strength of a specimen depends on its previous history. When annealed, or softened by heating, its strength is about 36,000 lb per sq in. for large wire. When cold-drawn, the same size has a strength of 49,000 lb per sq in.

Chemical Properties of Copper. The resistance of copper to atmospheric corrosion is well known. A bright-red coating of oxide (Cu_2O) forms, especially in moist air or under salt water, but this slowly turns to an attractive, dull-green "patina." Drainpipes for rain water also sometimes acquire a green coating. This coating is considered to make bronze statues more attractive as they age. The composition of the green material is now known to be the basic sulfate [$CuSO_4 \cdot Cu(OH)_2$] or the basic copper chloride.

When copper is heated in air, a black coating of cupric oxide (CuO) forms. $2Cu + O_2 \rightarrow 2CuO$. Some of the red cuprous oxide (Cu_2O) also forms.

Copper joins readily with sulfur. Under ordinary conditions of placing copper in sulfur vapor the action forms cuprous sulfide.

Thin sheets of copper placed in chlorine burst into flame spontaneously. Hydrochloric acid cleans the oxide film from its surface but fails to attack the metal since copper is less active than hydrogen. The same applies to dilute sulfuric acid, but hot concentrated sulfuric acid oxidizes and dissolves copper.



Courtesy of Dun & Bradstreet, Inc.

FIG. 27-8.—Character of normal copper consumption.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

Concentrated nitric acid acts on copper, producing dense, poisonous, brown fumes of nitrogen dioxide gas.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

With dilute nitric acid the decomposition of the nitric acid is less vigorous, forming nitric oxide (NO) in the solution, which oxidizes as soon as it comes in contact with the air.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$

Notice that, in every case given of attack by an acid on copper, no hydrogen is liberated. In this respect copper differs from the more active metals, such as zinc, cadmium, and iron.

Uses of Copper. Copper shingles make a lasting and attractive roof. Ships sheathed with copper below the water line resist the attack of barnacles and other marine creatures. Copper and sometimes cuprous oxide are ingredients of many antifouling paints used on the bottom of both wooden and steel boats.

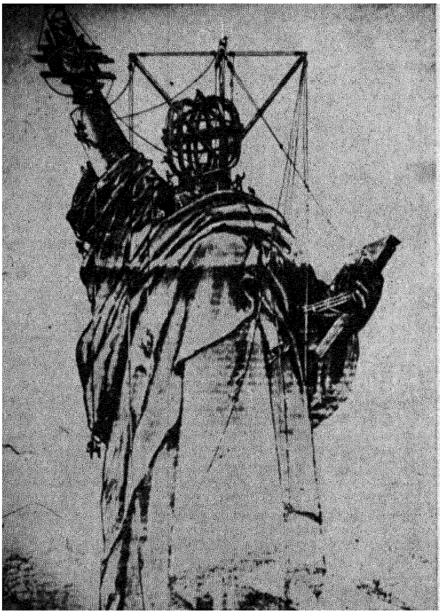


FIG. 27-9. This rare old photograph shows the operation of putting the copper garment on the Statue of Liberty.

The chief use of copper is for making wire and other electrical equipment. Almost three-quarters of the annual production of the metal, over 2 million tons, is used directly as the metal. A large steamship requires immense amounts of copper for condenser tubes and other purposes. Over 3 million pounds of copper was used in building the "Queen Mary." The average automobile contains about 45 lb of copper, most of it in the radiator. Electrified railroads require great tonnages of copper.

At home, copper is used for roofing gutters, flashings, and conductor pipes. Copper tubing may be used for plumbing. In other forms copper is used for screening, lightning rods, heating coils, and hot-water storage tanks. These are in addition to the electrical and hardware equipment of the home.

The famous Statue of Liberty (Liberty Enlightening the World), located on Bedloe Island in New York harbor, is made of sheet copper riveted together. (See Fig. 27-9.)

Copper Alloys. Brass, the most important alloy of copper, has already been mentioned under the topic of zinc (see page 476). Bronze contains copper and tin, sometimes with zinc added. It is used for statues, ornamental work, hardware, and memorial tablets. Its permanence and beauty are well known. Today all United States coins contain copper in the alloy, silver coins having 10 per cent copper. Sixteen-carat (k) gold is one-third copper, added for hardening.

Tests for Copper. The red color of copper is usually sufficiently distinctive to identify the metal. Sulfur tarnishes it black, and nitric acid forms a blue solution of copper nitrate. Copper compounds form a deep-blue solution when ammonia water is added in excess. The blue color is that of the complex ion $[Cu(NH_3)_4]^{++}$. When a nail is added to a solution of a copper compound, a red precipitate of copper is formed.

$$Cu^{++} + Fe \rightarrow Fe^{++} + Cu$$

Copper in Printing. If we wish to prepare a picture for publication in a book, a copperplate is made. The printing of class pictures in a classbook, for example, is done from a copper half-tone. The metal is treated on the surface with a photo-sensitive coating. After being exposed through a half-tone screen and treated, it is etched with acid. The resulting high and low spots, some taking ink and others not, are capable of printing a picture.

The actual printing of a book such as this one is done from copper electrotypes, or "electros" (see page 480). The type (see page 470), line cuts (see page 476), and half-tones are assembled in a printer's form, pressed into wax, the wax dusted with graphite (carbon), and electroplated with copper. The resulting copper shell, properly mounted, forms the printing surface.

QUESTIONS

45. Write the symbols for these elements: copper; gold; silver; lead; tin; antimony; mercury. From what language are the symbols derived? Account for their common origin.

46. Cite references to the use of copper or brass in ancient classic or religious writings, such as Caesar's *Commentaries*, Vergil's *Aeneid*, or the Bible.

47. What is the chief use of copper?

48. A beautiful, polished, green semiprecious stone is a copper ore. What is its probable composition?

49. What treatment is given to copper sulfide ore (*a*) in order to concentrate it; (*b*) in order to remove the sulfur?

50. What is the percentage of copper in the following ores: (*a*) chalcopyrite, 2 per cent $CuFeS_2$; (*b*) chalcocite, 1 per cent Cu_2S?

51. Write formula equations for (*a*) action of zinc on copper sulfate solution; (*b*) union of copper with sulfur; (*c*) union of copper with phosphorus; (*d*) action of cuprous oxide and hydrochloric acid.

52. What fact about copper probably gave rise to the legend that copper could be tempered?

53. Write the formula equations for the action of copper oxide (CuO) on (*a*) dilute nitric acid; (*b*) dilute sulfuric acid; (*c*) concentrated sulfuric acid; (*d*) dilute hydrochloric acid.

54. Write equations for the action of copper, if any, on the acids mentioned in the previous question.

55. What properties of copper make it a suitable material for shingles? State a disadvantage of copper shingles.

56. Compare copper-tubing plumbing with threaded and jointed iron piping in a home in respect to (*a*) convenience in installation; (*b*) cost of material; (*c*) resistance to corrosion.

57. What weight of copper is needed to make 200 class rings, weighing $\left\{\begin{matrix}6\\5\end{matrix}\right.$ grams each $\left\{\begin{matrix}10\\12\end{matrix}\right.$-carat gold?

58. (*a*) How can metallic copper be identified? (*b*) How can copper ions in solution be identified?

59. For what purpose is copper used in each of the following industries: (*a*) fishing; (*b*) plumbing; (*c*) printing; (*d*) electroplating; (*e*) furniture making; (*f*) farming: (*g*) automobile making?

60. (*a*) Why should copper kitchen utensils be kept bright? (*b*) Why are copper utensils sometimes tin-lined?

61. A common method to prepare steel for marking is to wash it over with copper sulfate solution. What change is thus made on the steel so that it shows scratches readily? Write an equation in ionic form for the reaction.

62. What volume of nitric oxide is liberated when $\left\{\begin{matrix}63.6\\95.4\end{matrix}\right.$ grams of copper is dissolved in dilute nitric acid?

Nickel

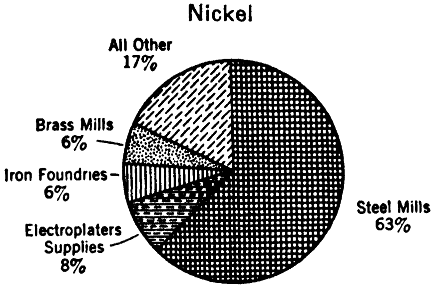
Nickel Ores. About 90 per cent of the world's nickel comes from Sudbury, Ontario, Canada. The sulfide ore found there contains copper, iron, and cobalt in addition to nickel and may be made directly into the Ni-Cu alloy, ***Monel*** metal. Some nickel is found in New Caledonia. The United States produces very little.

Nickel is obtained from its ore by a complicated process. It is roasted, treated in a converter that resembles a Bessemer converter, freed of copper, purified by use of carbon monoxide in the Mond process, and finally refined by electrolysis.

Properties of Nickel. Refined nickel is sometimes 99.95 per cent pure. It is a silvery-white metal. Its density, 8.9 g per ml, is a little more than that of iron. It melts at 1450°C. Nickel is malleable, ductile, and somewhat magnetic. Its tensile strength is about 70,000 lb per sq in.

Nickel rusts very slowly. It is less active than iron. It liberates hydrogen from dilute acids very slowly and resists the attack of hot alkaline solutions. Nitric acid dissolves nickel, forming nickel nitrate. Carbon monoxide combines directly with the metal, forming nickel carbonyl $[Ni(CO)_4]$.

Uses of Nickel. About two-thirds of all the nickel produced is used with steel in nickel-steel alloys. In general, the addition of nickel to steel improves many of the desirable qualities of the steel, including tensile strength. The SAE handbook recommends nickel steel 2345 (3 per cent Ni) for structural purposes where great strength is desired, as for propeller or axle shafts. Nickel is used extensively as an electroplate over plumbing fixtures and on automobiles, bicycles, and small machine parts, for it combines resistance to corrosion with pleasing appearance.



Courtesy of Dun & Bradstreet, Inc.

FIG. 27-10.—Character of normal nickel consumption.

Nickel Alloys. Monel metal, a trade-marked alloy, contains 60 to 72 per cent nickel with copper and some iron and manganese. It is used for covering table tops and cabinets in dining cars and large kitchens and for many purposes that require a noncorrosive, nonpoisonous, shiny metal for food-handling equipment. Monel metal has a slightly red color, from the copper in it.

Invar (63.8 per cent Fe, 36 per cent Ni, 0.2 per cent C) is an alloy that changes size very little with changes in temperature. It is used for precision instruments, measuring tapes, airplane-engine parts, and pendulum rods. The seal-in wire in electric light bulbs is an alloy of this type. It has a core of 45 per cent nickel and 55 per cent iron covered with a copper sheath that comprises one-fifth the volume of the entire wire. It has the same expansion characteristics as glass to which it adheres in a vacuum-tight seal. The entire lighting industry depends on the use of this alloy.

The wire in an electric toaster, flatiron, or similar heating device gets red-hot but does not burn or corrode readily in the air. This wire is frequently made of nichrome, an alloy of 75 per cent nickel, 11 per cent chromium, 12 per cent iron, and 2 per cent manganese.

Permalloy, 80 per cent nickel with 20 per cent iron, shows great magnetic permeability when small electric currents are near it. It is used in magnetic apparatus, telephone cables, and other electrical equipment.

Nickel-silver, formerly called German silver, has copper 57 per cent, zinc 19 per cent, and nickel 24 per cent. This alloy is bright, shiny, weather resistant, and hard. It is the base metal for silver-plated tableware.

A nickel coin is a sort of Monel metal. It contains only one-fourth nickel; the rest is copper.

Wartime Coinage. The composition of United States coins was affected by wartime conditions in the metal market. "Nickels," formerly 75 per cent copper and 25 per cent nickel, were changed to 56 per cent copper, 35 per cent silver, and 9 per cent manganese. These alloys have almost identical colors.

Wartime pennies were of zinc-coated steel. Other pennies are a bronze that contains 2.5 per cent tin and 2.5 per cent zinc with copper. Silver coinage contains 10 per cent copper as formerly.

Powder Metallurgy. A technique of forming useful shapes from high-melting or very hard metals has become important recently. The metal is prepared as an extremely fine powder by reduction of oxides or by spraying. Then it is packed into a mold under pressure and brought to the sintering[1] point, thereupon taking the form of the mold. Some pieces are allowed to remain very porous. They absorb oil and serve as "oilless" bearings, as they require no further oiling.

Many laboratories use powerful Alnico magnets. These are made from a mixture of the powders of iron, aluminum, nickel, and cobalt molded into shape by powder metallurgy technique. This method permits us (1) to produce alloys otherwise impossible to make, (2) to mold intricate shapes cheaply, and (3) to fabricate high-melting tungsten, tantalum, and molybdenum that cannot be melted and cast.

SUMMARY

Lead has been known and used since ancient times. It is found chiefly in the ore galena (PbS). The ore is roasted and blasted with air to remove sulfur, then reduced with carbon.

The physical properties of lead are as follows: It is a dense, soft, silvery metal. It can be melted readily.

Its chemical properties are as follows: It tarnishes quickly on the surface, but slowly thereafter. It is not rapidly attacked by strong acids or alkalies, but it is readily corroded by some weak acids and by concentrated nitric acid. Its compounds are poisonous to the body. Lead forms oxides when heated in air.

Minium, or red lead (Pb_3O_4), forms below 585°C.

Litharge (PbO) forms above 585°C.

---

[1] Sintering is a process by which some materials are brought to a coherent mass by heating, but not by completely melting.

Lead dioxide (PbO_2) forms when nitric acid is used with lead.

Lead is used for lining chemical apparatus, for making weather-resisting sheathing, for storage batteries, and for sinkers. It is also used in alloys, including solder (with Sn), shot (with As), and type metal (with Sb). A lead compound, tetraethyl lead, raises the octane number of gasoline. Many other compounds are important.

Tin was also known to ancient peoples; it is found chiefly in the ore cassiterite (SnO_2). The metal is easily prepared by reducing the oxide with carbon. It is then refined by remelting and electrolysis.

The physical properties of tin are as follows: It has a soft, silvery, bright, metallic luster and a relatively low melting point. It changes into a powdery form at a low temperature.

Its chemical properties are as follows: It is attacked by strong acids but resists corrosion by weak acids and the atmosphere. It protects iron well while the coating is unbroken.

Tin is used for block tin pipes, collapsible tubes, and tin-foil wrappings. Tin alloys include solder (with Pb), bronze (with Cu), and pewter (with Pb or Sb).

Zinc is also a metal known and used since ancient times, but it was sometimes confused with tin. The ores of zinc are zinc blende (ZnS), zincite (ZnO), smithsonite ($ZnCO_3$), and franklinite ($ZnO \cdot Fe_2O_3$).

The metallurgy of zinc is relatively simple. (1) Roasting in air and reducing with coal produce zinc from the sulfide or carbonate. (2) Leaching zinc oxide with sulfuric acid produces zinc sulfate; the metal is obtained on the cathode by electrolysis of solution of zinc sulfate. (3) Zinc is refined by electrolysis or by distillation in a vapor of natural gas.

The physical properties of zinc are as follows: It is bluish gray; it has a metallic luster; its melting point is 419.4°C; it is malleable between 200 and 300°C; its density is about the same as that of iron.

Its chemical properties are as follows: It corrodes slowly in air, forming a gray tarnish. It is a fairly active metal. It burns in air and is attacked readily by acids. It dissolves slowly in strong alkalies.

Zinc is used as the cathode in dry cells; for galvanizing steel; as sheet metal for protective coverings; for recovering other metals; for making jar tops; for making alloys, especially brass (with Cu).

Cadmium occurs in ores with zinc and is similar to it chemically. It has a lower melting point than zinc and is less active chemically. It is used in the form of electroplated coating and for making low-melting alloys.

Copper has been known and used extensively since before the dawn of written history. It is found both free and combined, as oxides and sulfides chiefly.

The metallurgy of copper is complicated. Copper ores are usually concentrated by froth flotation. Roasting removes part of the sulfur. Iron is removed as slag in a reverberatory furnace, forming matte. Matte is converted in a blast furnace to blister copper. Blister copper is refined by electrolysis. Leaching and replacement methods are also used with some ores.

The physical properties of copper are as follows: It is a pink-colored metal, soft, ductile, and malleable, that hardens when cold-worked. It is an excellent conductor of heat and electricity.

Its chemical properties are as follows: It corrodes in air very slowly. It joins sulfur and chlorine directly. It is attacked by concentrated sulfuric acid and by nitric acid. It does not replace hydrogen from nonoxidizing acids.

Copper is used extensively as an electrical conductor; for making pipes; for weather-resisting parts of houses; and for making electrotypes and half tones in printing. Copper alloys include brass (with Zn) and bronze (with Sn). Copper is alloyed with gold and silver to harden those metals. Compounds of copper are used extensively as fungicides.

Nickel occurs chiefly as sulfide ores in the Sudbury region, Canada. In its metallurgy, nickel is freed of sulfur, purified by use of carbon monoxide, and refined by electrolysis.

Nickel is a silver white metal, strong, ductile, and malleable. It corrodes very slowly and is attacked by nitric acid and by carbon monoxide.

Nickel is used as an electroplating metal for covering other metals with bright, wear- and tarnish-resisting surfaces. Alloys of nickel with steel are used for many purposes; a popular alloy of nickel and copper is Monel metal. Other alloys include nichrome (with Cr), permalloy (with Fe), nickel silver (with Cu and Zn), and stainless steel (with Cr and Fe).

QUESTIONS

63. What is the chief source of nickel?

64. What is the chief use of nickel?

65. What is the composition of steel No. 2345?

66. What properties make Monel metal a popular covering for shelves in large kitchens?

67. How does the junkman aid in conserving natural resources?

68. Investigate the uses to which Alnico magnets are put.

69. For what purposes were the composition of nickels and composition of pennies altered during World War II? What specific requirements had to be met by the replacement alloys selected?

70. What chemical industry depends upon the catalytic properties of finely divided nickel?

MORE CHALLENGING PROBLEMS AND QUESTIONS

71. A copper coin liberated $\left\{\begin{matrix}4.48\\5.60\end{matrix}\right.$ liters of sulfur dioxide under standard conditions when it was dissolved in concentrated sulfuric acid. What weight of copper was in the coin?

72. A 2-gram sample of brass precipitates $\left\{\begin{matrix}2.5\\2.4\end{matrix}\right.$ grams of copper sulfide (CuS) after it has been dissolved and the solution saturated with hydrogen sulfide. What is the percentage composition of the brass?

73. What is the difference between hard solder, soft solder, and silver solder? What is the composition of electric fuse wire?

74. (*a*) Lye is dissolved in water and placed in (1) a galvanized iron pail; (2) a tin can; (3) an aluminum pan. Write equations for any reactions that may take place. (*b*) If the lye solution stays in a metal vessel exposed to air, what change in composition takes place? Write the equation for the reaction. (*c*) Does this change affect the usefulness of the lye in neutralizing acids? Write equations to show the effect of hydrochloric acid on the lye both before and after the lye has been standing exposed to air.

UNIT SIX - - - - - - - - - - - - - - CHAPTER XXVIII

CORRORSION—HARMFUL OR HELPFUL

When men produce iron by placing iron ore in a blast furnace and heating it with coke and limestone, they are reversing a process of nature. Iron is an active metal that rusts easily. Most iron found in nature occurs as iron oxide. The blast-furnace process reduces, or deoxidizes, the iron ore. Consequently unprotected iron, attacked by water, oxygen, and carbon dioxide together in the air, tends to produce iron ore again. The rusting of iron articles represents an enormous waste of the energy used in their production, as well as a loss of the articles themselves. Everyone agrees that such waste should be avoided. As a result, increasing attention is being given today to the cause and prevention of rusting, or corrosion.

Another way to consider the matter is to say that iron is at the top of a hill and iron ore is at the bottom. Iron can roll toward the bottom of the hill, becoming iron ore, and do work on the way. But to get iron up to the top of the hill (from iron ore to iron) requires the heat from fiercely burning coke. At the top, the level of potential energy is high, and work must therefore be done to reach that position. In going down, the changing of iron to iron oxide is accomplished by a change of chemical energy to heat: indeed, the rusting of iron is accomplished by the evolution of ***measurable*** quantities of heat.

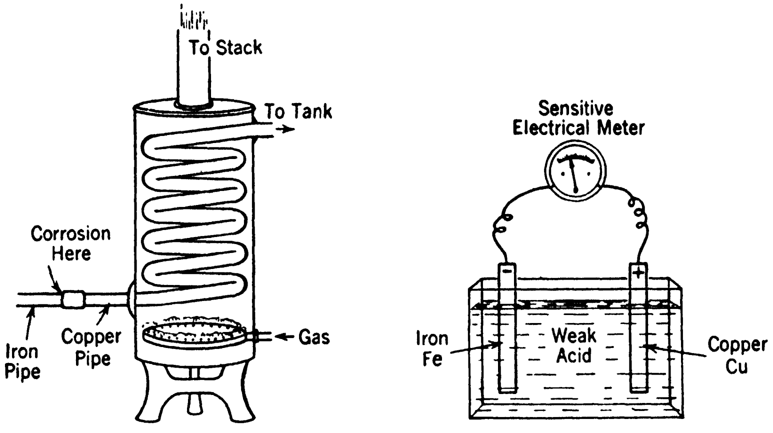
We shall now consider (1) the reasons why metals, chiefly iron, corrode; and (2) how to stop rusting or, better, how to prevent rusting from starting.

Iron Rusting. Experiments show that under water all forms of iron—cast, wrought, and steel—rust at the same rate. In air, under identical conditions, steel rusts fastest of the three; cast iron and wrought iron rust much more slowly.

New Terms

corrosion
passive iron
oxidation
reduction
electron transfer
depolarizer
vehicle
white lead

Experiments also show that, unless moisture and oxygen both are present, the rusting of iron in air is very slow. The presence of sulfur dioxide hastens the process. The end compound formed by ordinary rusting of iron is hydrated ferric oxide ($Fe_2O_3 \cdot 3H_2O$) or ferric hydroxide [$Fe(OH)_3$].



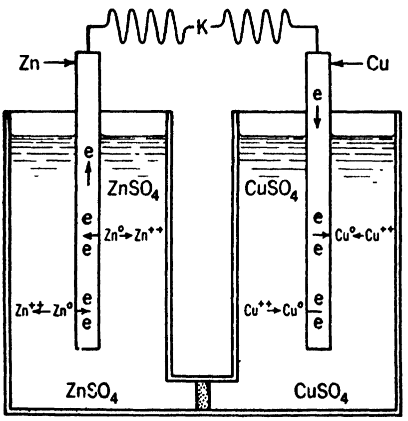
IN PRACTICAL LIFE

IN LABORATORY

FIG. 28-1.—When iron and copper are connected in contact with slightly corroding liquid, the iron soon becomes pitted with corrosion.

Two-metal Corrosion. A heating coil made of copper is connected to a water-supply system that uses iron pipes. (See Fig. 28-1.) After a relatively short while in service, a leak is noticed at the joint between the copper and iron pipes. Examination of the leak shows that the iron pipe is badly corroded, or "eaten away."

The explanation of this corrosion is that, when two ***unlike*** metals are in contact with each other in the presence of even very dilute salt solutions, the more active metal is attacked to a slight degree. The active metal in this case is iron. A little electric cell is set up. (See Fig. 28-2.) Iron is the cathode, or fuel, for the cell. Copper is the anode and is uncorroded. Impure water is the weak electrolyte. Any hydrogen that tends to accumulate and to stop the electrochemical action is oxidized to water by the oxygen dissolved in the water. Thus the iron pipe rusts.



Courtesy of Journal of Chemical Education

FIG. 28-2.—The mechanism of cell action. Notice that electrons leave the less active metal (Zn) and that this metal goes into solution as ions (Zn^{++}).

This sort of corrosion may be expected where any two unlike metals are in contact with the same corroding liquid. Salt water acts faster than fresh water as a corroding liquid. Consequently, ship's fittings are readily subject to two-metal corrosion wherever two-metal joints have been used in their equipment.

An experimental study of common industrial metals and alloys exposed to common water, salt water, weak acids, and weak alkalies has been made. An activity list based on these experiments is given below. The most active materials come first. Those grouped together have little action on each other. Obviously, the further separated in the list, the more rapid the corrosion of the upper one of a pair of metals is expected to be.

ELECTROCHEMICAL SERIES OF THE IMPORTANT INDUSTRIAL METALS*

— Easily corroded
Magnesium, aluminum, duralumin
Zinc, cadmium
Iron, chrome-iron (active), chrome-nickel-iron (active)
Solder, tin, lead
Nickel, brass, nickel-copper, copper
Chrome-nickel-iron (passive), chrome-iron (passive)
Silver solder
Silver, platinum, gold
+ Slowly corroded

* McKay, R. J. and R. Worthington, *Corrosion Resistance of Metals and Alloys*, Reinhold Publishing Corporation, New York, 1937.

Acid Corrosion. We have learned that aluminum, magnesium, zinc, iron, and lead are easily attacked by dilute acids, forming hydrogen. For example, in terms of ions,

$$Fe + 2H^+ \rightarrow Fe^{++} + H_2\uparrow$$

This action is greatly hastened if oxygen is present to change the hydrogen into water as fast as it forms. The oxygen in this case is called a depolarizer, for an accumulation of hydrogen on the metal tends to stop the action of the acid.

In general, the rate of corrosion of iron becomes rapid if the acidity (see page 225) of the corroding liquid is as high as pH 4 and if a good supply of oxygen is on hand to act as a depolarizer. If the supply of oxygen is low, the evolution of hydrogen starts at pH 5, but the rate of corrosion is very much slower than when oxygen is abundant. Thus we see that the amount of dissolved oxygen is an important factor in determining the rate of corrosion of iron in very dilute acids.

Concentration Effects. Assume that the same piece of iron is in contact with impure ordinary water. (See Fig. 28-3.) At one region the water has plenty of dissolved oxygen, but at another region for some reason the water lacks dissolved oxygen. This difference in concentration of dissolved oxygen is cause enough for corrosion to take place. The area at which the oxygen is lacking becomes the anode (+) in a tiny electrolytic cell. The aerated iron becomes the cathode (−). The rust formed is porous and rich in available dissolved oxygen, and therefore deep pitting is produced. Many iron pipes that corrode in soil or cinders are attacked because an oxygen concentration cell forms.

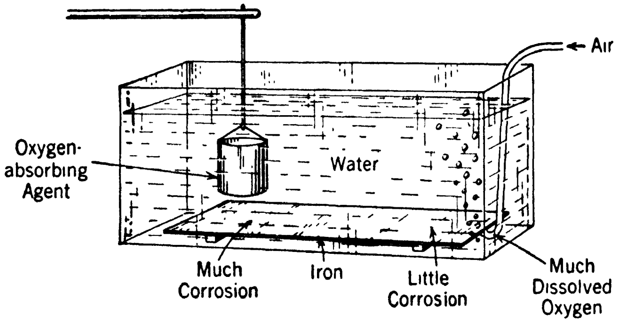


FIG. 28-3.—An oxygen concentration cell. The two electrodes differ in the amount of dissolved oxygen in the electrolyte at each.

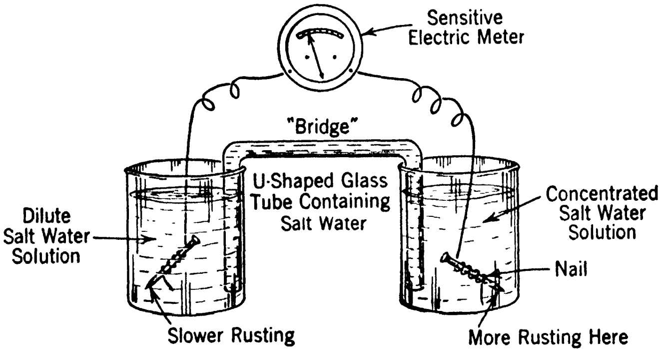


FIG. 28-4.—An electric cell may be set up when identical electrodes are used—one is placed in a solution, the other in a similar solution, differing only in concentration.

Another possible cause of corrosion can be seen from an experiment. Two iron nails are placed in separate beakers. One contains a dilute salt solution, the other a concentrated salt solution. The beakers are connected by an inverted U-shaped tube of salt water that serves as a bridge or liquid connection between the beakers. The two nails are connected by iron wires to a sensitive electrical meter. (See Fig. 28-4.) A slight movement of the meter needle shows that a current is flowing, or that more electrons are being liberated on one nail than on the other. The nail in the concentrated salt solution corrodes faster.

Electrolysis. The earth is a storehouse of electrons. Feeble stray electric currents from numerous sources are continually surging under and on the surface of the earth.

Let us assume that a long pipe line is buried in the earth. At one damp spot many stray earth electrons come to it. The iron of the pipe carries these electrons in the pipe through a length of dry nonconducting soil. At the next wet spot the electrons leave the pipe. At this spot the pipe is the anode of an electroplating cell, or the electrode that is eaten away. Serious corrosion may result where the electrons leave the pipe. (See Fig. 28-5.)

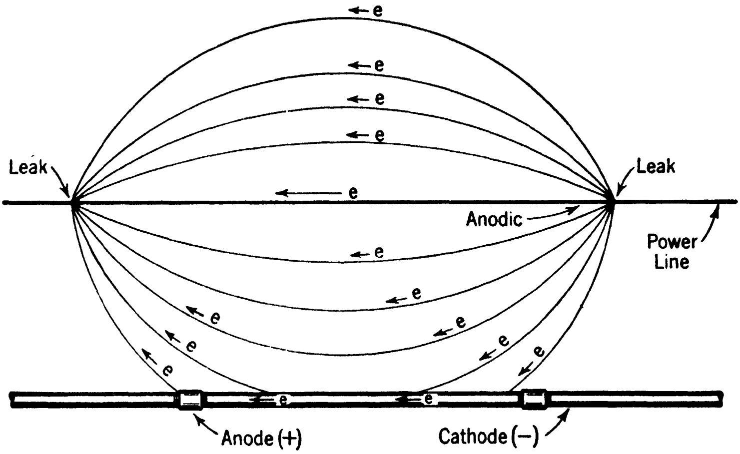


Fig. 28-5.—Stray-current corrosion. Where does the underground pipe corrode?

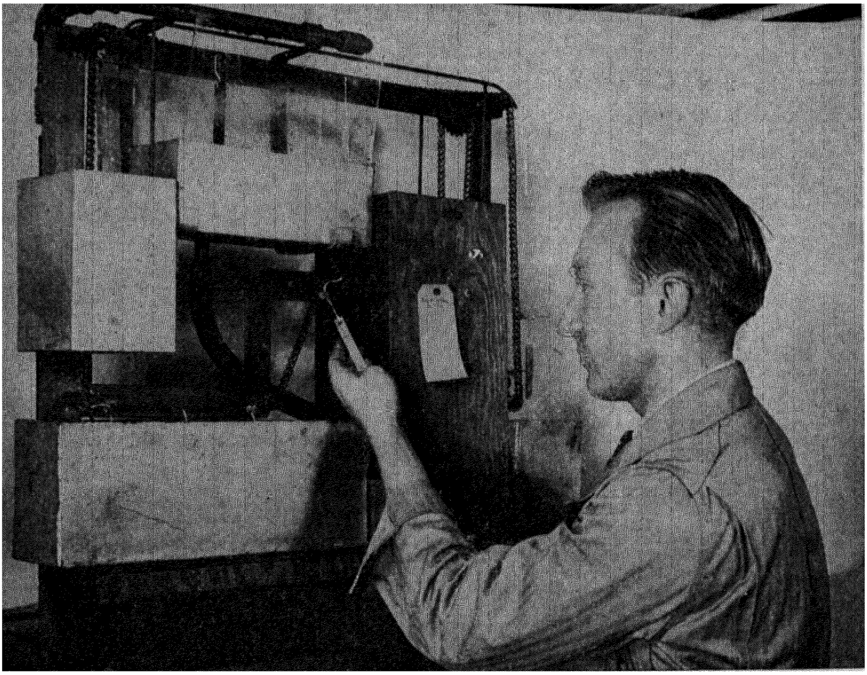
Other Causes of Corrosion. When alloys are made hurriedly, they are sometimes not uniform in composition. This may be true of Bessemer steel in which the added manganese has not had time to distribute itself evenly. Irregularity in composition causes the steel to corrode more readily. Duralumin corrodes more readily than aluminum alone, possibly owing to irregularities in its composition. Lack of uniform composition is equivalent to a two-metal cell.

Metals under stress corrode more readily than those without any force acting on them. This is especially true of metals that have been cold-worked. A small crack in a tightly fastened nut becomes a serious failure if the atmosphere is moist and somewhat corroding. The effect is something like crumbling the keystone in an arch.

Sometimes lubricants may cause corrosion. If the oils present break down into fatty acids (see page 560) or if petroleum oils are improperly refined so that acid remains in them, these acids may attack metals, especially lead (see page 469.)

Prevention of Corrosion. 1. The obvious method of stopping corrosion is to protect the metal. Painting is used extensively for this purpose. The linseed- or tung-oil "vehicle" of the paint carries a pigment, or "body," to aid in its covering power. When oxidized, or "dried," the oil forms a horny impervious coating over the metal, effective as long as it is unbroken.

2. Electroplating (see page 240) iron with other metals less active chemically has been discussed. Nickel, cadmium, chromium, silver, and even brass are among the metals applied by electroplating.



Courtesy of Armour Research Foundation

FIG. 28-6.—Chemist L. E. Anderson demonstrates corrosion-testing apparatus that was designed at a research chemical laboratory.

3. Mechanically applied metal coatings are also used. A cleaned base metal may be dipped in molten protective metal, or the protective metal may be warmed and rolled onto sheet iron or aluminum. Gold-filled jewelry has merely a gold coating. Tin, lead, and zinc are used for rolling onto steel, forming a sandwich of the steel between two waferlike sheets of protecting metal.

4. Enamels or porcelain surfaces applied to iron are well known. Kitchen utensils of enamelware have a baked, glasslike coating.

5. Another way to avoid corrosion is to make a corrosion-resisting alloy of the iron. Even 0.2 per cent of copper in steel increases its corrosion resistance greatly. Stainless steels, which must contain 12 per cent of chromium or more (see page 443), are known to all. The common type of stainless steel contains 18 per cent chromium and 8 per cent nickel.

Surface-treating Steel. Ordinary brown rust is porous and flaky. It does not protect the iron beneath. In fact, rust adsorbs acidic gases and moisture, hastening more corrosion. If the surface of steel could be treated so that a tough inactive oxide coating was formed, then ordinary rust could not gain a foothold.

Several metals furnish examples of self-protection by tough oxide films. Aluminum is protected by a tough layer of aluminum oxide (Al_2O_3); and magnesium, alloyed with about 5 per cent of other metals, resists weather well and corrodes no faster than aluminum.

When hot iron acts on steam, a protective film (Fe_3O_4) is formed.

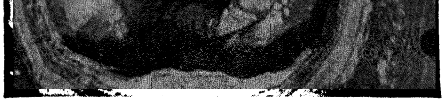
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$$

Dipping steel into hot phosphoric acid (H_3PO_4) also produces a good corrosion-resisting coating. This treatment is often given to steel that is to be sprayed with lacquer or enamel. The coating bonds well with modern steel finishes, such as those applied to automobile bodies and household machines.

Courtesy of Aluminum Company of America

FIG. 28-7.—A strong aluminum-alloy mast reduces dead weight on the sailing yacht "Rainbow." Aluminum alloys are available that resist salt-water spray corrosion.

Tacks, razor blades, and small firearms are sometimes blued. This corrosion-resisting finish is applied by heating the metal with bone black.



Courtesy of D. W. Haering & Company, Inc.

FIG. 28-8.—This scale deposit was found in a 12-in. steam line 400 ft. from the boilers in a 29-story building. Corrosion can take place on both sides of a metal pipe.

Passive Iron. When iron is immersed in concentrated nitric acid, it is made unreactive, or ***passive***. That is, the iron no longer acts chemically like ordinary iron but is attacked much less by common chemicals, resembling lead chemically more than iron. Passive iron will not replace copper from copper sulfate solution. Chlorides destroy the passive state, and the chromate ion (CrO_4^{--}) preserves the passive condition. Investigators claim that razor blades become dull because of a slight rusting on the cutting edges. A blade kept between shaves in a solution of sodium chromate (Na_2CrO_4) will keep its cutting edge for a long time, for the passive condition of the steel prevents rusting.

Strangely enough, if the oxygen concentration of a solution that normally corrodes iron is kept high, the passive condition is preserved—just the reverse of ordinary corrosion.

In stainless steels containing over 12 per cent chromium, the iron is in the passive state. The steels remain stainless just as long as the iron remains in the passive condition. When the oxygen supply is low in a corroding liquid, stainless steels rust. Pitting occurs because the active form and the passive form of the same metal act as if they were two different metals (see table, page 493).

QUESTIONS

1. Bicycle handle bars are usually made of steel plated with nickel. Many water pails are made from sheet steel and galvanized by dipping them into molten zinc. Explain how each coating protects the steel.

2. Give an example of an article that has lost its usefulness owing to corrosion.

3. Which of the two metals in contact corrodes the more rapidly in each of the following examples: (*a*) On a seagoing boat a phosphor-bronze propeller shaft has a steel guide. (*b*) An iron water pipe is connected directly to a copper water tank. (*c*) Aluminum and silver (in contact) are heated in a weakly alkaline solution for the purpose of cleaning tarnish from the silver. (*d*) Carbon and zinc are in contact with ammonium chloride in a dry cell. (*e*) Sulfuric acid from a storage battery sprays on both steel and copper. (*f*) A dentist using a steel instrument touches a silver filling in a tooth that is moist with saliva.

4. Point out how the nature of the surface corrosion of iron differs from that of aluminum.

5. Why must steel be perfectly clean before an enamel coating is applied to it?

6. Point out the effect of high content of dissolved oxygen on the rate of corrosion of ordinary iron as compared with the rate of corrosion of stainless steel otherwise under the same conditions.

7. What is one important reason for razor blades becoming dull while standing? How may they be kept sharp?

8. A successful antifreeze liquid must not corrode three materials. Name them.

9. An airplane made of magnesium-aluminum alloys makes a crash landing in a swamp that contains slightly acid water. If the airplane cannot be removed for several days, what damage does the metal undergo?

10. If an organic (carbon compound) antifreeze liquid is used in an automobile radiator, sodium chromate must not be used for an antirusting agent. Explain.

11. Why is calcium chloride considered to be an unsatisfactory antifreeze material?

Helpful Corrosion. Owing to improvements in modern metallurgy, many metals can be made almost 100 per cent pure. They are suitable and often economical starting materials for making compounds (salts) of the metals.

Copper, burned in chlorine, effectively corrodes and produces copper chloride of high purity.

$$Cu + Cl_2 \rightarrow CuCl_2$$

Tin on scrap tin plate (tin coated on iron) is recovered in the form of the compound stannic chloride ($SnCl_4$) by treating the metal at fairly low temperatures with chlorine.

$$Sn + 2Cl_2 \rightarrow SnCl_4$$

This process is controlled in such a manner that very little of the iron is attacked.

About one-fourth of all the lead produced is deliberately corroded in the manufacture of white lead [approximate formula $Pb(OH)_2 \cdot 2(PbCO_3)$], or basic lead carbonate, the most important white pigment in paints. The Dutch process of making white lead uses earthenware crocks (see Fig. 28-9) that have a reservoir in the bottom containing 500 ml of 28 per cent acetic acid ($H \cdot C_2H_3O_2$). Perforated lead disks, called buckles, are piled on shoulders in the crocks. The perforations in the disks are so arranged that the circulation of acetic acid fumes, moisture, and carbon dioxide cannot be shut off. The crocks fill a room in layers. Fermenting tanbark from a leather tannery is strewed between each layer. With this combination of carbonic and acetic acids in the warmth from the fermentation, the lead corrodes to form a white powder, the basis of much of the outside white house paint used today.

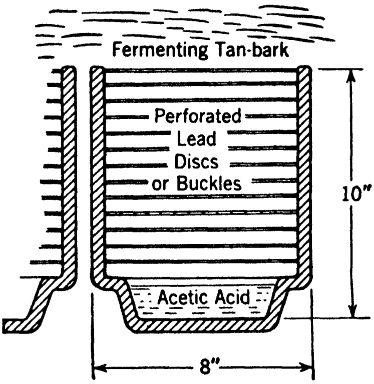
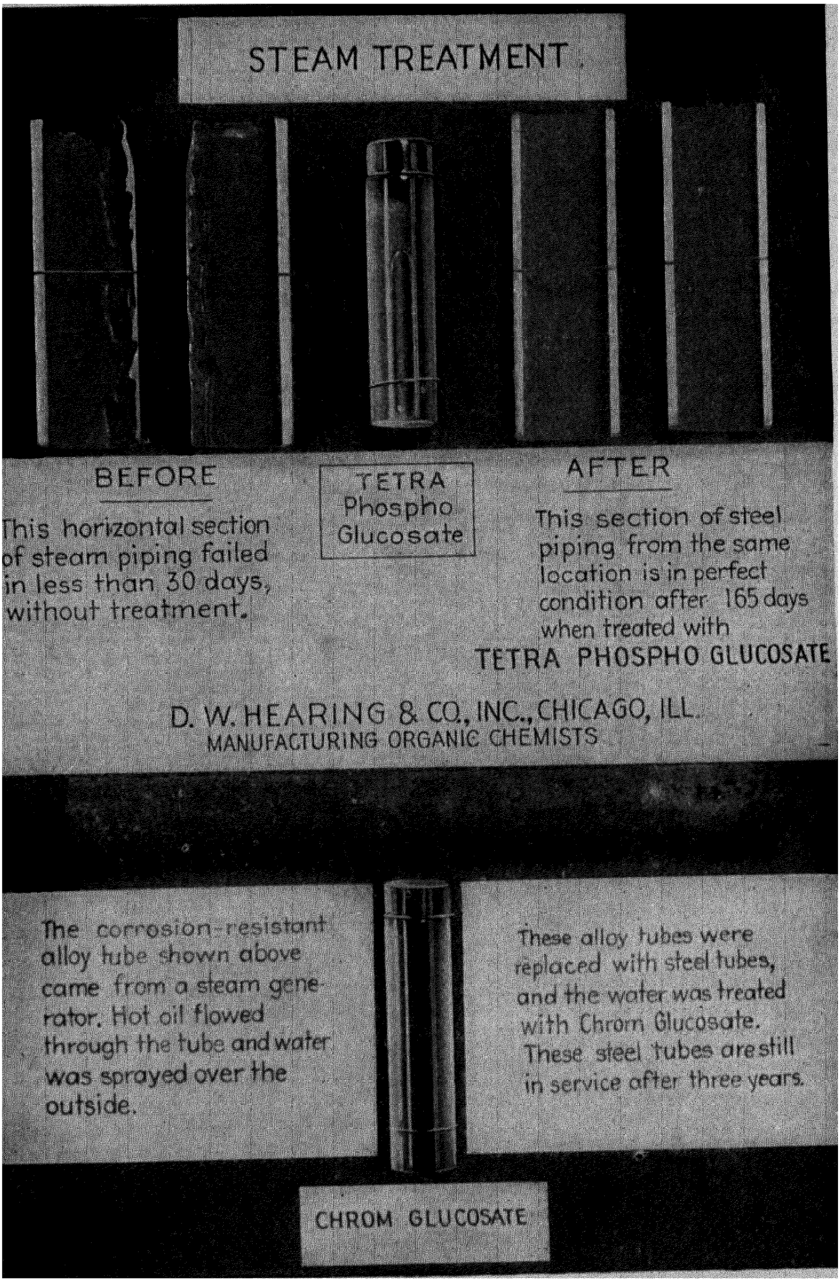


FIG. 28-9.—When lead is corroded in a warm, moist atmosphere containing carbon dioxide, white lead forms. White lead is used in many types of paints.



This horizontal section of steam piping failed in less than 30 days, without treatment.

This section of steel piping from the same location is in perfect condition after 165 days when treated with TETRA PHOSPHO GLUCOSATE

The corrosion-resistant alloy tube shown above came from a steam generator. Hot oil flowed through the tube and water was sprayed over the outside.

These alloy tubes were replaced with steel tubes, and the water was treated with Chrom Glucosate. These steel tubes are still in service after three years.

Courtesy of D. W. Haering & Company, Inc.

FIG. 28-10.—The effect of the use of a chemical inhibitor in preventing corrosion is clearly shown in this display.

Thus we see that corrosion is helpful in two cases,

1. When it forms a protective coating over the metal
2. When useful compounds of the metals are formed.

An Ounce of Prevention. Further examples of how to prevent corrosion are interesting.

The water in the cooling system of an automobile flows from the bronze radiator to the iron water jacket of the motor. In the summer, corrosion may be prevented by adding 1 oz of sodium or potassium chromate (K_2CrO_4) to the water. This renders the iron passive. Borax ($Na_2B_4O_7$) and trisodium phosphate (Na_3PO_4) also work well for the same purpose, but not for the same reason; they render the solution alkaline, which reduces the rate of corrosion.

Antifreeze preparations also contain an inhibitor to prevent corrosion in the cooling system. In this case the inhibitor must be soluble in the antifreeze fluid. Organic compounds, such as sodium chrome glucosate, ethanol amine, and quinoline ethiodide, are used.

To remove rust from a file, dip it in $6N$[1] hydrochloric acid (dilute HCl of the laboratory) to which aniline ($C_6H_5NH_2$) has been added. The rust dissolves but not the steel, for the aniline acts as an inhibitor. The use of such a preparation to clean out rusty plumbing or to clean steel before electroplating is suggested.

Corrosion in steam boilers is prevented by suitable water treatment. Salt-water corrosion of magnesium alloys used in the construction of certain seaplanes is prevented by a selenium coating. Pure aluminum coated on aluminum alloys has a similar effect.

Compounds of the Metals. Many useful compounds of the metals are in everyday use. Everyone has heard of Epsom salts or hydrated magnesium sulfate ($MgSO_4 \cdot 7H_2O$), blue vitriol or hydrated copper sulfate ($CuSO_4 \cdot 5H_2O$), and bichloride of mercury or corrosive sublimate ($HgCl_2$).

Some of these compounds, especially salt (NaCl), are found in nature. Others are made by treating the metal, metal oxide, hydroxide, or carbonate with the proper acid. For example, Epsom salts can be made by treating magnesium carbonate ($MgCO_3$) with sulfuric acid.

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2CO_3$$

The solution is filtered from the excess of magnesium carbonate that should be used and the salt crystallized from the clear solution.

In making magnesium from sea water, magnesium hydroxide [$Mg(OH)_2$] is obtained by treating the sea water with a solution of slaked

---

[1] See Appendix. $6N$ hydrochloric acid may be made by adding 516 ml of concentrated (36 per cent) hydrochloric acid to enough water to make 1 liter.

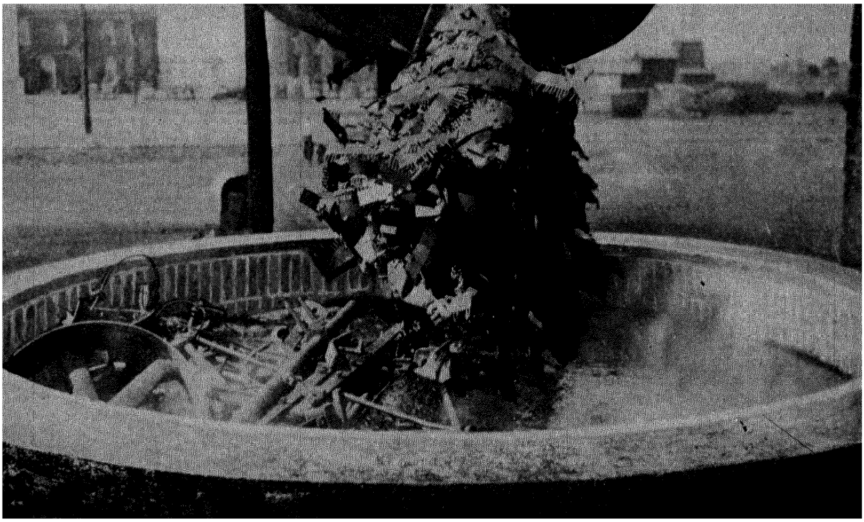
lime [$Ca(OH)_2$].

$$\underset{\text{in sea water}}{MgCl_2} + \underset{\text{slaked lime}}{Ca(OH)_2} \rightarrow \underset{\text{a precipitate}}{Mg(OH)_2\downarrow} + \underset{\text{left in solution}}{CaCl_2}$$

The less soluble magnesium hydroxide precipitates and is retained by a filter cloth, removed, and treated with hydrochloric acid to convert it to the chloride.

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

A solution of magnesium chloride free from the other metal ions originally present in sea water results. This, when evaporated, dried, and fused, is used in the electrolysis cell to obtain metallic magnesium.



Courtesy of Pennsylvania Salt Manufacturing Company

FIG. 28-11.—Deliberate corrosion produces useful compounds. Above, scrap iron is lowered into hot hydrochloric acid as the first step in manufacturing ferric chloride. The tank is lined with acid-resisting bricks.

The making of both soluble and insoluble metal salts has already been discussed (see page 226). These general methods should be reviewed at this point. A list of the more useful metal compounds together with their common names, formulas, and uses is given for reference in the Appendix.

Oxidation-reduction. When iron rusts, a compound of iron is formed. The action may be represented imperfectly by the equation

$$4\overset{0}{Fe} + 3O_2 + 6H_2O \rightarrow 2(\overset{+++}{Fe}_2O_3 \cdot 3H_2O)$$

A similar corrosion is seen in the slower oxidation of zinc,

$$2\overset{0}{Zn} + O_2 \rightarrow 2\overset{++}{Zn}O$$

or the tarnish on household silverware,

$$2\overset{0}{Ag} + S \rightarrow \overset{+}{Ag}_2S.$$

An examination of the metal (or sulfur) in each of these examples of corrosion shows that the element changes its combining number. A gain in the combining number is evident. More accurately, a loss of electrons has taken place. The oxygen or sulfur in these examples has gained electrons and is reduced from O^0 to O^{--}. In fact, all examples of so-called oxidation come under this classification. Oxygen is not necessary—merely an increase in the combining number of the metal. The equations following show more cases of oxidation and reduction. Let us examine with care the change in the combining number of the various elements. We also observe that as oxidation occurs other atoms are undergoing a decrease in combining number. This process is called ***reduction.***

$$\overset{0}{H}_2 + \overset{++}{Cu}O \rightarrow \overset{0}{Cu} + \overset{+}{H}_2O \qquad \left\{\begin{array}{lcll} \overset{0}{H}_2 & \rightarrow & \overset{+}{H} & \text{(oxidation)} \\ \overset{++}{Cu} & \rightarrow & \overset{0}{Cu} & \text{(reduction)} \end{array}\right.$$

$$\overset{+++}{Fe}_2O_3 + 3\overset{++}{C}O \rightarrow 2\overset{0}{Fe} + 3\overset{++++}{C}O_2 \qquad \left\{\begin{array}{lcll} \overset{+++}{Fe} & \rightarrow & \overset{0}{Fe} & \text{(reduction)} \\ \overset{++}{C} & \rightarrow & \overset{++++}{C} & \text{(oxidation)} \end{array}\right.$$

Just as borrowing and lending are two different aspects of the same transaction, so oxidation and reduction are two aspects of the same chemical process. We have just noticed that oxidation increases the combining number of a metal. Reduction, on the other hand, means a decrease in the combining number of a metal or nonmetal. More explicitly, since oxidation is a loss of electrons, then reduction is a gain of electrons. The whole process is oxidation-reduction.

In each of the following examples oxidation and reduction can be distinguished by noting the change in the combining number:

$$\overset{+++}{Fe}_2O_3 + 2\overset{0}{Al} \rightarrow \overset{+++}{Al}_2O_3 + 2\overset{0}{Fe}$$

(loss of $3e^-$ per atom of Al)
(gain of $3e^-$ per atom of Fe)

$$2\overset{+++}{Fe}Cl_3 + \overset{0}{Fe} \rightarrow 3\overset{++}{Fe}Cl_2$$

(loss of $2e^-$ from each atom of metallic iron)
(gain of $1e^-$ per atom of Fe in $FeCl_3$)

In short, oxidation-reduction actions are simply those chemical actions in which an ***electron transfer*** takes place. Balancing such equations involves making the electron transfer balance.

SUMMARY

The corrosion of iron and other metals causes great economic loss. Under water, all forms of iron rust at the same rate. In moist air, steel rusts faster than cast iron or wrought iron. Local conditions, such as the presence of mild acid, may greatly hasten the rusting of iron.

1. Corrosion takes place when two different metals are in contact in a corrosive liquid. The more active metal dissolves. An activity list of commercial metals and alloys is available.

2. In acid corrosion, the extent of corrosion depends in a measure on the amount of dissolved oxygen available. Dissolved oxygen acts as a depolarizer, changing hydrogen to water.

3. In concentration corrosion, the differing concentrations of the same electrolyte in contact with a metal cause corrosion at the area in contact with the more concentrated part or parts.

4. In electrolysis, the stray electric currents set up electrochemical cells in which the anode is corroded.

5. Less frequent causes of corrosion include lack of uniform composition of alloys, presence of strains, and presence of acids developed by breakdown of lubricants.

Corrosion is prevented by

1. Painting. A horny coating of oxidized oil containing pigments increases wear and attractiveness.

2. Electroplating. A corrosion-resisting metal is deposited electrically over a less resistant base.

3. Mechanically applied coatings. A surface coating of one metal is applied on another. Examples are galvanized iron or tin plate.

4. Surfacing with enamel or porcelain. An enamel or porcelain glasslike surface is melted onto metal.

5. Surface treating. Oxide films form naturally on aluminum. Other types of films are formed by chemical treatment, as in the case of iron. Insoluble oxide films resist further corrosion.

6. Passive metal. The passive condition of the metal is developed. In the case of iron, the passive condition is preserved by the chromate ion and destroyed by the chloride ion.

Corrosion may be helpful in the following respects:

1. Some surface corrosion protects the metal beneath from further attack. Red-brown iron rust, however, is flaky and porous and does not act in this way. Black magnetic iron oxide (Fe_3O_4) protects iron, and aluminum oxide (Al_2O_3) is an effective covering agent for aluminum.

2. Preparation of certain compounds, notably white lead, is accomplished by means of corroding the metal.

Compounds of metals may be formed as a result of corrosion. Many metallic compounds are used extensively, such as common salt ($NaCl$), blue vitriol ($CuSO_4 \cdot 5H_2O$), and Epsom salts ($MgSO_4 \cdot 7H_2O$) and some are the source of the metal.

Oxidation-reduction reactions comprise a common type of chemical change. They are electron-transfer reactions that involve a change in combining number (valence). The element that is oxidized has a higher combining number due to loss of electrons. The element that is reduced has a lower combining number due to gain of electrons. Oxidation-reduction equations may be balanced conveniently by considering the electron transfer.

QUESTIONS

12. Point out two examples of useful corrosion.

13. The addition of either potassium chromate or trisodium phosphate solution to the cooling water of an automobile radiator retards the rate of rusting. Explain the action of each.

14. Show by formula equations how to make (*a*) copper chloride ($CuCl_2$) in five different ways; (*b*) copper nitrate in five different ways.

15. Define oxidation-reduction in terms of (*a*) combining-number change; (*b*) electron transfer.

16. Show that the burning of carbon is an oxidation-reduction process.

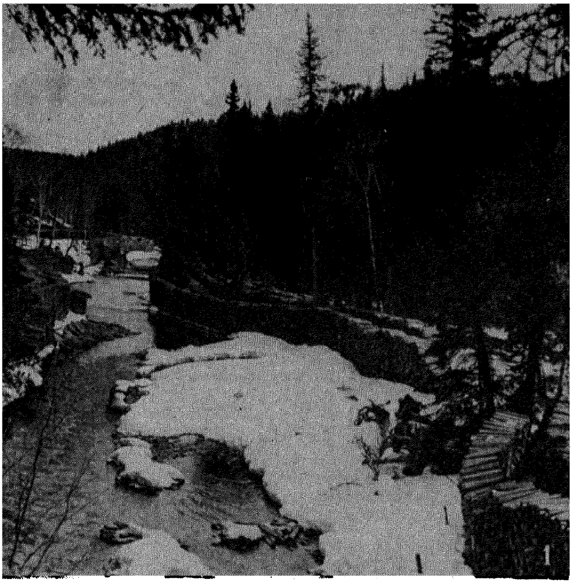
17. Illustrate oxidation-reduction by showing combining-number changes in each of the following equations (*do not write in this book*):

(*a*) $ZnO + C \rightarrow Zn + CO\uparrow$
(*b*) $SnO_2 + C \rightarrow Sn + CO_2\uparrow$
(*c*) $2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$
(*d*) $CO_2 + C \rightarrow 2CO$
(*e*) $SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2\downarrow$

18. When metals corrode, do they gain or lose weight?

19. Describe the Dutch process for corroding lead, using a labeled diagram.

UNIT SEVEN


1

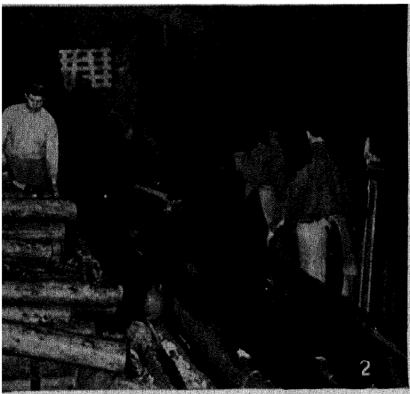
THE CHEMISTRY OF CARBON COMPOUNDS

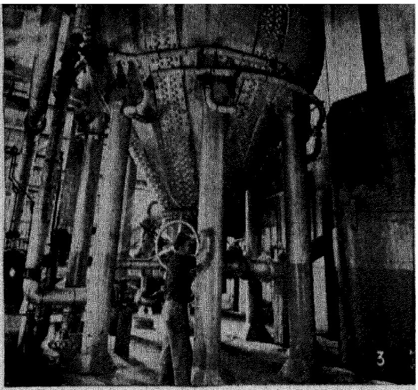
Logs are made into pulp, and pulp is made into paper. The process is both mechanical and chemical. The number of uses for paper is increasing, and more and more varieties of paper are coming into daily use.

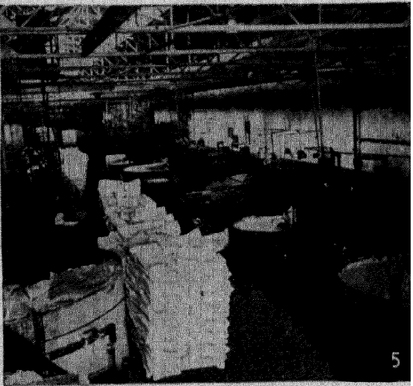
Logs are piled along a river (1), where they await the spring thaw for transportation to the pulp mill. Log jams are broken up by blasting with dynamite.

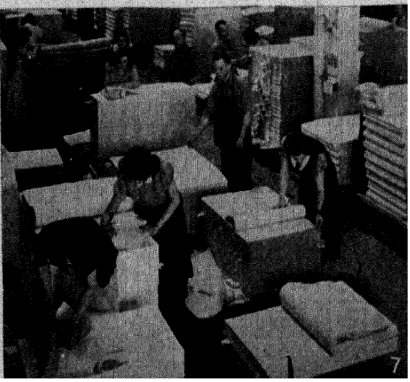
In the pulp mill (2), logs are barked and prepared to be cut into chips. When wood chips are cooked with chemicals in the digester (3), pulp is produced. The lignin, or natural binder in the wood, is destroyed, and a mass of fibers remains. This wood pulp is carried through the bleacher (4) with a huge volume of water. The beaters, tublike machines (5), are used to prepare a uniform suspension of pulp in water. The portable platforms are loaded with sheets of pulp.

The Fourdrinier papermaking machine is over 200 ft long. It converts a uniform soup of pulp and water into a continuous sheet of paper. On the left of (6) is shown a portion of the drier rolls. Finished paper is counted, inspected, and packed (7) for shipment.









Courtesy of Hammermill Paper Company

UNIT SEVEN .... CHAPTER XXIX

THE NATURE OF CARBON COMPOUNDS

A story is told about an organic chemist who, having a headache, sought relief at a drugstore. He explained his need to the clerk in this manner: "I'd like to buy some tablets of acetylsalicylic acid."

"Oh," replied the clerk, "you mean aspirin."

"That's it," responded the chemist. "I can never remember that name."

One reason why chemists give such strange, long names to organic compounds is because there are so many of them. The organic compounds, compounds of carbon, almost half a million in all, are ten times as numerous as the inorganic compounds, that is, compounds of all the rest of the 95 chemical elements. This great number, however, should not discourage the beginner. Learning about a few organic compounds will serve to give a general view of the entire field, for it is possible to classify organic compounds into groups, thus simplifying study.

As the term implies, ***organic*** compounds were once considered to be produced only through mysterious forces by living organisms. This view is not held today, for many organic compounds are made in laboratories without the use of materials directly connected with living creatures or plants. Organic chemistry is the study of compounds of carbon with hydrogen, nitrogen, sulfur, phosphorus, oxygen, the halogens, and relatively few other elements.

Comparison of Organic and Inorganic Compounds. ***1. Likenesses.*** All previously learned laws describe the behavior of both organic and inorganic compounds. The law of conservation of matter (see page 29), Gay-Lussac's law of volumes (see page 140), and Dalton's law of multiple proportions (see page 143) all hold true in both fields. Heat

---

New Terms

organic
inorganic
unsaturated
carboxyl group
wood alcohol
grain alcohol
enzyme
diastase
denatured alcohol
structural formula
double bond

speeds up the rate of reaction, and the effect of a catalyst is the same where both types of compounds are involved. Valence (combining-number) rules hold for both, but fewer ionic compounds are encountered among the organic group.

*2. **Differences.*** 1. All organic compounds have carbon as a constituent. Examples are sugar ($C_{12}H_{22}O_{11}$) and alcohol (C_2H_5OH).

Aside from carbon dioxide, carbon monoxide, and carbonates very few compounds that contain carbon are classified as inorganic.

2. In organic compounds, carbon shows a tendency to form long chains of atoms. Other elements do not show this property to any great extent.

3. We are aware that sodium hydroxide (NaOH) is a polar, saltlike solid compound which when melted or in solution conducts electricity well (see page 245). We explain this by saying that the compound is made of ions which dissociate easily and that its chief valence bond is of the ionic or electrovalent type; that is, an electron has actually been transferred from the sodium atom to the hydroxyl group (OH^-).

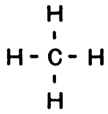
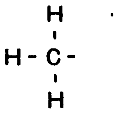
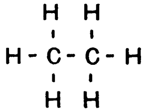
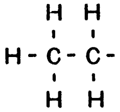
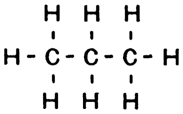
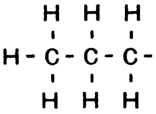
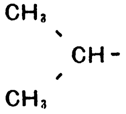
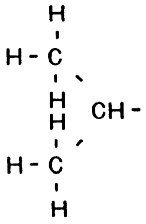
Alcohol (C_2H_5OH), on the other hand, is a volatile, mobile liquid, a carbon compound containing the hydroxyl group (—OH) that does not conduct electricity. We explain this by saying that the compound is not made of ions; and neither alone nor in water solution does it dissociate to produce conducting solutions. The hydroxyl group is attached to one of the carbons of the ethyl group (C_2H_5—) by means of a shared pair of electrons, a covalent bond (see page 191).

4. Chemical reactions in inorganic chemistry, when ionic, are frequently rapid. In organic chemistry hours and sometimes days are required for the completion of a given chemical process. Organic reactions frequently go in steps or stages. Only a very few of them are rapid.

5. A great number of inorganic compounds like salt (NaCl) dissolve in water. Very few organic compounds dissolve well in water. Compounds like sugar ($C_{12}H_{22}O_{11}$), alcohol, and glycerol are exceptions. Organic compounds do dissolve readily in organic solvents, such as benzene (C_6H_6), ether [$(C_2H_5)_2O$], and acetone [$(CH_3)_2CO$].

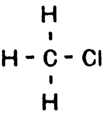
6. The structure (arrangement of atoms in the molecule) of most organic compounds is well established, but the structure of inorganic compounds is more difficult to determine. Up to the present, relatively few have been completely worked out.

Series of Compounds. Let us consider hydrocarbons. These are compounds of carbon and hydrogen only. The simplest is methane (CH_4). In this formula carbon has valence 4 and hydrogen 1. The next two members of the methane series of compounds are ethane (C_2H_6) and propane (C_3H_8); many others in the series are known (see page 535).

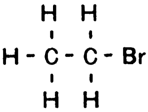
Hydrocarbon		Derived radical	
Molecular formula	Structural formula	Formula	Structural formula
CH_4 methane	 $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$	CH_3- methyl radical	 $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-$
C_2H_6 or CH_3-CH_3 ethane	 $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$	C_2H_5- or CH_3-CH_2- ethyl radical	 $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-$
C_3H_8 or $CH_3-CH_2-CH_3$ propane	 $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$ normal propane	C_3H_7- or $CH_3-CH_2-CH_2-$ normal propyl radical	 $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-$
		 $\begin{array}{l}\text{CH}_3\diagdown \\ \qquad\text{CH}- \\ \text{CH}_3\diagup\end{array}$ iso-propyl radical	 $\begin{array}{l}\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\diagdown \\ \qquad\quad\text{CH}- \\ \text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\diagup\end{array}$

Organic Radicals. Radicals with valence 1 may be considered to be related to a series of hydrocarbons by the removal of a single hydrogen atom, as shown in the table. Thus the methyl radical (CH_3—) is related to methane (CH_4), the ethyl radical (C_2H_5—), to ethane (C_2H_6), and so on. The beginner should write these formulas out both as given here and in the structural form given in the table, checking to see that each carbon atom possesses four bonds, each hydrogen atom one, and each oxygen atom (if present) two.

We can now see how to represent the formula for methyl chloride, a compound sometimes used as a refrigerant. It is methyl (CH_3—) chloride (—Cl), or CH_3Cl. Again, ethyl bromide, an important material in synthesis, is ethyl (C_2H_5—) bromide (—Br), or C_2H_5Br. Their structural formulas are

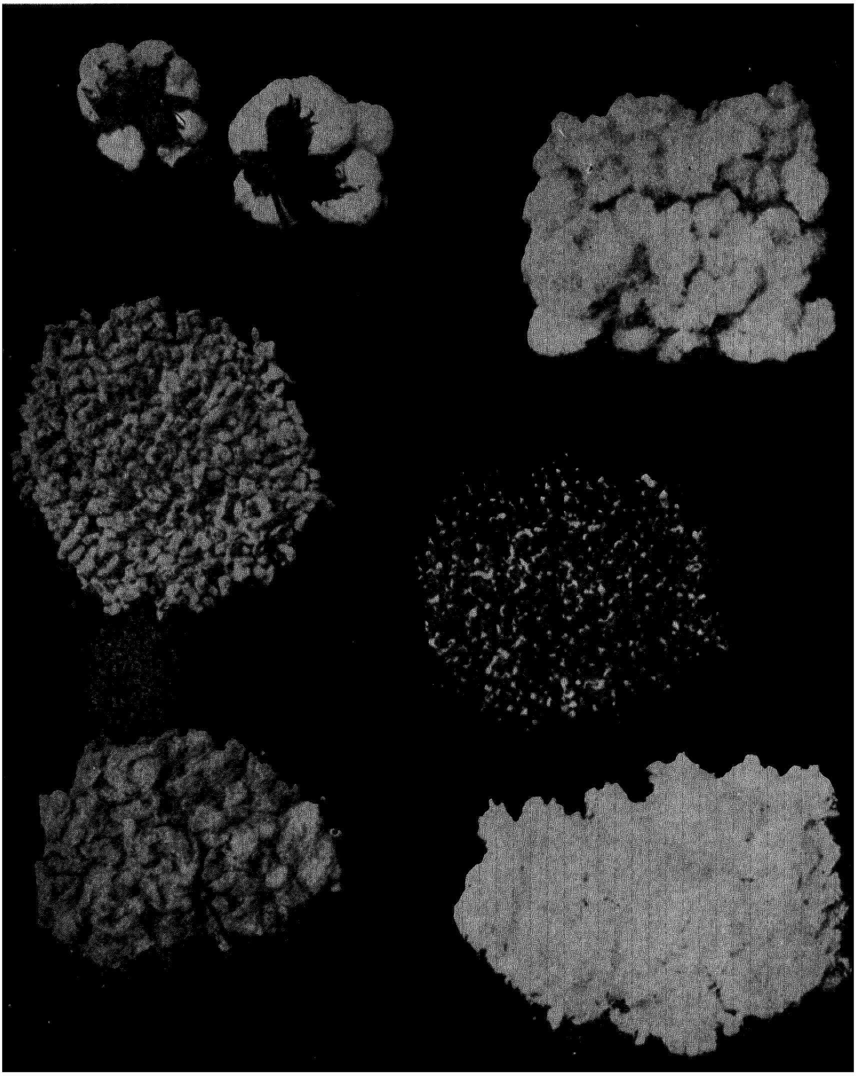

$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{Cl}$

methyl chloride


$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{Br}$

ethyl bromide

Carbon to Carbon to Carbon. Important and easily noticeable from the structural formulas already given is the fact that carbon atoms

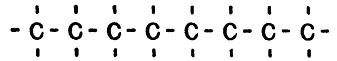


Courtesy of Celluloid Corporation

Cotton bolls	Staple cotton
Cotton seed before removing linters	Cotton seed after removing linters
Linters before purification	Chemical cotton

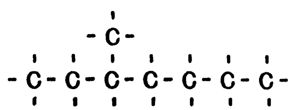
FIG. 29-1.—The organic chemist views cotton as a source of cellulose and of oil. Cotton can be made into nitrocellulose, a material of extensive uses.

join together by means of covalent bonds. In the examples given, chains of carbon atoms are formed. Such chains may be either straight or branched. Here are the structural formulas of two octanes, omitting the hydrogen:



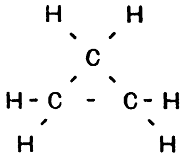
$$\begin{array}{c}| \;\; | \;\; | \;\; | \;\; | \;\; | \;\; | \;\; | \\ -C-C-C-C-C-C-C-C- \\ | \;\; | \;\; | \;\; | \;\; | \;\; | \;\; | \;\; |\end{array}$$

normal octane

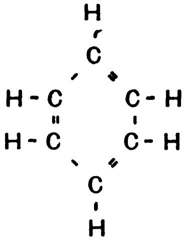


an iso-octane

Again, owing to the chain-forming tendency of carbon, the atoms may take the form of a ring. An example is cyclopropane, which is now an important anesthetic.



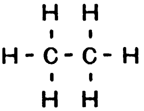
cyclopropane



benzene

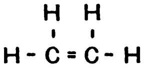
Benzene (C_6H_6) is an important ring compound in which some of the carbon atoms are attached doubly to each other. The derived radical, C_6H_5—, valence 1, is called the phenyl radical. Thus, phenyl (C_6H_5—) iodide (—I) is C_6H_5I.

Saturated and Unsaturated Compounds. Let us consider three different compounds of hydrogen and carbon that contain two atoms of carbon: ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2). A satisfactory way to account for the formulas is seen by the structural diagrams for these compounds.



$$\begin{array}{c} H \;\; H \\ | \;\;\; | \\ H-C-C-H \\ | \;\;\; | \\ H \;\; H \end{array}$$

ethane
(single bond)



$$\begin{array}{c} H \;\; H \\ | \;\;\; | \\ H-C=C-H \end{array}$$

ethylene
(double bond)

$H-C \equiv C-H$

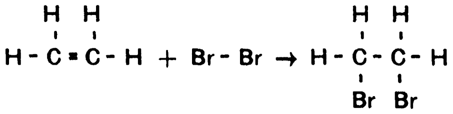
acetylene
(triple bond)

In ethane the carbon to carbon linkage is a ***single bond;*** in ethylene the linkage is a ***double bond;*** and in acetylene it is a ***triple bond.*** This situation is explained in terms of electrons. Each line in the bond represents a pair of shared electrons. There are thus two shared pairs of electrons in the carbon-to-carbon bond in ethylene and three pairs in acetylene.

The existence of double and triple bonds is supported by the laboratory fact that compounds thought to contain them are ready to add chemically at the point where the bond occurs in the compound. For example,

$$C_2H_4 \quad + Br_2 \quad \rightarrow C_2H_4Br_2$$

or



$$\mathrm{H{-}\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}H + Br{-}Br \rightarrow H{-}\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}{-}H}$$

or

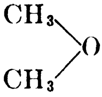
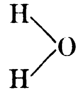
$$\underset{\text{ethylene}}{CH_2=CH_2} \quad \underset{+\ \text{bromine}}{+\ Br{-}Br} \quad \underset{\rightarrow\ \text{ethylene dibromide}}{\rightarrow CH_2Br{-}CH_2Br}$$

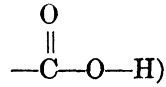
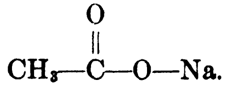
Acetylene adds bromine even more readily than does ethylene and takes double the amount.

Such compounds as ethylene or acetylene that contain double bonds or triple bonds are called ***unsaturated compounds.*** They are important especially in rubber, petroleum, and plastic chemistry.

Helpful Comparisons. We have seen that the radicals CH_3— (methyl) and C_2H_5— (ethyl) have combining numbers of 1. Comparing their position in compounds, as in CH_3Cl (methyl chloride), with HCl (hydrochloric acid), we see that the methyl radical is in the place corresponding to the hydrogen alone. Thus, at least for the purpose of writing formulas, the organic radicals mentioned may be considered similar to hydrogen.

The hydrocarbon methane, CH_3—H, usually written CH_4, corresponds to H—H, molecular hydrogen. The compound CH_3—OH is called methyl alcohol and corresponds to H—OH, water, which is also a hydroxyl compound.

Oxides are known in organic chemistry; dimethyl oxide,  is an example. They are called ***ethers*** and correspond to water  considered as an oxide, in which both the hydrogen atoms have been replaced by an organic radical.

The formulas for the so-called carboxylic acids all contain the group —COOH (better  $\mathrm{{-}\overset{O}{\overset{\|}{C}}{-}O{-}H}$), called the ***carboxyl*** group, containing an ionizable hydrogen atom. Methyl (CH_3—) carboxylate (—COOH), or CH_3COOH, is called acetic acid. One common method of representing this compound is $H{\cdot}C_2H_3O_2$. The position of the replaceable hydrogen atom is shown by the formulas for sodium acetate, $Na{\cdot}C_2H_3O_2$, CH_3COONa, or  $\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}Na}$.

The three hydrogen atoms of the methyl radical are not ionizable.

Organic "Neutralization." The chemical action called neutralization has been shown to be merely the transfer of a proton (see page 222).

$$H_2O{\cdot}H^+ + OH^- \rightarrow H_2O + H_2O$$

and

$$\underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-} \rightarrow \underset{\text{un-ionized product}}{NH_3} + \underset{\text{water}}{H_2O}$$

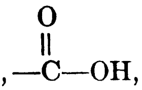
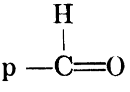
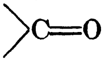
In the previous paragraph we saw that the compound corresponding to a hydroxide is an alcohol. Now we can make the comparison.

$$\underset{\text{organic acid}}{CH_3COOH} + \underset{\text{alcohol}}{CH_3OH} \rightarrow \underset{\text{an ester, un-ionized product}}{CH_3COO-CH_3} + \underset{\text{water}}{H_2O}$$

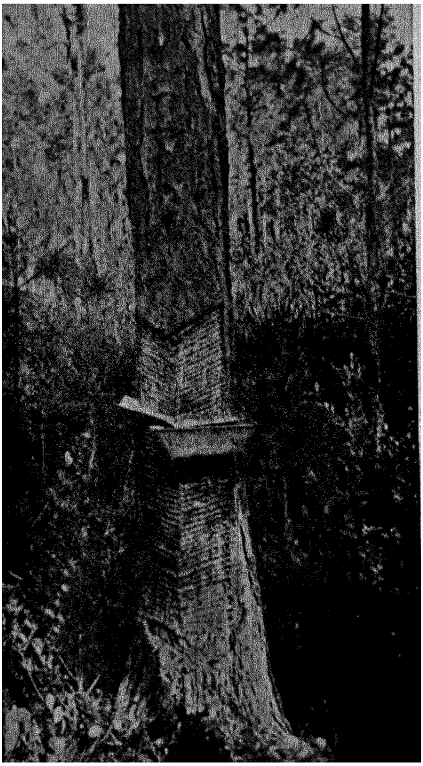
Thus ester formation, or esterification, corresponds closely to neutralization; esters are organic compounds that may be considered to be derived from an organic acid (or sometimes a mineral acid) with the replaceable hydrogen atom(s) replaced by an organic radical. Natural fats, oils, and waxes are mixtures of esters.

To summarize, a tabulation of the comparisons may be made.

	Inorganic compounds		Organic compounds
	Ionized	Un-ionized	
Positive part.	Na^+	H -	CH_3 -
Hydride....	Na^+H^-	H - H	CH_3 - H (CH_4), methane
Hydroxide..	Na^+OH^-	H - OH (water)	CH_3 - OH, methyl alcohol
Oxide..........	Na^+ O^{--} Na^+	H O H	CH_3 O, dimethyl ether CH_3
Sulfide...........	Na^+ S^{--} Na^+	H S H	CH_3 S, dimethyl thioether CH_3
Acid...........	......	H - Cl	CH_3COO - H, acetic acid
Salt.............	Na^+Cl^-	....	$CH_3COO^-Na^+$, sodium acetate
Ester............	....	.....	CH_3CO - OCH_3, methyl acetate

Other Organic Groups. In addition to the carboxyl group,  $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$, which is found in all carboxylic acids, the group  $-\overset{\overset{\displaystyle H}{|}}{C}{=}O$ is found in all aldehydes, and the group  $>C{=}O$ is found in all ketones.

Alcohols. Chemically, alcohols are similar to water (HOH), except that the first hydrogen in the formula is replaced by an organic radical. Thus the simplest alcohol is methyl alcohol, or methanol (CH_3OH), commonly called wood alcohol.



Courtesy of American Forest Products Industries, Inc.

FIG. 29-2.—Trees are a source of resins, lignin, and cellulose. This tree has been tapped for turpentine.

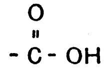
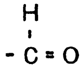
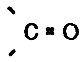
Wood Alcohol, or Methanol. Wood alcohol obtained its name because it is among the volatile materials driven off when wood is heated. Formerly it was obtained in quantity by the destructive distillation of wood. It is made synthetically, 100 per cent pure, by passing carbon monoxide and hydrogen from water gas over a catalyst.

$$CO + 2H_2 \xrightarrow{(ZnO,Cr_2O_3)} CH_3OH$$

Methanol, a colorless liquid that boils at 64.5°C, has about four-fifths the density of water. It mixes completely with water. It vaporizes easily, the fumes being poisonous. If it is taken internally, such disastrous effects are produced on the optic nerve that blindness may result. It may even cause death.

The compound is used as an antifreeze in automobile radiators and as a solvent for gums, as in shellac and varnishes; it is also used in some types of denatured alcohol and in making formaldehyde.

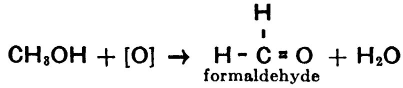
CHARACTERISTIC GROUPS FOR SOME CLASSES OF ORGANIC COMPOUNDS

Carboxylic acids	Aldehydes	Ketones
 $\overset{O}{\overset{\|}{-C-OH}}$	 $\overset{H}{\overset{\|}{-C=O}}$	 $>C=O$

Obviously, preparations of this sort are not beverages. Drinking them may produce fatal consequences. Like most organic compounds, "wood spirits" burn.

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$$

When a warmed piece of heated platinum or copper is held in a mixture of methanol vapor and air, the oxidation is partial, and the vapor of the formaldehyde produced is very irritating to the eyes.



$$CH_3OH + [O] \rightarrow \underset{\text{formaldehyde}}{H-\overset{\overset{\displaystyle H}{|}}{C}=O} + H_2O$$

When this experiment is carried out, the odor of formaldehyde will recall that of the solution in which biological specimens, frogs, for example, are preserved. Formaldehyde is also used extensively in making Bakelite and urea plastics.

Courtesy of Rural Credits Department, Pierre, S.D.

FIG. 29-3.—Starch, oil, and cellulose, all organic compounds, are obtained from corn.

Grain Alcohol. Grain alcohol, or Cologne-spirits, received its name from its source. When grain sprouts or germinates, catalysts from the plant, called ***enzymes*** as a group, change the insoluble stored starch to soluble sugar, an available food for the growing plant. The enzyme in this case is called ***diastase,*** and the preparation of sprouting grain is called a ***malt.***

$$\underset{\text{starch}}{(C_6H_{10}O_5)_x} + xH_2O \xrightarrow[\text{from malt}]{\text{diastase}} \underset{\text{maltose (malt sugar)}}{xC_{12}H_{22}O_{11}}$$

In the presence of the enzyme ***maltase,*** the maltose is converted into glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

The glucose is now fermented by yeast, single-celled plants that contain many enzymes, ***zymase*** being used in this case.

$$\underset{\text{(glucose)}}{C_6H_{12}O_6} \xrightarrow[\text{zymase from yeast}]{\text{alcoholic fermentation}} 2C_2H_5OH + 2CO_2\uparrow$$

Much of the alcohol made today comes from alcoholic fermentation of the sugar left in molasses after the crystallization of cane sugar (sucrose).

$$\underset{\text{sugar (sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase in yeast}} \underset{\text{(a mixture of glucose and fructose)}}{2C_6H_{12}O_6}$$

This process is easily demonstrated in the laboratory by adding yeast to a mixture of molasses and water and allowing it to remain in a warm place. The fermentation stops when a concentration of about 14 per cent alcohol is reached (see Fig. 29-4). The alcohol may be separated from the mixture by distillation. This, on a small scale, parallels the commercial method. The product is called ethyl alcohol or, better, ***ethanol*** (C_2H_5OH) or just alcohol.

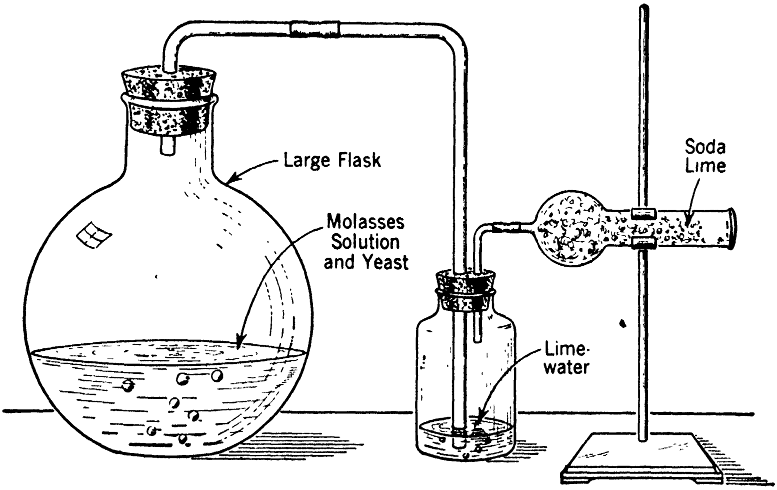


FIG. 29-4.—The alcoholic fermentation of sugar solution by yeast goes on when this apparatus is kept in a warm place. Alcohol, produced in the large flask, can be recovered by fractional distillation. The limewater turns milky, proving the production of carbon dioxide as a by-product—for no carbon dioxide from the air can enter the apparatus through the soda-lime tube.

What Is Pure Alcohol? Pure alcohol, 100 per cent, called absolute alcohol, is used for special laboratory and industrial purposes. It is a colorless liquid, boiling at 78.5°C. and freezing at the low temperature of −112°C. It vaporizes readily at room temperature and has a pleasant odor. Alcohol has a strong tendency to absorb water, with which it mixes in all proportions.

Commonly, alcohol is 95 per cent pure. The 5 per cent of water represents the water vapor that distills over when alcohol is distilled at 78°C with water. No matter whether one starts with a mixture that is stronger or weaker than 95 per cent, the vapor always has the same composition, 95 per cent alcohol, if water is present. (The vapor pressure of water at 78°C is 327 mm.)

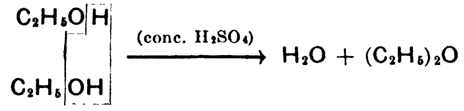
Alcohol can be partly oxidized in the presence of a catalyst to form acetic acid. This happens when hard cider changes to vinegar in the presence of "mother of vinegar," which contains *Bacillus aceti*. Unfiltered vinegar contains visible amounts of the cloudy "mother" that supplies the enzyme ***vinegar oxidase.***

$$C_2H_5OH + O_2 \xrightarrow[\textit{aceti}]{\textit{Bacillus}} H_2O + CH_3COOH$$

Uses of Alcohol. Alcohol is an excellent fuel, for it burns without soot. "Canned heat" is a jelly containing alcohol. Alcohol is used to some extent as a motor-vehicle fuel, but in most places its price is too high to compete with gasoline.

It is the most widely used solvent except water. The following common commodities contain alcohol: vanilla extract (37 per cent alcohol), peppermint extract (90 per cent), perfume (70 per cent), hair tonic (73 per cent), mouthwash (38 to 25 per cent), aftershave lotion (50 per cent). The concentrations given all represent information obtained from labels.

Alcohol is extensively used as an antifreeze liquid and for sterilizing. It is widely employed in the preparation of other compounds. Ether, for example, is made by dehydrating alcohol by means of sulfuric acid.



$$\begin{array}{l} C_2H_5O\boxed{H} \\ C_2H_5\boxed{OH} \end{array} \xrightarrow{\text{(conc. } H_2SO_4)} H_2O + (C_2H_5)_2O$$

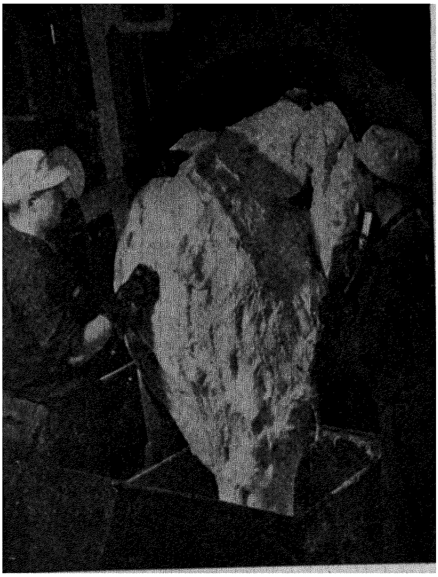
alcohol, 2 parts ether

At a higher temperature, the same process forms ethylene (C_2H_4).

A Compound with Social Significance. The effect of alcohol on the body depends on the amount drunk, the state of health of the person, and other factors. Hence no absolute statements can be made. In general, however, a small quantity causes deadening of some nerves, allowing blood to rush to the surface of the body, imparting a feeling of warmth, but actually chilling the body. The heart beats a little faster at first but later drops below the normal rate. Hence the use of alcohol as a stimulant is questionable. Social restraints, called inhibitions, apparently are removed as larger quantities are imbibed, and more nerves are paralyzed, causing intoxication (poisoning). If continued use of alcoholic beverages increases the amount of alcohol in the blood stream to 3 oz, alcohol is fatal. Even ½ pt of whiskey (16 oz), 100 proof (50 per cent alcohol), contains 8 oz of alcohol. Alcoholic poisoning is more frequently a contributing if not a direct cause of death than many people realize.

Alcohol slows the "reaction time," important in avoiding or causing automobile or industrial accidents. Many experiments have been conducted to determine the effect of alcoholic beverages on efficiency. The results point out that alcohol must be regarded as a narcotic.

Some authorities consider the use of alcohol, along with war, as a great handicap upon human progress. Alcohol has not an altogether black record, however. In some cases its stimulating action has saved lives. The use of beverages with slight alcoholic content instead of water is undoubtedly necessary in countries where the water supply is unreliable. In America, however, where reliable water supplies are common, no reason exists for drinking alcoholic beverages as a sanitary precaution.



Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 29-5.—Neoprene is being poured from polymerization kettles, one step in the processing of a type of synthetic rubber. Neoprene is an organic chemical.

Denatured Alcohol. Governments have found alcoholic beverages a convenient source of revenue. If, for example, the cost of 1 gal of 95 per cent alcohol is $6, only about 40 cents or less is the actual cost of the material. The rest is chiefly tax. But as we have seen there are many uses for alcohol other than that as a beverage. With these commercial uses the government should have no desire to interfere. Commercial alcohol may be sold tax-free if it is ***denatured,*** that is, has substances added to it which cannot be removed easily by distillation or any other means. These substances render the alcohol a direct, violent poison. A number of combinations of denaturants are permitted; the industrial user chooses the type of added impurity that will interfere least with the intended application. Radiator alcohol often contain pyridine (C_5H_5N), a disagreeable-smelling compound, or methyl alcohol (CH_3OH) as denaturants. Rubbing alcohol is a mixture of denatured alcohol, water, and isopropyl alcohol [$(CH_3)_2CHOH$].

Other Alcohols. Propyl alcohol (C_3H_7OH -iso) is used in medicine. Butyl alcohol (C_4H_9OH) is used in making esters for solvents. Both may be made by catalytically reducing the corresponding acid or by special fermentations.

In addition to the alcohols having just one hydroxyl group some important dihydroxy and trihydroxy alcohols are known. Ethylene glycol [$C_2H_4(OH)_2$] is widely used as a nonevaporating antifreeze. Glycerol [$C_3H_5(OH)_3$, glycerin], a by-product from soapmaking (see page 603), is a sirupy liquid of high boiling point used for the making of explosives, toilet creams, and rubber-stamp pads. It absorbs moisture from the air.

The compound commonly called carbolic acid is really an alcohol, phenol (C_6H_5OH). This compound is extensively used for making Bakelite plastic and as a vigorous antiseptic. It has an acid reaction—hence the name carbolic acid. Hundreds of other alcohols are known.

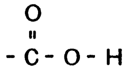
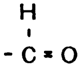
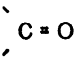
SUMMARY

Organic compounds are similar to covalent inorganic compounds in all fundamental essentials. The term "organic compounds" includes only certain compounds of carbon. In organic compounds the carbon often shows a tendency to form chains or rings. These compounds are seldom dissociated owing to covalent (electronic-pair sharing) bonds. They react relatively slowly. Few are soluble in water; organic compounds are better solvents for organic compounds. ("Like dissolves like.") Structural formulas are helpful in classifying organic compounds.

Hydrocarbons are compounds of hydrogen and carbon only. Methane (CH_4) is related to methyl radical (CH_3—). Ethane (C_2H_6) is related to ethyl radical (C_2H_5—). Many hydrocarbons exist in chain and ring forms. Some hydrocarbons have two or three covalent bonds between adjoining carbon atoms. These are called double or triple bonds and are points of chemical activity of the molecule.

Organic compounds are classed according to groups and may be compared with inorganic compounds of similar structure. Organic reactions are somewhat similar to inorganic reactions; for example, ester formation is often compared with neutralization, although many differences between the reactions are prominent.

Typical organic groups include:

Carboxyl.................	 $-\overset{O}{\overset{\|}{C}}-O-H$	Typical of organic acids
Aldehyde.................	 $-\overset{H}{\overset{\mid}{C}}=O$	Typical of aldehydes
Ketone...................	 $>C=O$	Typical of ketones
Hydroxyl.................	$-O-H$	Typical of alcohols

Methanol, or wood alcohol, is prepared from destructive distillation of wood. An impure product results. Synthetic methanol, 100 per cent pure, is prepared from carbon monoxide and hydrogen.

Methanol is a poisonous, colorless liquid. It has low boiling and freezing points. It is an excellent solvent for gums. It burns readily and oxidizes partly, to form formaldehyde in the presence of platinum catalyst.

Methanol is used as a solvent in shellac and to make formaldehyde; also, it is an effective antifreeze.

Ethanol, or grain alcohol, is prepared from grain by the change of starch to sugar by the enzymes diastase and maltase. The glucose formed is then fermented to alcohol and carbon dioxide by use of the enzyme zymase from yeast. Alcohol is separated from the ferment by fractional distillation.

Ethanol is a colorless, pleasant-smelling liquid. It is an excellent solvent, absorbs water readily, and mixes with it in all proportions. It burns in air. Dilute solutions of ethanol can be oxidized to acetic acid, as in the manufacture of vinegar. It reacts with acids and a great variety of organic compounds.

Ethanol is used as a fuel and an antifreeze. It is also used as a solvent in medicines, tinctures, extracts, and spirits. It is a component of all alcoholic beverages. It has a part in the preparation of ether, synthetic rubber, explosives, and many other compounds.

QUESTIONS

1. Tabulate the compounds represented by the following formulas in two groups, organic and inorganic: CH_4; SiH_4; CO_2; Na_2CO_3; $HCHO$; $H{\cdot}C_2H_3O_2$; $MgCO_3$; $NaHCO_3$; CCl_4; CH_3OH.

2. Contrast organic with inorganic compounds in four ways.

3. Name three elements that are very important in organic compounds.

4. Contrast in two respects the behavior of inorganic and organic compounds toward water.

5. Butane has the formula C_4H_{10}. Write the formula for the butyl radical. What is its valence?

6. Write the structural formula for (*a*) normal (straight-chain) butane; (*b*) iso- (branched-chain) butane.

7. Write the formula for (*a*) ethyl nitrate; (*b*) methyl bromide; (*c*) isopropyl chloride; (*d*) ethyl acetate; (*e*) dimethyl sulfate.

8. In what three ways can two carbon atoms be joined together? What does each type of bonding represent in terms of electrons?

9. Make a "dot" diagram showing electrons in the outermost orbits of each atom in (*a*) ethane; (*b*) ethylene; (*c*) acetylene.

10. Write the formula for (*a*) acetic acid; (*b*) sodium acetate; (*c*) calcium acetate. Also, write the structural formulas for these compounds.

11. What evidence shows that acetic acid possesses hydrogen atoms with two differing sorts of chemical activity?

12. List three different classes of organic compounds, and opposite each write its corresponding inorganic compound.

13. Write formula equations for the reaction of acetic acid with (*a*) sodium hydroxide solution; (*b*) calcium hydroxide solution; (*c*) methyl alcohol; (*d*) ethyl alcohol; (*e*) propyl alcohol.

14. Write the structural formula for the characteristic group of elements found in all (*a*) aldehydes; (*b*) ketones; (*c*) organic acids; (*d*) alcohols.

15. Point out the difference between burning methyl alcohol and oxidizing it in the presence of platinum as a catalyst.

16. Which produces the greater lowering of freezing point when added to a liter of water, 100 grams of methyl alcohol or 100 grams of ethyl alcohol? Give a reason for your answer.

17. Tell how to distinguish methyl alcohol from ethyl alcohol and from a mixture of the two.

18. Formaldehyde solution is a good preservative for biological specimens. Why is it not used for preserving foods, such as meats and fish?

19. Name two by-products of bakeries that are usually wasted.

20. Tell the steps in changing starch to alcohol. Include three equations.

21. Distinguish absolute alcohol from denatured alcohol and from ordinary grain alcohol.

22. List two disadvantages of alcohol for motor fuel, as compared with gasoline.

23. For what purpose is alcohol used in many "patent" medicines?

24. When ether is prepared from alcohol, how is the formation of ethylene retarded?

25. What weight of alcohol can be produced from $\left\{\begin{matrix}540\\720\end{matrix}\right.$ grams of glucose?

26. What volume of carbon dioxide at STP is formed when $\left\{\begin{matrix}1026\\1368\end{matrix}\right.$ grams of sucrose ferment?

27. What is the percentage composition of methyl alcohol?

28. A gas is composed of 40 per cent carbon, 6.7 per cent hydrogen, and the balance oxygen. The weight of 200 ml of it at STP is 0.27 gram. Find its correct molecular formula.

29. In what volume proportions should air and methyl alcohol vapor be mixed when formaldehyde is to be produced by aid of a catalyst?

30. Account for the fact that repeated distillation of 95 per cent alcohol fails to lower the percentage of water that it contains.

31. What volume of liquid alcohol is needed to produce a liter of diethyl ether? The density of ether is 0.71 gram per milliliter and that of alcohol 0.79 gram per milliliter.

UNIT SEVEN - - - - - - - - - - - - CHAPTER XXX

OUR FUELS

If we watch a fire of soft coal burning, we see tongues of flame spurt from the lumps of coal from time to time. These jets of flame are caused by burning gas that escapes from the coal while it is being-roasted in the fire.

From this observation comes the suggestion that the making of this flammable gas might be separated f[illegible]e burning. This indeed can be done if we place the coal in an oven, airtight except for an outlet, and then apply heat outside the oven. The heated coal gives off gases. The gases can be carried away in pipes, purified, and used at a distance from the place where it was made.

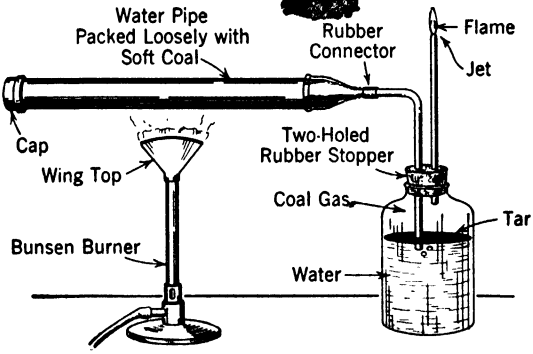


FIG. 30-1.—This working model brings the gas works into the laboratory. The destructive distillation of coal is carried on conveniently on a small scale in a capped water pipe provided with an opening for the escape of volatile products.

Making a miniature gasworks is a simple and instructive experiment. A piece of iron water pipe is fitted with a cap at one end and a tapered fitting at the other. (See Fig. 30-1.) The pipe is filled loosely with soft coal. The tapered fitting is attached by a rubber tube to a glass tube inserted through a stopper in a bottle,

---

New Terms

destructive distillation
producer gas
natural gas
water gas

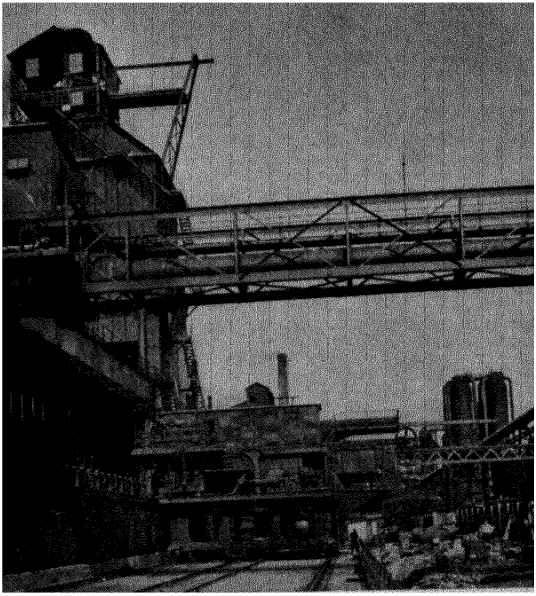
hydrocarbon
octane number
lignite

bituminous coal
Btu
methane series

which serves as a scrubber. The glass tube dips just below the surface of the water in the bottle. This scrubber apparatus is thus simply a bottle fitted with a two-holed stopper. The glass delivery tube is in one of these holes, and a jet shaped like the glass part of a medicine dropper is in the other.

When we apply heat to the iron water pipe, the coal inside decomposes. The products formed by this process of heating coal shut off from the air are different from the coal. Any such decomposition carried out by applying heat to material shut off from the air is called ***destructive distillation.***

In commercial practice the oven is called a ***retort.*** If all or part of the vapors from the heated coal are allowed to escape directly into the air and there burned, the retort is called a beehive coke oven, named from its general shape. Beehive coke ovens waste valuable by-products from the coal; they are an extravagant means for making coke to supply the hungry mouths of the nation's blast furnaces. Modern practice saves the vapors that come from the heated coal.



Courtesy of Koppers Company, Inc.

FIG. 30-2.—By-products from soft coal distillation come through the off-take main (central pipe) to the by-product plant (right). Coke-pushing machine is also shown.

Gaseous Fuels

By-product Coke Ovens. A vertical wall of coal about 14 ft high and 8 in. thick is poured into a section of a multiple retort. The walls of the retort are kept hot by burning cheap fuel gas between adjacent retorts. Vapors escape from the coal for perhaps 18 hours. The solid material that remains behind after the heating is coke—a porous, gray substance, chiefly carbon. It is used for blast furnace and foundry fuel, as a reducing agent, and for heating homes.

Coal Tar and Coal Gas. The hot vapors that are drawn off a by-product coke oven are passed through water and further cooled to condense tar. Some coal tar floats on the water; the soluble portions of the coal gas, chiefly ammonia (NH_3), remain dissolved in the water. A little of the ammonia joins the water to form ammonium hydroxide.

$$NH_3 + HOH \rightarrow NH_4^+OH^-$$

This solution is then run into sulfuric acid until the ammonium sulfate crystals form.

$$2NH_4OH + H_2SO_4 \rightarrow 2H_2O + (NH_4)_2^+ SO_4^{--}$$

The crystals are washed and whirled dry in the basket of a centrifugal machine.

The tar is used as a binder in making roads, or it may be subjected to further distillation and treatment to make coal-tar products (see page 581).

Coal gas, chiefly hydrogen and methane with some carbon monoxide and nitrogen, is purified to free it from several objectionable impurities. Then it serves as a household and industrial fuel.

A ton of coal might produce 10,000 cu ft of gas with 537 Btu[1] heat value per cubic foot, 10 gal of tar, and 25 lb of ammonium sulfate and leave ¾ ton of coke in the retort after the distillation.

Opportunities for Improving Coal Distillation. Experts in the destructive distillation of coal agree that the process is far from perfect. For example, most coke ovens are intermittent; only a few are continuous. As a rule, continuous processes are preferred for commercial operations.

When the red-hot coke is pushed out of the oven with a single stroke of a powerful ram, the coke burns furiously while it is being carried in a steel car to an enormous showerbath. This is a startling and wasteful sight. Some work has been done toward eliminating this obvious loss, but more is needed.

Changing the temperature at which coal is distilled results in a definite change in the products, favoring liquid oils and less tar. Here again possibilities of development in the future are indicated.

Water Gas. To make water gas, a firebrick-lined cylinder, called a generator, which is as large as a squatty farm silo, is well filled with coke or hard coal. A fire is made within the cylinder and forced to furious

---

[1] Btu means British thermal unit. This is the quantity of heat needed to raise the temperature of one pound of water through one degree Fahrenheit.

intensity (1400°C) by powerful motor-driven fans. Then the air draft is shut off and steam sent through the glowing coals. The steam is reduced by the hot carbon, liberating carbon monoxide and hydrogen gases. The mixture is known as water gas. $H_2O + C \rightarrow CO + H_2$. This chemical action takes in heat (endothermic), and after 3 minutes the coke has cooled to 1000°C, necessitating sending more air through the coals for 2 minutes, to brighten the fire. While the air is reviving the fire, the gasmaking machine sends a bright glare into the sky, a brilliant sight at night. Thus the process of making water gas is one of alternately heating coal red-hot in air and then sending steam through it.

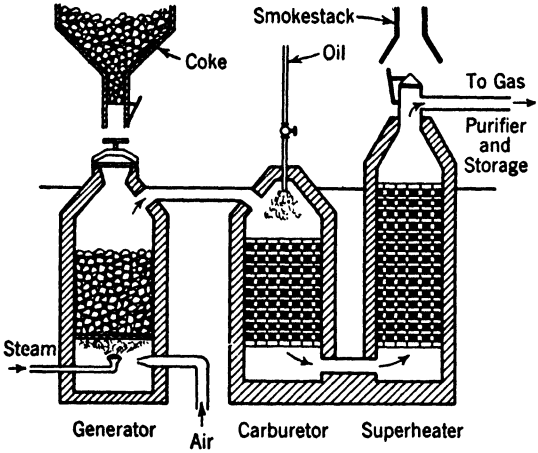


FIG. 30-3.—The water-gas machine is composed of three principal parts: generator, carburetor, and superheater.

Straight water gas does not meet the legal heat requirements for fuel gas of most states. Oil gas, therefore, is added to it. This is made by spraying oil onto hot checker-bricks in a second cylinder, the carburetor, through which the hot blast from the generator is passed. When the oil strikes this very warm region, it "cracks" (see page 537), and most of it remains in the form of a stable, permanent gas mixed with the water gas by the time it has passed over another checker-brick-lined heating chamber, the superheater. (See Fig. 30-3.)

Not only has water gas higher heat value when enriched with oil gas, but the flame of burning is changed from pale blue, as seen when hydrogen or carbon monoxide burns, to a light-giving, or luminous, sooty flame. This gas is purified as coal gas is.

Water gas is interesting to us because it illustrates how coke can be made into gas, even after coming from the coke oven. The process, a convenient one, is often run to supplement coke-oven gas at times of peak loads.

Steam may be introduced into coke ovens or into producer-gas machines (see page 526). The mixture of carbon monoxide and hydrogen produced by the water-gas machine is the starting material for making synthetic alcohol and other valuable synthetic chemicals.

QUESTIONS

1. Name four products of the destructive distillation of bituminous coal.

2. In what way are beehive coke ovens wasteful?

3. What product is formed when cooled coke-oven gas is run through hydrochloric acid?

4. What weight of coal must be distilled daily in order to supply the needs of a city that consumes 12 million cubic feet of gas per day?

5. What weight of ammonia is available from a ton of coal if 25 pounds of ammonium sulfate is made from it? HINT: Find the percentage of ammonia in ammonium sulfate.

6. Explain why the process of making water gas is an intermittent one.

7. In the water-gas-making machine, what purpose is served by (*a*) the generator; (*b*) the carburetor; (*c*) the superheater?

8. What products are formed when water gas burns?

9. Assuming that no time is lost in adding fuel and that water gas is made by a machine at the rate of 500 cubic feet per minute, what is the daily output of the machine

10. The gas from a water-gas machine is immediately passed through a large tank containing water. State two changes brought about by this treatment.

Producer Gas. Another gas that is used as a fuel is producer gas. To manufacture it, a revolving cylindrical tank as large as a railroad car, lined with firebrick, is used. A cheap fuel, coke for example, is burned inside, while air is sent through the bottom of the deep fuel bed. The nitrogen of the air passes through it unchanged, but the oxygen at the bottom of the bed joins carbon to form carbon dioxide. $C + O_2 \rightarrow CO_2$. The carbon dioxide rises and is reduced by hot carbon to carbon monoxide. $CO_2 + C \rightarrow 2CO$.

Often steam is put into the machine also, adding hydrogen to the mixture of fuel gases. $C + H_2O \rightarrow CO + H_2$. Thus producer gas contains nitrogen, carbon monoxide, and hydrogen.

Producer gas is always made for definite direct use. It may be used to heat coke ovens, to run gas (not gasoline) engines, or for industrial fuel. It is too poisonous for use in homes, and its fuel value is low.

Natural Gas. Some borings into the earth produce flammable gas, which is chiefly methane (CH_4). Oil wells are usually gas wells, also.

The "wet" gas, as taken from wells, sometimes contains a little vapor of gasoline. This vapor is absorbed in oil or condensed and saved. The gases that do not condense to form liquids are used directly for fuel.

Natural gas is being made wherever leaves and vegetable matter decay. It can be found by stirring the mud at the bottom of a pond. In certain places, sometimes thousands of feet below the surface, great quantities of such gas are imprisoned in pores of the earth's rocks.

Special Gases. Blast furnaces for making iron produce such great excess of carbon monoxide that the gas can be burned. This gas is a lean fuel, but it will provide power for engines that move materials around the furnaces.

Compressed gas in strong steel tanks is used extensively for fuel. This gas comes chiefly from petroleum refineries and natural gasoline plants as a by-product, and it is composed of compounds of carbon and hydrogen only. Such compounds are called ***hydrocarbons.*** The gas may be propane (C_3H_8), butane (C_4H_{10}), and possibly pentane (C_5H_{12}), or a mixture of these. It is used for fuel for trucks, for industrial heating, and for household fuel gas in the country.

Acetylene. When water is added to calcium carbide, a colorless gas called acetylene (C_2H_2) is evolved. This gas, 92.3 per cent carbon, burns with so sooty a flame that a special type of burner must be used when it is burned to produce light.

$$\underset{\text{calcium carbide}}{CaC_2} + \underset{\text{water}}{2H_2O} \rightarrow \underset{\text{slaked lime}}{Ca(OH)_2} + \underset{\text{acetylene}}{C_2H_2\uparrow}$$

Acetylene is a hydrocarbon gas, exceptionally high in heat value. It is used in the oxyacetylene torch to produce a heat so intense that it melts steel. It decomposes easily when warmed, liberating heat (exothermic reaction). We may represent this change as

$$C_2H_2 \rightarrow 2C + H_2 \ (+ \text{heat})$$

Three results follow from this fact. (1) Acetylene can be used as a source of pure carbon with hydrogen, as a by-product. (2) The heat of burning is added to the heat of decomposition, a very hot flame being thus produced. The equation that represents the complete burning of acetylene is $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$ (+ heat). (3) Acetylene cannot safely be compressed and stored in tanks directly, for it may explode. There is no danger of explosion if the tanks contain asbestos soaked with acetone.

Acetylene has many uses as a gas for lighting or for heat. It is also the starting material for making some synthetic rubber and some plastics.

Gas Flames. The fact that a handful of fuel gas can be ignited and the burning gas carried in the hands (see Fig. 30-4) illustrates clearly that flames come from burning gas. Solids glow when they burn, as does burning charcoal; flames from solids or liquids, however, are produced only if the substances (1) are changed to vapor by heat, (2) give off gas by destructive distillation, or (3) form gas by chemical action. Alcohol in a spirit lamp burns with a flame because the liquid alcohol is changed to gaseous form by the heat of the burning. A piece of wood burns with flame because the vapors of wood alcohol and other substances formed by destructive distillation are burning. Coke or charcoal may burn with a flame when the oxygen of the air forms carbon monoxide, which in turn burns.

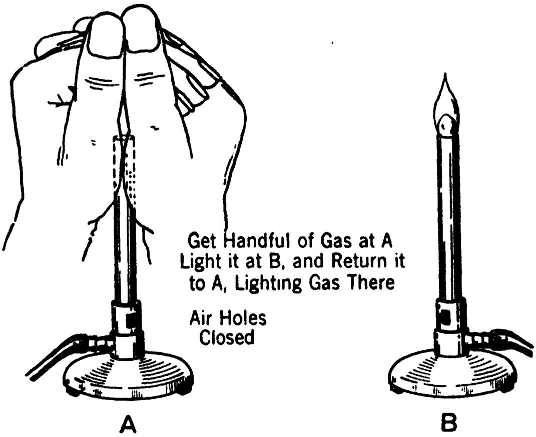


FIG. 30-4.—While this experiment illustrates the hard way to save a match, it also clearly shows that flames are produced from substances burning in the gaseous state. When solids burn, they glow.

Bunsen's Gas Burner. The Bunsen burner, invented by Robert Wilhelm Bunsen (1811–1899), is in general a most satisfactory gas burner. It is simply a vertical tube. At one end are a small opening to admit the gas and an adjustable opening for air; at the other end the gas and air mixture burns. A gas range at home has many small Bunsen burners.

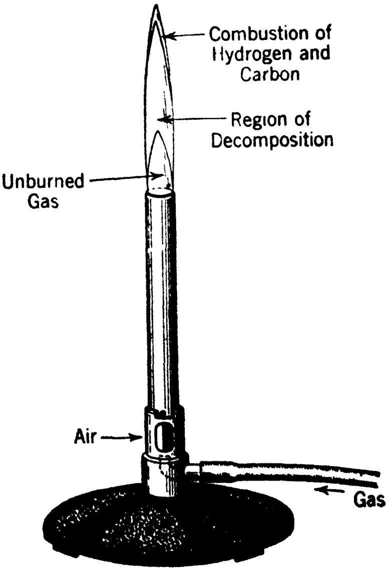


FIG. 30-5.—The Bunsen burner is the type commonly used in laboratories that are supplied with fuel gas.

When adjusted correctly, a Bunsen burner flame consists of two distinct cones. The inner cone consists of unburned gas, surrounded by a darker region. In the second cone, decomposition of hydrocarbons takes place. Surrounding the latter cone, the hot decomposed material meets the oxygen of the air. Here vigorous burning takes place in a third region, which is visible only under favorable light. (See Fig. 30-5.)

If the supply of air is limited, the carbon formed by decomposition glows, forming a yellow, sooty flame. Such a luminous, or light-giving, flame is much cooler than the blue Bunsen flame. If blown about by a breeze, the hot carbon may not burn when it reaches the outer edge of the flame but forms smoke instead.

QUESTIONS

11. Some producer-gas machines are made in such a way that the surroundings are almost entirely open to the outdoor air. Of what benefit is this arrangement to the workers?

12. Why is producer gas considered a "lean" gas?

13. Name the chief constituent of natural fuel gas.

14. Do all natural gases burn?

15. Describe a method for securing gas for cooking in regions removed from city gas mains.

16. Write equations for (*a*) producing acetylene from "carbide"; (*b*) burning acetylene.

17. What percentage of acetylene is hydrogen?

18. Account for the very high temperature produced in the oxyacetylene torch.

19. In attempting to synthesize acetylene from coke and hydrogen, does the expected reaction absorb heat, or does it give out heat?

20. A match head can be held unburned in the lower central part of a Bunsen burner flame. Account for the low temperature in this region.

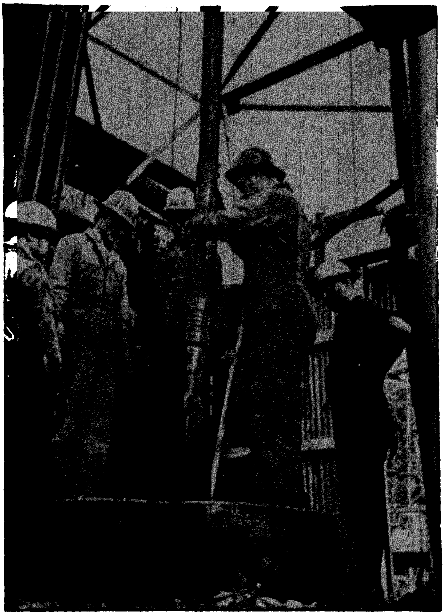
Liquid Fuels

Motor Fuels. An ordinary automobile engine uses gasoline for fuel. In the carburetor the gasoline is forced into a fine spray that evaporates easily when it is mixed with a large amount of air. The vapor mixture thus formed is then drawn into the automobile cylinders. Here the fuel-air mixture is compressed and set on fire by sparks from spark plugs. The burning or exploding fuel in the cylinder expands, forcing the piston downward. The downward movement of the piston is transmitted to the rotary movement of the wheels. All this takes place very quickly.

Fuel requirements for modern motors, namely, a cheap liquid that will vaporize readily and burn violently when mixed with air, are at present met by only two common substances, gasoline and alcohol.

Sources of Gasoline. Gasoline is produced (1) by the distillation of petroleum, (2) by "cracking" of oils, (3) by absorbing the gasoline vapors from natural gas (see page 530), (4) by combining hydrogen with low-grade coal or oil, (5) by "polymerizing" small molecules into clusters. Gasoline is such an important fuel that its story is interesting to us all.

Petroleum. The liquid remains of animal and vegetable life of ages past are stored in cracks and pores of some rocks. This dark, ill-smelling liquid is called petroleum. In most places petroleum is found far below the surface of the earth, but in a few instances it occurs fairly close to or even on the surface. The first oil well was sunk by Col. Edwin L. Drake in Titusville, Pennsylvania, in 1859. He struck oil 70 ft below the surface. Today in some wells oil must rise from great depths—the deepest well is 3 miles deep. Deposits of petroleum-like material on the surface of the earth are different from petroleum below the surface. We have, for example, the asphalt "lake" in Trinidad and the La Brea tar pits in Los Angeles, California.



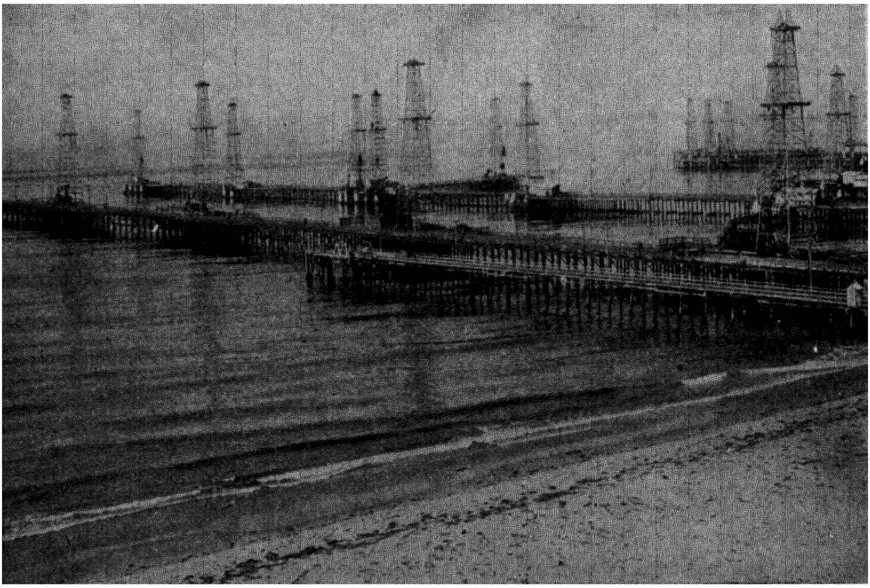
Courtesy of American Petroleum Institute

FIG. 30-6.—This oil-well drilling crew is inserting a "knuckle-joint" into the well hole to begin directional drilling. Directional drilling is a technological advance that increases immeasurably the nation's oil reserves.

How Petroleum Is Obtained. Oil-well drilling is a specialized occupation. Except in the case of "wildcat" wells, location of the place to be drilled is established by scientific experimenting with earth vibrations and by other methods. A derrick is set up to lift the heavy tools and pipes. In one type of drilling a diamond-studded collar is revolved by a powerful motor. This hard cutting tool on the end of a long steel stem cuts its way through the hardest rock. When seams of the rock are cut, they may allow oil or water to seep into the hole. To prevent this, the hole must be lined with cement. Bentonite clay in colloidal form is often used as a drilling mud to aid in removing rock chips (see Fig. 15-10).

So highly developed is the art of well drilling that holes, many thousands of feet deep and sometimes at an angle, are pierced in rocks. A derrick on the seashore may start a hole directionally drilled a quarter of mile out under the sea. (See Fig. 30-7.)

Oil is found in many places. The principal oil-producing states in the United States are Texas, California, Oklahoma, Illinois, and Louisiana. Paraffin-base oils in important quantities come from the vast mid-continent and Pennsylvania fields. Asphalt-base oils come from the Texas Gulf coastal region. The United States leads in the production of petroleum. Large supplies are produced in the U.S.S.R., Venezuela, Iraq, the Netherlands East Indies, Rumania, Mexico, and elsewhere.

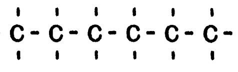


Courtesy of Snider-Triangle

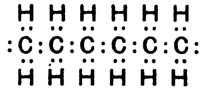
FIG. 30-7.—Shown here is a score of petroleum wells drilled in the ocean.

Oils from different wells may be very different. Petroleum is sometimes found together with much natural gas. Other oil wells produce very little or no natural gas. Some petroleum leaves a thick tarlike remainder when it is refined and is therefore called asphalt-base. Other oils produce much paraffin when refined. These are the paraffin-base oils. Many of the Russian oils are naphthene-base. Some oils are mixed-base.

What Petroleum Is. Petroleum is a mixture of hundreds of compounds of carbon and hydrogen, called hydrocarbons. Some compounds in petroleum are members of the methane series of hydrocarbons.

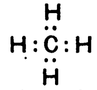


$$\begin{array}{c} |\;\;\;|\;\;\;|\;\;\;|\;\;\;|\;\;\;| \\ -C-C-C-C-C-C- \\ |\;\;\;|\;\;\;|\;\;\;|\;\;\;|\;\;\;| \end{array}$$



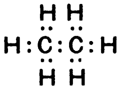
$$\begin{array}{c} H\;\;H\;\;H\;\;H\;\;H\;\;H \\ :\ddot{C}:\ddot{C}:\ddot{C}:\ddot{C}:\ddot{C}:\ddot{C}: \\ H\;\;H\;\;H\;\;H\;\;H\;\;H \end{array}$$

Chemists have made diagrams to show the arrangement of the atoms in the hydrocarbons. These show clearly that carbon has valence 4 and that a carbon atom shows marked ability to join with other carbon atoms. The carbon-hydrogen bond is of the covalent type, the electron pair of the bond serving jointly to fill the outer orbit of both the hydrogen and the carbon atoms.



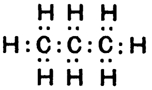
$$\begin{array}{c} H \\ H:\ddot{C}:H \\ H \end{array}$$

methane (CH_4)



$$\begin{array}{c} H\;\;H \\ H:\ddot{C}:\ddot{C}:H \\ H\;\;H \end{array}$$

ethane (C_2H_6)

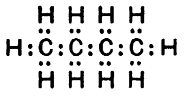


$$\begin{array}{c} H\;\;H\;\;H \\ H:\ddot{C}:\ddot{C}:\ddot{C}:H \\ H\;\;H\;\;H \end{array}$$

propane (C_3H_8)

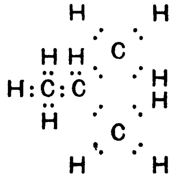
The Importance of Arrangement. Three letters, T, R, and A, for example, may be arranged in several ways, as A R T, T A R, or R A T. Just so in chemistry we find that different arrangements of the same atoms within a molecule make different molecules.

We can make diagrams of two sorts of butane (C_4H_{10}) known in the laboratory. One, called normal butane, has a straight chain of carbon atoms and a boiling point of −0.6°C; the other, called isobutane, has a branched chain of carbon atoms and a boiling point −10.2°C. These two compounds are almost alike, except for the arrangement of atoms within the molecule. They are called ***isomers.***



$$\begin{array}{c} H\;\;H\;\;H\;\;H \\ H:\ddot{C}:\ddot{C}:\ddot{C}:\ddot{C}:H \\ H\;\;H\;\;H\;\;H \end{array}$$

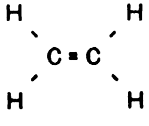
normal butane (C_4H_{10})

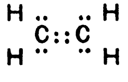


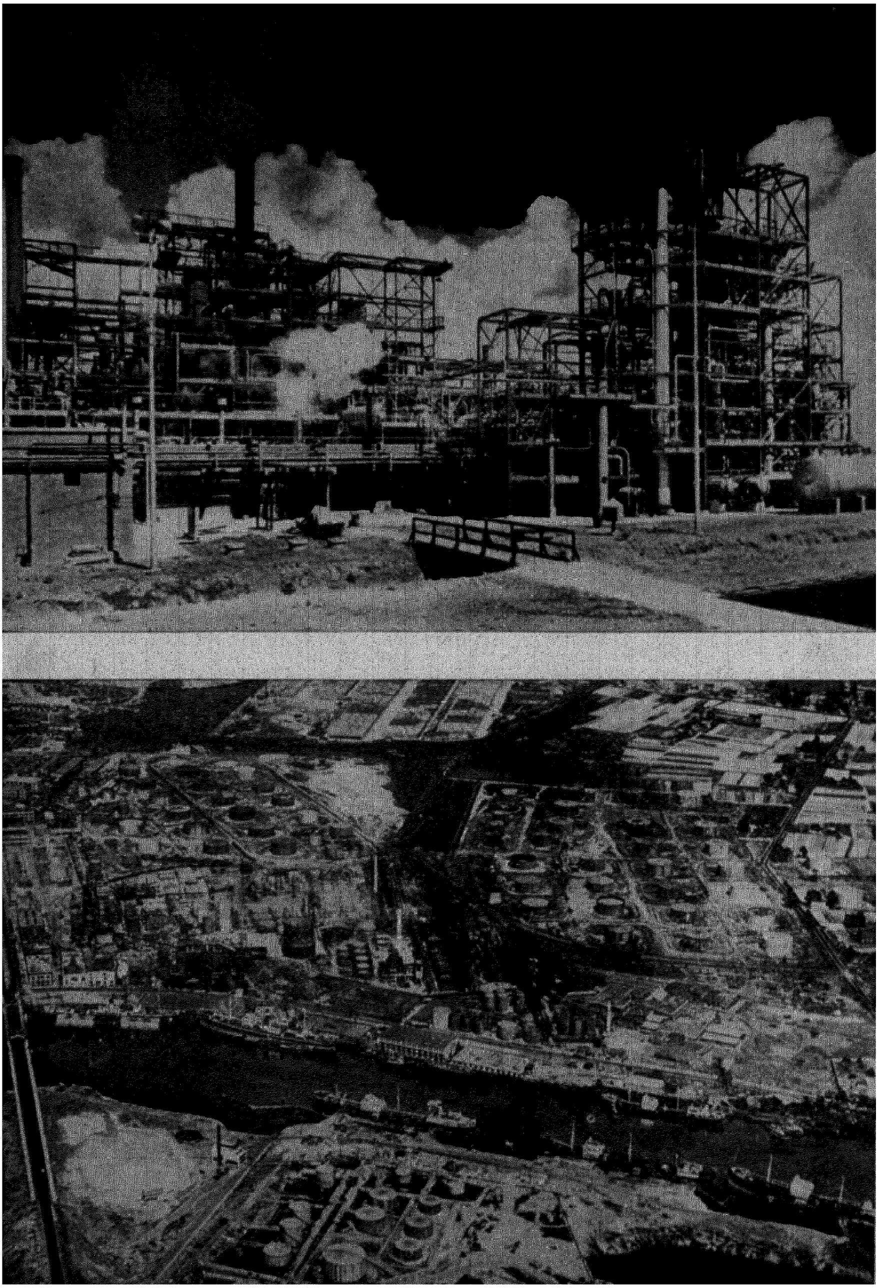
isobutane (C_4H_{10})

When there are more carbon atoms in the molecule of a hydrocarbon, the number of isomers increases. Seventy-five different decanes ($C_{10}H_{22}$) are possible.

To make the situation even more complicated, many other classes of hydrocarbons are known. Some are related to benzene (C_6H_6), a cyclic compound in which the carbon atoms are arranged in a ring; others are related to ethylene (C_2H_4), a compound in which a "double-bond" or "unsaturated" linkage is known between the carbon atoms.





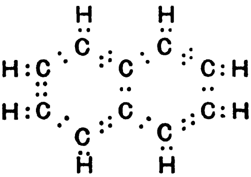


Courtesy of Atlantic Refining Company

FIG. 30-8.—A close-up and an air view of modern petroleum refineries.

Two pairs of electrons shared between two atoms is called a double bond.

Chemically, a mixture of normal and isomeric compounds, saturated and unsaturated, cyclic, branched, and straight chains of carbon atoms, but all hydrocarbons, is petroleum. Moreover, petroleum is a mixture of liquid hydrocarbons that contains solid and gaseous hydrocarbons all dissolved in each other. Usually, the liquid hydrocarbons contain 4 to 10 and more carbon atoms per molecule, the gases fewer, and the semi-solids even more.



naphthalene, an unsaturated cyclic hydrocarbon ($C_{10}H_8$)

How Petroleum Is Prepared for Use. The first "coal oil" was bottled and sold, to the accompaniment of a banjo entertainer, as a cure-all, good for man and beast. Later, the chief use of petroleum was for making kerosene for lighting when burned in coal-oil lamps.

Today petroleum is in most cases piped directly to a refinery. (See Fig. 30-8.) Many methods of refining are used, but let us assume that a maximum yield of gasoline, the product most used, is desired.

The petroleum is heated in a huge boiler called a still. The vapors are cooled and condensed within pipes. The part boiling between 104 and 436°F is the gasoline fraction. This fraction is kept separate from the next higher range of boiling points, 437 to 572°F, the kerosene fraction. At a higher range of temperatures, fuel oils, light lubricating oils, heavy lubricating oils, and paraffin or asphalt are vaporized. Petroleum coke is left in the retort. This process of separating a liquid according to range of boiling points is called ***fractional distillation.***

We should notice carefully that benzene, sometimes called benzol, is a definite compound (C_6H_6) obtained from the fractional distillation of coal tar. Benz*i*ne, on the other hand, is a mixture of hydrocarbons obtained from the fractional distillation of petroleum. The term benz*i*ne is rapidly becoming obsolete in the petroleum industry. It is principally a drugstore product used in dry cleaning. This product is more volatile than gasoline.

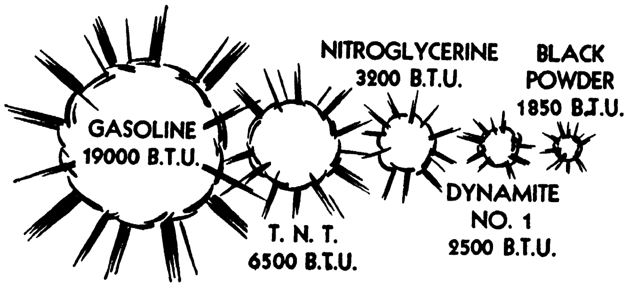
The various fractions must now be refined, or purified from assorted foreign substances that are present in the original petroleum. This is done in several ways. One method washes the fraction with concentrated sulfuric acid, sodium hydroxide solution, and water in turn. Sulfur may be removed by sodium plumbite (Na_2PbO_2). The purified fraction is now redistilled, and the gasoline so prepared is ready for the market as "straight-run" gasoline.

Cracking. The fuel-oil fractions are sent to another part of the plant, where they are heated under pressure. As a result of this treatment the hydrocarbon molecules split, or "crack," into fragments, or simpler molecules, that correspond to the more volatile compounds.

One possibility illustrates in general the chemical change accomplished.

	$C_{10}H_{22}$ →	C_7H_{16} +	C_3H_6
at ordinary temperatures	decane saturated kerosene-like liquid	heptane saturated gasoline-like liquid	propene gas, unsaturated

The fractions used for cracking stock, however, usually have more than 10 carbon atoms. Almost any breakdown of the higher boiling-point hydrocarbons is possible, but the process is controlled to produce the greatest possible amount of gasoline. The cracking process has greatly extended the yield of gasoline from petroleum.



Courtesy of General Motors Corporation

FIG. 30-9.—Gasoline is one of the most powerful packages of energy.

The portion of the oil that resists cracking is sold for fuel oil. The unsaturated compounds may be used to make plastics, alcohols, synthetic rubber, or other by-products, but they can also be used to make gasoline.

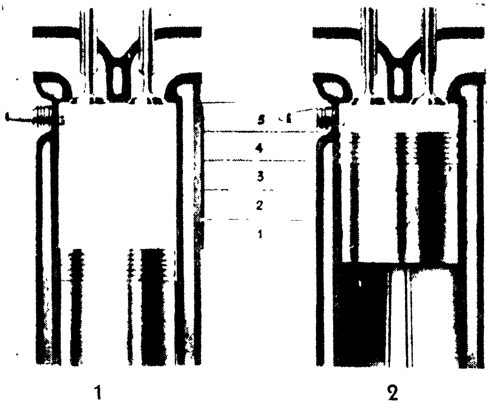
Polymer Gasoline. The process of making gasoline from small molecules is just the reverse of cracking. The joining of small molecules to make larger ones is a process called ***polymerization.*** This can be accomplished by the help of catalysts. The difficulty is to stop the molecules from joining when gasoline has been formed. Hydrocarbon molecules that continue to join may form gums when the gasoline is stored.

Gasolines made in the several different ways are blended and then offered for sale.

Octane Number. The most important fact about a gasoline today is its octane number. This number is a measure of its "knock" rating. A high octane number, 72 for example, indicates high antiknock gasoline. Straight-run gasoline, composed of straight-chain saturated hydrocarbons, knocks easily. Its octane number is low. Branched-chain or ring hydrocarbons have much higher octane numbers. Hence certain oils are naturally high in antiknock value, while others are naturally low.

The octane number of a gasoline is improved (1) by the method of refining, (2) by blending, and (3) by the use of inhibitors (negative catalysts).

The inhibitor most used is tetraethyl lead [$Pb(C_2H_5)_4$], a compound that together with ethylene dibromide ($C_2H_4Br_2$) and a dye constitutes the "Ethyl fluid" that is added to many gasolines. In the motor, the carbon and hydrogen parts of these molecules burn. Lead bromide ($PbBr_2$) forms. At the high temperature of the motor, this is a gas; it is exhausted through the tail pipe of the car.



Courtesy of Ethyl Corporation

FIG. 30-10.—A compression ratio of five to one is shown here. Note that the piston at the bottom of cylinder (1) encloses five times as much volume as it does when at the top of cylinder (2).

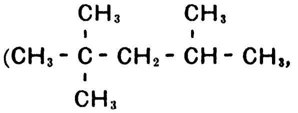
Motor Knock. Effective use of gasoline in an automobile engine requires that the gasoline-vapor-air mixture be highly compressed before it is exploded. The compression ratio in modern engines may be 7 or 8 to 1 (see Fig. 30-10), and many gasolines knock badly when they are compressed to such a high extent and exploded.

In order to prevent knocks, gasoline with octane rating 70 to 80 or over must be used if the compression ratio is high. The required octane rating depends on the design of the engine as well as the compression ratio. For airplane engines, gasoline with octane values 100 or over may be demanded. Such demands require skill and economy in all steps of the petroleum industry. Small wonder that about one-half of the chemists in the United States are employed by oil industries. "Triptane," a powerful aviation gasoline, is a fuel that has a very high knock rating.

The cause of knocking is interesting. The spark from the spark plug sets the gasoline-air mixture on fire at one spot in the cylinder. If this mixture burns steadily and smoothly, it will deliver steady power to the piston, owing to the expansive force of the hot gases formed by the burning. If, on the other hand, the gasoline-air mixture burns too rapidly or explodes, the gases expand faster than the piston can move, and the motor "knocks."

A badly knocking motor gives poor power, wastes fuel, and is under extra strain. It may be compared to hitting a stone wall with a baseball bat. The stone wall pushes back with as much force as the bat pushes forward. The power of the stroke is wasted. A smoothly running motor may be compared to striking a ball with a baseball bat with a "follow-through" swing. The full power of the stroke is used in driving the ball.

Technically speaking, pure iso-octane

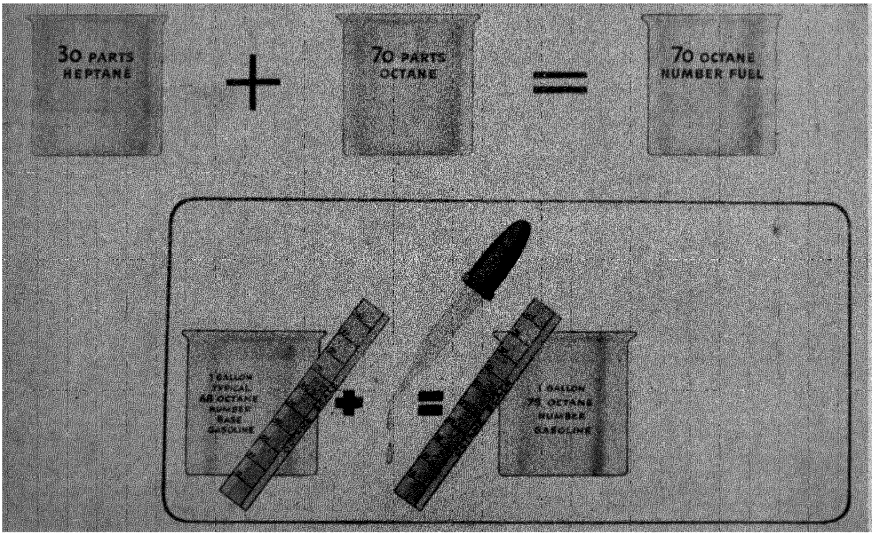


$$(CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{CH}-CH_3,$$

2-2-4 trimethylpentane) is rated as 100 in octane number, for it burns nicely under high compression. Normal heptane

$$(CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3),$$

with no branched-chain structure, knocks badly under compression. Gasoline, when compressed and ignited, that causes knocks to exactly the same extent as a mixture of 72 per cent iso-octane and 28 per cent normal heptane is given a 72 octane rating.



Courtesy of Ethyl Corporation

FIG. 30-11.—Octane number, and the effect on octane number of adding a catalyst.

Oil Resources. In spite of the great amount of oil that has already been used, the total volume used is only a small fraction of the total supply. Also, in recent years we have discovered extensive oil reserves, although some existing fields have been exhausted. Improved methods enable us to reach oil at a lower depth than could be reached a few years ago. Forcing the natural gas back into the wells has extended the "life" of oil wells. Drawing the oil out at a slow rather than at a rapid rate has also increased total yield.

On the other hand, we are certain that the oil supply of the world is limited. We cannot get all the oil from any well. Some oil we cannot reach. The cost of getting oil is slowly becoming higher.

From these facts we can reasonably conclude that (1) we should conserve oil, that is, we should use it carefully, without waste; (2) we should extend the use of oil, for example, by adding hydrogen and reclaiming used oil wherever economically possible; and (3) we should develop petroleum substitutes.

The Burning of Gasoline. Gasoline burns easily. It vaporizes readily. It forms an explosive gasoline-air mixture at ordinary temperatures.

THE BURNING OF GASOLINE
in an automobile cylinder

[Gasoline assumed to be octane (C_8H_{18})]

Exhaust tail-pipe gases

1. When air is abundant and flame is free,

$$2C_8H_{18} + 25O_2 \rightarrow \overset{\text{carbon dioxide}}{16CO_2} + \overset{\text{steam}}{18H_2O}$$

2. When air is abundant, hot flame strikes water-cooled cylinder wall,

$$2C_8H_{18} + 17O_2 \rightarrow \overset{\substack{\text{Carbon monoxide}\\ \text{(poison)}}}{16CO} + \overset{\text{steam}}{18H_2O}$$

3. When air is limited and flame strikes cooled metal,

$$2C_8H_{18} + 9O_2 \rightarrow \overset{\text{Carbon}}{16C} + \overset{\text{steam}}{18H_2O}$$

Carbon dioxide is 7.7 per cent and poisonous carbon monoxide 7.1 per cent by volume of the exhaust from an average car.

Gasoline Substitutes. A liquid substitute for gasoline is alcohol. It burns with abundant heat, vaporizing readily. Moreover, it can easily be made from a number of annual crops—sugar cane, corn, or potatoes, for example. In peacetime, however, most of it, is made by fermenting the sugar in commercial molasses, although synthetic methods are important also.

$$\underset{\text{sugar}}{C_6H_{10}O_5} + H_2O \rightarrow \underset{\text{alcohol}}{2C_2H_5OH} + \underset{\text{carbon dioxide}}{2CO_2\uparrow}$$

Two disadvantages of this liquid may be mentioned: alcohol absorbs water readily, taking it even from the air; and at present, in the United States, it costs more than gasoline. Also, the entire alcohol production is only about 3 per cent of the volume of gasoline used. In spite of these objections, alcohol-gasoline mixtures are used for motor fuel in other countries where alcohol may not cost more or where its use may be subsidized.

The countries where gasoline is scarce furnish us with a preview of the fuels that cars and buses will use when petroleum is almost gone. Some gasolineless cars use compressed fuel gas in large clumsy tanks. Others carry little gas generators, using coal or wood for fuel. Such cars travel a much shorter distance with a lot more bother than a car with a tank full of gasoline. They also lack power on hills.

Dangers with Gasoline. Three facts should be remembered about the use of gasoline. (1) Gasoline-vapor-air mixtures are explosive. Such explosive mixtures are always formed when gasoline is used for cleaning or when a tank is being filled with gasoline. (2) Gasoline with tetraethyl lead (leaded gasoline) is poisonous. The poison may be absorbed through the skin. (3) The fumes from gasoline make some persons ill.

Lubricating Oil. Oil from the higher boiling fractions of petroleum is an important lubricant. Waxes may be removed by chilling and filtering, and other impurities are sometimes extracted by solvents. It is interesting to note that most lubricating oils used today are far better than are needed for the purpose of automobile lubrication.

Tests show that oil in service under differing conditions oxidizes slowly and becomes diluted by gasoline that "blows" by the piston rings. The oxidized oil is a satisfactory lubricant, and the gasoline evaporates through a "breather." In fact, after 2000 miles of service, oil is found to change less than 2 per cent in all its important properties. "Studies of used oil show that a good oil retains its lubricating qualities much longer than was formerly supposed, although the point at which it becomes unfit for use cannot be accurately determined—at the present time."[1]

Under some conditions lubricating oil used in a car may be all right at the end of 2000 miles or more; under others, such as driving in a dust storm, it may be unfit for use after 300 miles. The demands of the modern car on lubricating oil are severe, and oil may deteriorate rapidly. No hydrocarbon can withstand excessive heat without decomposition. It is good insurance in case of doubt to change oil rather than to have expensive repair bills.

Smoke. Incomplete burning (see page 541) forms carbon, a black soot that clouds the sky of some manufacturing cities. Smoke smudges

---

[1] Holmes, Edward O. Jr., "The Changes in the Physical and Chemical Characteristics of Lubricating Oil with Use," *Report of the N.E.A. of Chemistry Teachers*, vol. 42, No. 3, March, 1941.

everything—curtains, clothes, buildings, and people. Worst of all, it is an unnecessary and preventable waste.

To avoid smoke, burn it up. This may be done by (1) keeping the fire hot enough, (2) supplying enough air, and (3) being sure that fuel and air are well mixed.

Tobacco smoke (the visible part) is not a gas as some people assume, but a collection of tiny solid particles, formed by the incomplete burning of the tobacco.

QUESTIONS

21. State the requirements for a liquid automobile fuel.

22. What is petroleum with respect to composition?

23. *Petroleum Facts and Figures*, 1941, published by the American Petroleum Institute, lists the 1940 use of petroleum in barrels in the United States (times 100,000) as: motor fuel, 5900; light fuel oil, 1640; heavy fuel oil, 3360; kerosene, 690; lubricants, 246; other products, 1364. What percentage of the total does each use represent?

24. In 1940 the United States had 390,000 producing oil wells; in 1917, it had 197,000. What is the per cent increase? Was the increase in petroleum production necessarily the same percentage?

25. Total world production of petroleum in 1940 was 2,146,105 thousand barrels. Outside the United States, 794,258 thousand barrels were produced. What percentage of the world's supply was produced in the United States?

26. Make a diagram showing the arrangement of carbon and hydrogen atoms and bonding electrons in normal (straight-chain) pentane (C_5H_{12}).

27. Distinguish destructive distillation from fractional distillation.

28. Show two possible structural arrangements for isomers of pentane.

29. Contrast "cracking" hydrocarbons with "polymerizing" them.

30. What is the meaning of 80 octane number as applied to gasoline?

31. Point out three ways by which the existing supply of petroleum is being extended.

32. For what reason are lead compounds added to gasoline?

33. Production of 150 octane number gasoline is now possible. What does this figure mean in respect to the standard scale?

34. What causes a motor to knock?

35. What is the real source of the motive power of a gasoline engine?

36. Why are the exhaust fumes from any gasoline engine always poisonous?

37. Point out the hazard of keeping containers of gasoline in a garage.

"You'll Never Know What Hit You." This ominous title appeared on a warning against the danger of carbon monoxide in closed garages. Slight amounts of carbon monoxide cause a headache. Larger amounts produce quick unconsciousness, followed by death. The gas is colorless and odorless so it gives absolutely no warning to its victims. The only way to guard against it is by knowledge and intelligent actions.

To balance the comfort and service of fires to mankind, we must pay the price of continual watchfulness. Out of control, fires destroy property and people. The product of normal burning, carbon dioxide, may suffocate persons. The product of improper burning, carbon monoxide, is an insidious danger.

Carbon Monoxide. When carbon monoxide is to be made, a well-ventilated fume hood must be used. The gas should not be prepared in an ordinary room. To make carbon monoxide, formic acid is heated to boiling and concentrated sulfuric acid allowed to enter slowly. The acid is dehydrated.

Courtesy of The Travelers Insurance Company

FIG. 30-12.—A closed cab and a leaky exhaust pipe may mean death from carbon monoxide.

$$\underset{\text{formic acid}}{H{\cdot}COOH} \xrightarrow{\text{(conc. } H_2SO_4)} H_2O + CO\uparrow$$

The production of the gas industrially has already been described (see page 529).

Carbon monoxide burns easily in air, with a blue flame.

$$2CO + O_2 \rightarrow 2CO_2$$

As we have learned, it is found in many fuel-gas mixtures.

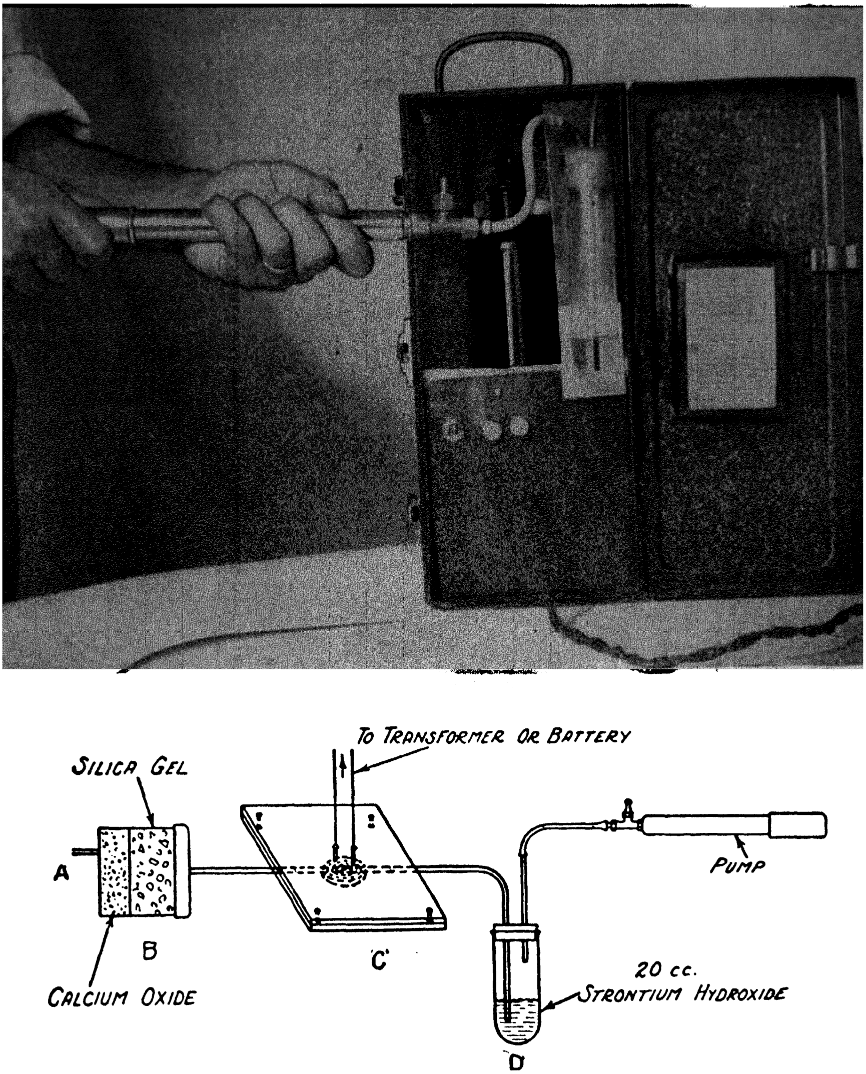
Carbon monoxide can take oxygen from hot oxides, also. It is an excellent reducing agent. In the laboratory we can easily show this by its action on hot copper oxide or lead oxide.

$$PbO + CO \rightarrow Pb + CO_2$$

Industrially, it is used to make our iron from the ore,

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

to refine nickel, and to make wood alcohol (CH_3OH) and phosgene ($COCl_2$).



Courtesy of The Travelers Insurance Company

Fig. 30-13.—In this portable carbon monoxide detector, the sample is first freed of carbon dioxide (*b*). Then the carbon monoxide is oxidized to carbon dioxide (*c*) and absorbed in strontium hydroxide solution to which an indicator is added (*d*). Twenty pump strokes will decolorize 20 ml of solution if CO in the sample is 100 parts per million.

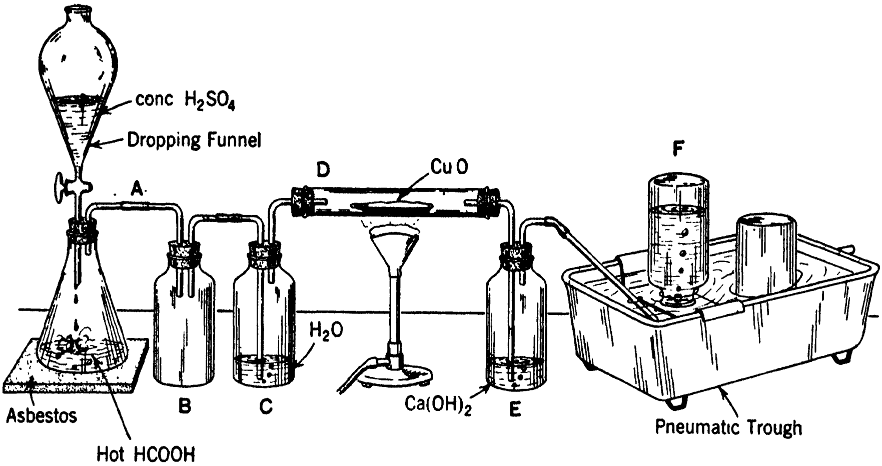


FIG. 30-14.—Carbon monoxide may be prepared in the laboratory and its properties demonstrated by using the apparatus shown above. Complete ventilation is essential.

Solid Fuels

Fossil Fuel. Many of the same processes that have gone on in the past on the earth are going on today. The formation of coal is one example. In swampy places plant and animal matter became decayed and matted together. Peat was formed. This can be dried and used for fuel, but it is not satisfactory for industrial uses. In some places layers of peat became covered by soil and rocks. The pressure of the material on top made it lose water and gases and change in chemical nature. Brown coal, or ***lignite,*** was the result. Increased pressure gradually changed the lignite to soft, or ***bituminous,*** coal. Special conditions of high pressure produced the hard, or ***anthracite,*** coal. An authority estimates that 20 ft of plant accumulations forms 3 ft of peat, and in turn, 1 ft of coal. The material in a seam of coal 1 ft thick thus represents the accumulation of plant matter for about 300 years.

Our coal supply has a limit. When we use it, we are drawing on our capital stock of the sunshine of other ages. Although we have a large supply, it follows that we should use coal with care and not waste it.

Nature of Coal. Plant stalks, fibers, and wood are composed chiefly of cellulose, a compound that has the formula $(C_6H_{10}O_5)_x$. When plant tissue is changed into coal, it loses water, carbon dioxide, and methane (CH_4). The coal formed contains less oxygen and hydrogen and a relatively larger amount of carbon as we go from lignite to bituminous to anthracite.

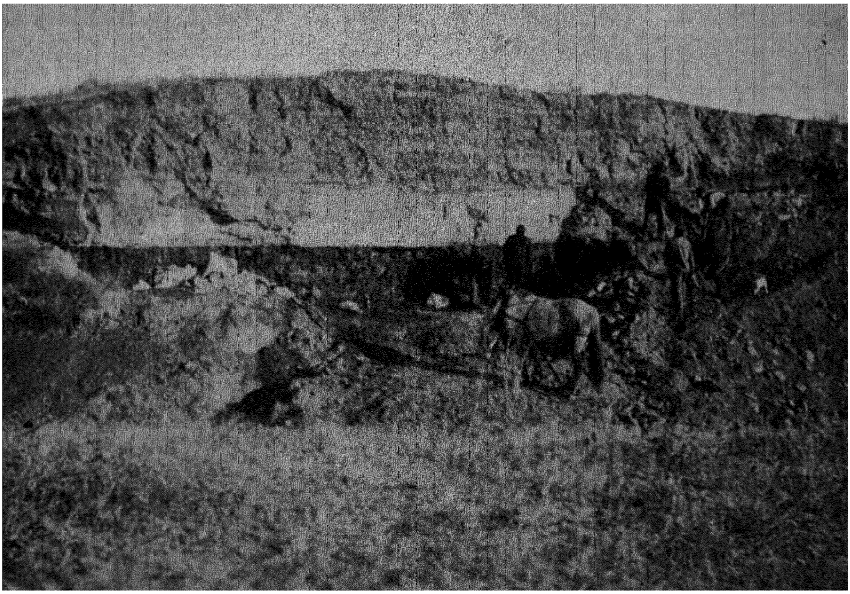
Coal is a mixture of compounds. Most of these compounds are able to join with oxygen and form carbon dioxide and water vapor. In addition, all the mineral matter that was present in the original plants is left in the coal and remains as ashes when coal is burned. Sulfur, an unwanted impurity, is frequently found in coal.

COMPOSITION AND FUEL VALUE OF THE SOLID FUELS*

Fuel	Carbon, %	Hydrogen, %	Oxygen, %	Relative fuel value
Cellulose	44.5	6.2	49.3	7.5
Wood	50.0	6.0	44.0	7.4
Peat	60.0	5.9	34.1	9.9
Lignite coal	67.0	5.2	27.8	11.7
Bituminous coal	88.4	5.6	6.0	14.9
Anthracite coal	94.1	3.4	2.5	15.7

* Adapted from Alexander Findlay, *Chemistry in the Service of Man*, 5th ed., Chap. V, Fuels and Illuminants, Longmans, Green and Company, New York, 1939.

Use of Coal. Coal is one of the great raw materials of industry. If we trudge about the grounds of a large manufacturing company or power plant, we observe large coal piles—ample proof of the need for coal.



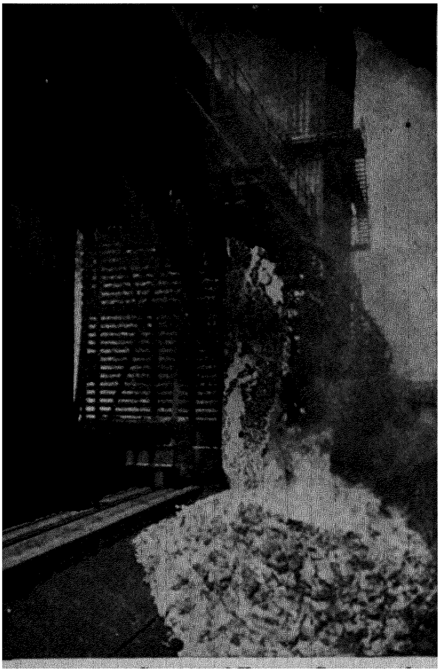
Courtesy South Dakota State School of Mines

FIG. 30-15.—These men are mining a seam of coal.

Much of our coal is wasted. Indeed, great need exists for studying the best ways of using coal effectively. In a modern steam power plant, the supply of coal represents two-thirds of that which started from the mine. About one-third is wasted or lost in mining and transportation. Two-thirds of the part burned in the fires of the boilers is wasted, and often less than 4 per cent is changed into useful work. A small steam locomotive is one of the most ingenious machines for wasting coal ever devised by man.

The most effective way of heating with coal is by the use of carefully designed grates or by burning it as a powder. Anthracite coal is entirely a fuel coal. Lignite is not used extensively, although when our better grades of coal are exhausted, more use may be made of this sort of fuel.

Smokeless Fuel. By outlawing it, the city of St. Louis, in 1940, eliminated the smoke nuisance, which in the past often made it necessary to turn on automobile headlights during the daytime. Outlawing smoke was economically possible because of the Curran-Knowles process of producing smokeless fuels from the inferior Illinois coals, which, though cheap and plentiful, burned with an appalling evolution of soot. This was accomplished after extensive research into the methods of making coke that would give full heat at a fuel-bed temperature below the melting point of the slag. The improved coke costs the St. Louis fuel consumer no more, and the benefits to health and cleanliness are tremendous.



Courtesy of K[illegible] Company, Inc.

FIG. 30-16.—Coke is shown here being pushed from by-product ovens after the "burn" has been completed. From this point, the coke will go to the quencher.

This is one example of how citizens can apply the advances of scientific research if they keep informed and are interested.

Charcoal. When wood is heated in a closed retort, or destructively distilled, interesting changes occur. A choking, smoky vapor arises. The wood becomes black and porous charcoal. The vapors are condensed by passing them through pipes cooled by running water. Wood alcohol (CH_3OH), acetic acid ($HC_2H_3O_2$), acetone [$(CH_3)_2CO$], and water are found in the condensed vapors.

Charcoal is a good household fuel since it burns readily, without smoke, and leaves little ash. Carefully made charcoal sticks are used by artists. Charcoal absorbs gases, sometimes undesirable ones. Decayed animal matter is made a bit more approachable when sprinkled with charcoal. Activated charcoal is made from carefully selected vegetable matter and is used in military and industrial gas masks.

Charcoal is frequently made without collecting the vapors. Piles of wood are placed in a pit and covered with sod. The whole mass is set on fire. Owing to lack of air the burning is incomplete, and the wood becomes changed into charcoal. Charcoal "burning" was done in the European forests in King Arthur's day and is carried on today in the same way. (See Fig. 30-17.)

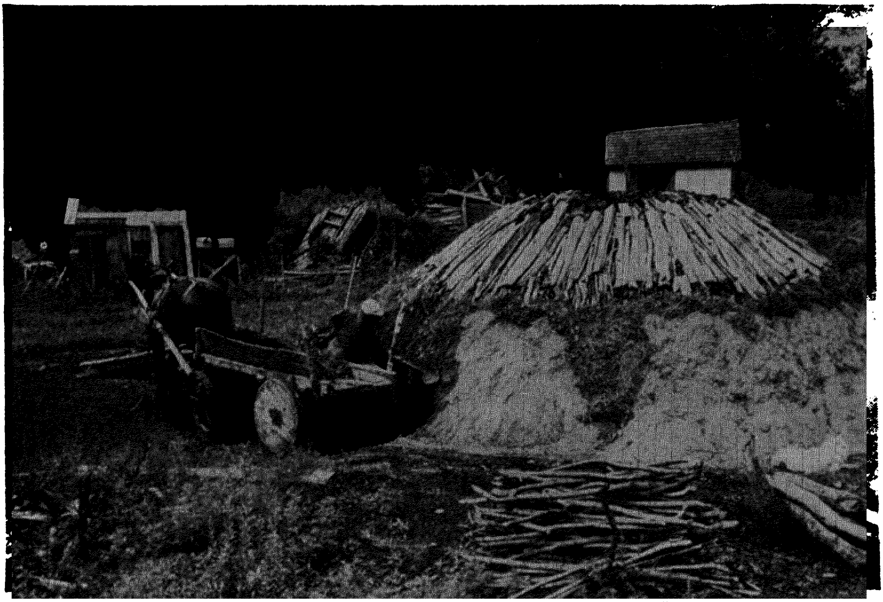


Photo by Philip Acquaviva

FIG. 30-17.—This is a rural method of making charcoal. A volcanolike heap of wood is covered with sod. Then it is set afire, burning partially in limited air. A heap of charcoal remains when the sod is removed.

SUMMARY

Among gaseous fuels, coal gas, the product of destructive distillation of bituminous coal, consists chiefly of methane and hydrogen. Destructive distillation is the process of heating a material in a closed retort in the absence of air and condensing the vapors formed. Water gas is made by an intermittent process. Steam is blown through hot coke, an endothermic change taking place. The resulting mixture of hydrogen and carbon monoxide is enriched with oil gas and the mixture stabilized by passing it over hot bricks. Water gas is the starting point for synthetic chemicals. Producer gas is made by passing air slowly through a deep bed of burning coal or coke. It consists chiefly of nitrogen and carbon monoxide and is a "lean" fuel and an inexpensive one. Natural gas is fuel from the earth, chiefly methane. Blast furnaces and oil refineries produce fuel gases as by-products.

Acetylene is prepared by the action of calcium carbide with water. It is a colorless gas that decomposes when heated and burns in oxygen with enough heat to melt steel. Acetylene is used as an illuminating gas because it burns with a sooty flame, as fuel for the oxyacetylene torch, and as a starting compound for synthetic chemicals.

Flames are burning gases. The Bunsen burner burns a mixture of gas and air, producing a luminous flame if the air holes are closed and a nonluminous flame when a mixture of air and gas is burned.

Among liquid fuels, petroleum, a natural mixture of hydrocarbons, is obtained by drilling into the earth. Fractional distillation separates petroleum according to a range of boiling points into fractions some of which are gasoline, kerosene, fuel oil, lubricating oil, and paraffin. Refining consists of removing unwanted impurities from petroleum fractions.

Sources of gasoline are (1) straight-run distillation, (2) "cracking" heavier hydrocarbons into smaller molecules, (3) condensing vapors from natural gas, (4) hydrogenation of lignite, and (5) polymerization of low molecular-weight hydrocarbons.

Hydrocarbons are compounds of hydrogen and carbon only. The simplest is methane, (CH_4). Some hydrocarbons are straight-chain compounds, some have branched chains, and others have a ringlike structure. Isomers are compounds having the same number of atoms and same molecular weight but differing in arrangement of atoms within the molecule.

The octane number is a rating of the knock performance of gasoline when compressed and ignited in an engine. High octane number (80 to 100) means that a gasoline will burn smoothly when compressed. The octane number can be raised by addition of lead tetraethyl and other inhibitors.

The petroleum supply is limited, although resources are extensive. Gasoline is very high in available energy. Burning gasoline evolves heat, which expands the gaseous contents of an automobile cylinder, pushing the piston down. Poisonous carbon monoxide is always formed by burning gasoline in an automobile engine.

Gasoline substitutes include alcohol and fuel gases. Wood gas from a generator carried with the vehicle is sometimes used.

Smoke represents unburned fuel. It can be avoided by (1) maintaining a high temperature in the fire, (2) a sufficient supply of air, and (3) adequate mixing of air and fuel.

Carbon monoxide is prepared by incomplete burning of carbon or carbon compounds, by reduction of carbon dioxide with hot carbon, and by action of hot formic acid on concentrated sulfuric acid. It is a colorless, odorless gas at room conditions. It is extremely poisonous, burns with a pale blue flame, and is an excellent reducing agent. It is used as an industrial fuel and as a reducing agent for metallic oxides. It is used to make methyl alcohol and to refine nickel.

Among solid fuels, coal, the vegetable matter of past ages, is found in extensive deposits in many different types. Coal is used as a fuel, to make coke, and to make coal gas. It is the main source of industrial energy.

Charcoal is made from wood by destructive distillation or by partial burning. It is used for fuel, for a reducing agent, and for adsorbing gases.

QUESTIONS

38. What part does the concentrated sulfuric acid play in the preparation of carbon monoxide from formic acid?

39. List three physical properties of carbon monoxide.

40. Write formula equations for (*a*) burning of carbon monoxide; (*b*) reduction of carbon dioxide by hot carbon; (*c*) reduction of ferric oxide (Fe_2O_3) by carbon monoxide; (*d*) reduction of magnetic iron oxide (Fe_3O_4) by carbon monoxide.

41. What percentage of nickel carbonyl [$Ni(CO)_4$] is due to carbon monoxide?

42. Distinguish three types of coal from each other.

43. What evidence shows the origin of coal?

44. Which is more valuable for heating, bituminous coal at $\left\{\begin{matrix}\$8\\ \$5\end{matrix}\right.$ per ton or anthracite coal at $\left\{\begin{matrix}\$14\\ \$6\end{matrix}\right.$ per ton?

45. Coal ashes are sometimes spread on the soil. Do they have fertilizing value?

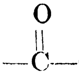
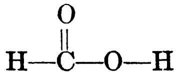
46. What advantage has the by-product method of making charcoal over the old method? Why is the old method still used?

UNIT SEVEN .... CHAPTER XXXI

PLANT AND ANIMAL CHEMISTRY

Acids

Picture an alchemist gathering ants. A supply of these creatures is obtained and crushed in a mortar with a pestle, and the carcasses are extracted with water. The resulting liquid is found to taste sour, and it is given the appropriate name ***formic acid*** (H—COOH) (ant acid from the Latin *formica*, meaning "ant"). In fact, this is the acid injected into the flesh by nettles, bees, mosquitoes, wasps, and hornets that "sting." A synthetic ant bite may be enjoyed by dipping a needle in a solution of formic acid and thrusting it into the flesh. If a less personal observation of swelling is desired, the needle may be pricked into prepared gelatin instead of the flesh.

All organic acids that contain the carboxyl group may be recognized by —COOH* or, better,  $-\overset{\overset{\displaystyle O}{\|}}{C}-O-H^*$. In the case of formic acid the remaining valence bond on the carbon atom is attached to a hydrogen atom by a covalent bond,  $H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H^*$. The replaceable hydrogen atom is starred (*).

Formic Acid (H—COOH*). Formic acid is the simplest of all the organic acids. When pure, it is a colorless liquid that has a sharp odor and taste, boils at 100.5°C, and is 1.22 times as dense as water. It dissolves in water in all proportions.

Formic acid can be made by heating oxalic acid [$(COOH)_2$] dissolved in glycerol [$C_3H_5(OH)_3$].

$$\underset{\text{oxalic acid}}{(COOH)_2} \rightarrow CO_2 + \underset{\text{formic acid}}{HCOOH^*}$$

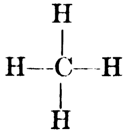
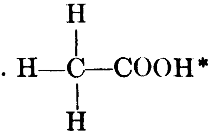
When heated, formic acid decomposes into carbon monoxide and steam.

$$HCOOH \rightarrow CO + H_2O$$

The acid is a good reducing agent.

New Terms

formic acid
aldehyde
hormone
ketone
ester
fat
anesthetic

Acetic Acid (CH_3COOH^*). The best-known organic acid is acetic acid ($CH_3—COOH$), since 4 to 10 per cent of it is found in vinegar. Acetic acid may be considered to be related to methane  $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$ by replacing one of the hydrogen atoms by a carboxyl group.  $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-COOH^*}$.

Vinegar forms when hard cider (which contains alcohol) oxidizes in air in the presence of certain bacteria (see page 519).

$$\underset{\text{alcohol}}{C_2H_5OH} + \underset{\text{from air}}{O_2} \rightarrow \underset{\text{acetic acid}}{CH_3\text{-}COOH^*} + H_2O$$

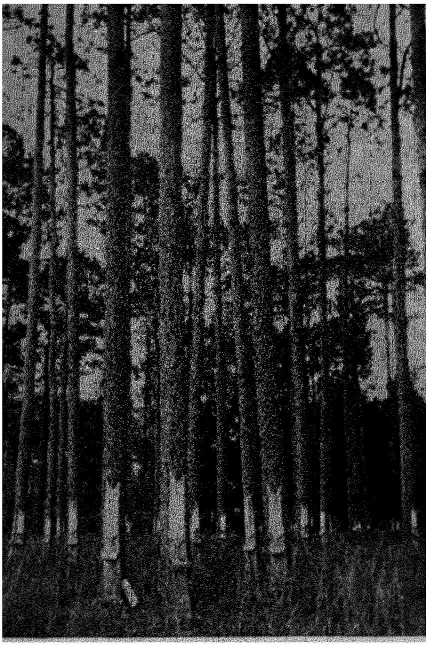
The change is slow when the cider is stored in barrels but relatively rapid when the hard cider is sprayed into air or allowed to trickle over wood shavings in a tower through which a current of air is flowing.

Acetic acid may also be prepared from acetylene in the presence of catalysts by the following synthesis:

$$\underset{\text{acetylene}}{C_2H_2} + H_2O \rightarrow \underset{\text{acetaldehyde}}{CH_3CHO}$$

$$2CH_3CHO + \underset{\text{from air}}{O_2} \rightarrow \underset{\text{acetic acid}}{2CH_3COOH}$$

Glacial acetic acid (100 per cent) is so called because of the icelike crystals that form from the pure liquid at 16.7°C. Both the sharp odor and the sour taste of a dilute solution of this liquid are observed in vinegar, which contains in addition some flavoring and coloring materials derived from the original fruit.



Courtesy of U.S. Forest Service

FIG. 31-1.—Plant chemistry is illustrated by this stand of longleaf pine being turpentined at Georgetown, S.C.

Acetic acid is a weak acid when compared with hydrochloric but relatively strong when compared with most organic acids. It dissociates

$$CH_3COOH \rightarrow \underset{\text{acetate ion}}{CH_3COO^-} + H^+$$

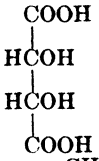
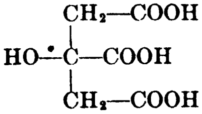
extensively enough to react with zinc and other active metals, carbonates, and hydroxides. It combines with alcohols in the presence of a dehydrating agent (concentrated H_2SO_4) to form esters.

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{methanol}}{HOCH_3} \rightarrow \underset{\text{methyl acetate}}{CH_3COOCH_3} + H_2O$$

Acetic acid is used to make acetates, such as sodium acetate (CH_3COONa or $NaC_2H_3O_2$) and lead acetate or sugar of lead [$Pb(C_2H_3O_2)_2$].

Other Crganic Acids. Other organic acids are known. Many refreshing soft drinks (soda water) contain citric acid or tartaric acid. Sour fruit or berries contain acids, or salts of organic acids.. In fact, some acids contain more than one carboxyl group per molecule. More information about carboxylic acids is contained in the following table:

SOME COMMON ORGANIC ACIDS

Acid Name	Formula	Remarks
Formic........	$H\cdot COOH$	Trace in honey—acts as a preservative
Acetic.........	$CH_3\cdot COOH$	Synthetic vinegar made from acetic acid (4 %) and water—lacks flavor
Propionic....	$C_2H_5\cdot COOH$	Also called propanoic acid
Butyric....	$C_3H_7\cdot COOH$	Found in rancid butter and in Limburger cheese
Palmitic.....	$C_{15}H_{31}\cdot COOH$	Found as esters of glycerol in fats or oils
Stearic........	$C_{17}H_{35}\cdot COOH$	Used to make cold, vanishing, shaving, and latherless shaving creams
Oleic..........	$C_{17}H_{33}\cdot COOH$	Its glyceryl ester found in oils. "Unsaturated," can add hydrogen
Linoleic.....	$C_{17}H_{31}\cdot COOH$	Found in linseed and cottonseed oil as esters. More unsaturated than oleic. Adds oxygen from air readily; also adds hydrogen
Oxalic.........	 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Found as potassium salt in sorrel. Has two carboxyl groups. Poisonous. Used as bleaching agent
Tartaric.......	 $\begin{array}{c}COOH\\ \vert\\ HCOH\\ \vert\\ HCOH\\ \vert\\ COOH\end{array}$	Potassium hydrogen tartrate ($C_4H_4O_6KH$); insoluble in alcohol and deposits inside wine casks. Crude deposit called "argols," refined, "cream of tartar"
Citric.......	 $\begin{array}{l}\quad\ CH_2-COOH\\ \quad\ \vert\\ HO-C-COOH\\ \quad\ \vert\\ \quad\ CH_2-COOH\end{array}$	Found in many fruits and berries. In lemons, 6 %. Many uses of citrates. Magnesium citrate used in medicine as a purgative

QUESTIONS

1. Write the formula for the radical found in all organic acids. Indicate the replaceable hydrogen atom.

2. Write the formula for (*a*) formic acid; (*b*) sodium formate; (*c*) calcium formate; (*d*) methyl formate.

3. Write the formula for (*a*) oxalic acid; (*b*) sodium oxalate; (*c*) calcium oxalate; (*d*) dimethyl oxalate; (*e*) methyl ethyl oxalate.

4. Name three organic acids, and tell the natural source of each.

5. Write an equation for the complete burning of (*a*) formic acid; (*b*) acetic acid; (*c*) oxalic acid.

6. By equations show the change of (*a*) oxalic acid to formic acid; (*b*) alcohol to acetic acid; (*c*) acetaldehyde to acetic acid; (*d*) acetic acid to sodium acetate; (*e*) acetic acid to lead acetate.

7. Name two industries in which the flavor of vinegar is important.

8. On standing in air, grape juice changes to wine, and in turn the wine changes to wine vinegar. Write two equations to represent these changes.

9. Write formulas for the (1) sodium and (2) calcium salts of (*a*) propionic acid; (*b*) butyric acid; (*c*) palmitic acid.

10. (*a*) Tartar emetic is potassium antimonyl tartrate. Write its formula. (*b*) Rochelle salts is the sodium potassium salt of tartaric acid. Write the structural formula.

11. Point out an essential difference between acetic, oxalic, and citric acids.

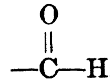
12. What weight of sodium hydroxide is needed to neutralize $\left\{\begin{matrix}240\\300\end{matrix}\right.$ grams of vinegar, 10 per cent acetic acid?

13. When $\left\{\begin{matrix}100\\500\end{matrix}\right.$ grams of dilute vinegar, 6 per cent acetic acid, is run onto an excess of sodium hydrogen carbonate, what volume of carbon dioxide gas at STP is liberated?

14. What difference, if any, would there be in the volume of carbon dioxide produced if sodium carbonate was used in the previous problem instead of sodium hydrogen carbonate?

15. Write equations for the complete neutralization by potassium hydroxide of (*a*) acetic acid; (*b*) formic acid; (*c*) oxalic acid; (*d*) tartaric acid; (*e*) citric acid.

Aldehydes

Formaldehyde. Aldehydes are so called because they can be made from ***al***cohol ***dehyd***rogenated. They all contain the characteristic grouping  $\overset{\overset{\displaystyle O}{\|}}{—C}—H$, or —CHO. Aldehydes represent an intermediate stage of oxidation between an alcohol and an acid. This can be seen from the following series of chemical changes, which show the steps in the oxidation of methyl alcohol:

$$\underset{\text{methanol}}{CH_3OH} + [O] \rightarrow \underset{\text{formaldehyde}}{HCHO} + H_2O$$

$$\underset{\text{formaldehyde}}{HCHO} + [O] \rightarrow \underset{\text{formic acid}}{HCOOH}$$

Some aldehydes are fragrant and give characteristic odors to so-called "essential" oils, as cinnamic aldehyde in oil of cinnamon, and benzaldehyde (C_6H_5CHO) in oil of bitter almonds.

Formaldehyde is made by the oxidation of methyl alcohol vapor by oxygen of the air in the presence of hot copper that has oxide on its surface. The equation for the reaction is the first of the two given above. The product of the reaction is a gas, irritating to the eyes. A solution of the gas dissolved in water to 37 per cent strength is called "formalin."

Formaldehyde is used for making resins (Bakelite, for example) and dyes. It is a good disinfectant. The solution is used to harden gelatin in photographic processes and by a similar action to preserve biological specimens.

Formaldehyde readily changes into a solid form called paraformaldehyde. This change is explained by assuming that formaldehyde is polymerized, that is, that the solid contains a multiple molecule composed of a number of units each having the simple formula HCHO. Formaldehyde gas is easily released from the solid form for use as a disinfectant and preservative. "Paraform candles" are burned for this purpose.

QUESTIONS

16. Point out the difference between the characteristic groups in aldehydes and in organic acids.

17. What product is formed (*a*) by oxidation of an aldehyde; (*b*) by reduction?

18. Balance this equation: (*Do not write in this book.*)

$$HCHO + NH_3 \rightarrow \underset{\text{hexamethylenetetramine}}{(CH_2)_6N_4} + H_2O$$

19. What weight of methanol must be used in order to fill an order for $\left\{\begin{matrix}5\\15\end{matrix}\right.$ tons of formaldehyde?

20. Formaldehyde is one ingredient of embalming fluid. What purpose does the formaldehyde serve in this mixture?

21. List three uses for formaldehyde.

Ketones

Acetone. Another class of organic compounds is called ketones and has the characteristic group $\rangle C = O$.

The most important member of this group of compounds is acetone [$(CH_3)_2CO$], or dimethyl ketone. Acetone is a colorless liquid with a penetrating pleasant odor, boiling at 56°C. It is a good solvent for resins, gums, and varnishes, including fingernail lacquer. It is used for making chloroform ($CHCl_3$) and iodoform (CHI_3). Like wood alcohol, acetone was formerly made from distilling wood. Today both methanol and acetone are made synthetically.

QUESTIONS

22. Write formulas for (*a*) diethyl ketone; (*b*) dimethyl ketone; (*c*) methyl ethyl ketone; (*d*) chloroform; (*e*) iodoform.

23. For what purpose is acetone used in lacquers?

24. Write an equation for the burning of acetone.

25. What weight of dry calcium acetate is needed to produce $\left\{\begin{matrix}1\\5\end{matrix}\right.$ liters of liquid acetone (density 0.79 grams per milliliter)? The equation for the reaction is

$$\mathrm{Ca(C_2H_3O_2)_2} \xrightarrow{\text{heated}} \mathrm{(CH_3)_2CO} + \mathrm{CaCO_3}$$

Courtesy of Commercial Solvents Corporation

FIG. 31-2.—Animal chemistry is illustrated by these rabbits lined up in stanchions in a penicillin factory. The rabbits are used for pyrogen tests. They are not injured, the same rabbits being used several times.

Ethers

Ether. Ethers correspond to organic oxides. For example, the common ether is diethyl oxide [$(C_2H_5)_2O$]. Note the difference between the characteristic grouping in an ether (=O) and that in a ketone (=C=O).

Ether is made by treating alcohol with concentrated sulfuric acid as a drying agent in the presence of an aluminum compound as a catalyst.

$$\underset{\text{ethanol}}{2C_2H_5OH} \rightarrow \underset{\text{ether}}{(C_2H_5)_2O} + H_2O$$

Ether is a liquid that boils at 34.5°C and evaporates quickly at room temperature. The vapor is flammable and is explosive when mixed with air. Ether has an advantage over chloroform ($CHCl_3$) as a general anesthetic because its effects are more easily controlled. However, it has several disadvantages as an anesthetic, and its use is giving way to more desirable ones.

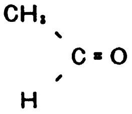
Ether is an excellent solvent. Natural fats and waxes are often extracted from plants by dissolving them in ether, evaporating and recovering the ether, and leaving the plant product.

QUESTIONS

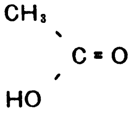
26. Write the formula for (*a*) dimethyl ether; (*b*) diethyl ether; (*c*) methyl ethyl ether.

27. To what class of compounds does each of the following belong?

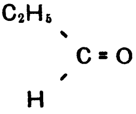
(*a*)



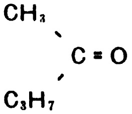
(*c*)



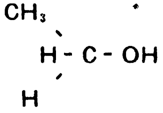
(*e*)



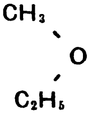
(*b*)



(*d*)



(*f*)



28. Why is ether sometimes used to remove spots from clothing? What danger accompanies its use?

29. State one advantage and one disadvantage of the use of ether for anesthesia.

30. Write an equation for the preparation of dimethyl ether.

31. What weight of alcohol should be used to prepare $\left\{\begin{matrix}1480\\370\end{matrix}\right.$ grams of common ether?

Esters

Ethyl Acetate. We have already seen (see page 555) that esters can be made from an acid and an alcohol by the removal of water.

When small amounts of ethanol and acetic acid are heated in a test tube with a few drops of concentrated sulfuric acid, a pleasant, "fruity" odor of ethyl acetate, an ester, can be noticed.

$$\underset{\substack{\text{acetic}\\\text{acid}}}{CH_3COOH} + \underset{\text{ethanol}}{HOC_2H_5} \rightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

By substituting different acids or alcohols in the above general reaction, a large number of esters can be made. For example, the popular wintergreen flavoring, identical with that found in the checkerberry plant, can be made in the laboratory by the action of salicylic acid and methanol.

$$\underset{\text{salicylic acid}}{C_6H_4(OH)COOH} + \underset{\text{methanol}}{HOCH_3} \rightarrow \underset{\substack{\text{methyl salicylate}\\ \text{or oil of wintergreen}}}{C_6H_4(OH)COOCH_3} + H_2O$$

The natural odors and flavors in fruits and flowers are due chiefly to esters. In some cases the identical plant product may be prepared synthetically, but in many others the perfumes of flowers are delicate mixtures of several scents. To imitate these requires the blending skill of a perfumer.

Esters, such as butyl acetate and ethyl acetate, are excellent solvents for the gums in lacquer finishes that are sprayed onto automobiles. These solvents evaporate quickly, leaving a tough coating. Esters of high molecular weight are used as internal lubricants, or plasticizers, in rubber and plastic products. Common fats are esters of the alcohol glycerol [$C_3H_5(OH)_3$].

Name	Formula	Remarks
Esters of simple alcohols		
Iso-amyl acetate........	$CH_3COOC_5H_{11}$	Called "banana oil"
Ethyl butyrate..........	$C_3H_7COOC_2H_5$	Odor resembles that of pineapples
Octyl acetate..........	$CH_3COOC_8H_{17}$	Odor resembles that of oranges
Esters of glycerol—fats		
Glyceryl butyrate.......	$(C_3H_7COO)_3C_3H_5$	In butter (5 %)
Glyceryl stearate.......	$(C_{17}H_{35}COO)_3C_3H_5$	In beef suet and mutton tallow
Glyceryl oleate..........	$(C_{17}H_{33}COO)_3C_3H_5$	In olive oil (72 %)

Fats. Fats are mixtures of the glycerol esters of the higher molecular weight acids of the formic acid series or esters formed from a combination of them. Esters commonly found are those of stearic, oleic, and palmitic acids. All fats and oils, regardless of natural source, are combinations of relatively simple parts. Because the esters of the acids mentioned are found in fats, the acids themselves are called the "fatty acids."

A fat can be made in the same general way in which an ester is produced. An alcohol (glycerol) and a fatty acid are brought together in the presence of a dehydrating agent.

$$\underset{\text{stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{glycerol}}{C_3H_5(OH)_3} \rightarrow \underset{\text{glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + 3H_2O$$

Notice that glycerol, a *tri*hydroxy alcohol, requires three molecules of the fatty acid for complete reaction. This equation may look complicated, but the learner who tries writing it our for himself will see that no new principles are involved, merely new and larger radicals.

Decomposing Fats. A supply of glycerol (glycerin) can be made for explosives by the action of steam on fat. This reaction is the reverse of the one showed in the preceding paragraph.

$$\underset{\text{glyceryl palmitate}}{(C_{15}H_{31}COO)_3C_3H_5} + \underset{\text{steam}}{3HOH} \rightarrow \underset{\text{glycerol}}{C_3H_5(OH)_3} + \underset{\text{palmitic acid}}{3C_{15}H_{31}COOH}$$

Esters also act with solutions of sodium or potassium hydroxide to form soaps or soaplike metallic salts. If a fat is treated with lye (NaOH) solution, the products are a sodium soap and glycerol. (See page 603.)

QUESTIONS

32. What is the percentage composition of ethyl acetate?

33. The formulas $C_4H_8O_2$ and $CH_3COOC_2H_5$ both represent ethyl acetate. Why is the second preferred?

34. Write equations for the preparation of the following, each from its appropriate organic acid and alcohol: (*a*) ethyl acetate; (*b*) methyl acetate; (*c*) methyl salicylate; (*d*) ethyl salicylate; (*e*) isoamyl acetate.

35. What is a plasticizer?

36. Define the general terms *ether; ester; aldehyde; ketone; carboxylic acid; alcohol.*

37. Most fats contain esters derived from what alcohol?

38. In what respect does the composition of glycerol differ from the composition of ordinary alcohol?

39. Palmitic acid has the formula $C_{15}H_{31}COOH$. Write the formula for (*a*) ethyl palmitate; (*b*) glyceryl palmitate; (*c*) sodium palmitate; (*d*) calcium palmitate.

40. Name two solvents for fat.

41. When butter turns rancid, an evil-smelling acid is formed by the decomposition of glyceryl butyrate (butterfat). Write the formula for this acid.

42. Write the formula of a fat, showing the glyceryl, stearate, oleate, and palmitate radicals all in one molecule.

43. What product made from fat is useful for (*a*) military purposes; (*b*) household purposes?

Waxes

Waxes, like fats, are esters, but they are esters of alcohols containing one hydroxyl group. One of the most extensively used waxes in furniture and floor polishes is carnauba wax, obtained from the coating on certain Brazilian palm leaves. It contains myricyl cerotate ($C_{26}H_{53}COOC_{31}H_{63}$), an ester. Beeswax contains another ester, myricyl palmitate

$$(C_{15}H_{31}COOC_{31}H_{63}).$$

While these formulas look large, they represent nature.

QUESTIONS

44. Distinguish in general the composition of a wax from that of a fat.

45. Write an equation to show the reaction produced by treating beeswax with lye.

46. What is the percentage of carbon in beeswax?

47. Give two uses for beeswax and one for carnauba wax.

Enzymes and Hormones

Enzymes. Let us stir one-half a yeast cake into a little warm water in a bottle, then fill the bottle with a solution of hydrogen peroxide, cover it with a glass plate, and immediately invert and place it mouth downward in a pan of water so that the mouth is below the water in the pan. (See Fig. 31-3.) The yeast cake contains catalysts produced by the living yeast plants that decompose the hydrogen peroxide.

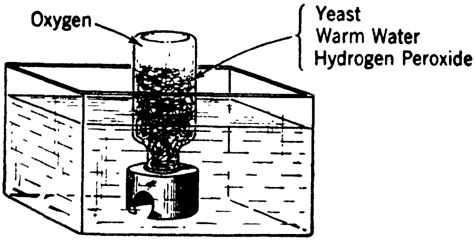


FIG. 31-3.—Enzyme at work is illustrated by this experiment. Yeast enzymes readily liberate oxygen from hydrogen peroxide.

$$2H_2O_2 \rightarrow 2H_2O + O_2\uparrow$$

The oxygen produced collects in the upper part of the bottle and expels the reaction mixture.

Such catalysts from living sources are called ***enzymes.*** Many useful and interesting changes are aided by enzymes. "Most life processes are accomplished in the presence of enzymes. The oxidation of food in the cells of animals can occur at rapid rates at body temperature only because enzymes serve as catalysts for the very complicated processes."[1]

We have seen that the enzyme in malt called ***diastase*** assists the change of starch to sugar (maltose) (see page 597). An enzyme in yeast called ***zymase*** catalyzes the oxidation of glucose to alcohol (see page 518). Another enzyme in yeast called ***invertase*** catalyzes the hydrolysis of sucrose into simple sugars.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

[1] **Erie Ball, Harvard University.**

It is well known that a cracker held in the mouth tastes sweet after a while.

A more convincing test may be made by boiling a chewed and unchewed cracker respectively with Benedict's solution. The former reduces the copper salt dissolved in Benedict's solution to a pink precipitate of cuprous oxide (Cu_2O), showing that a reducing sugar has been formed from the starch of the cracker. The unchewed cracker gives no evidence of sugar.

The change of starch to sugar in the mouth is carried on with the aid of ***ptyalin,*** an enzyme in saliva. Other changes aided by enzymes occur throughout the digestive system.

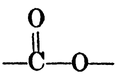
Hormones. The processes within the body itself are controlled by small amounts of chemical regulators in the blood stream called ***hormones.*** These chemical compounds are produced in the "ductless glands" in specialized organs of the body. In the neck the thyroid gland produces the hormone ***thyroxine,*** controlling growth. Thyroxine contains iodine, an element that must be supplied in small amounts for normal health. The adrenal glands produce the hormone ***adrenalin,*** which causes blood vessels to contract, heart to speed up, sugar to be released from the liver ready for fuel, and the body to be prepared generally for emergencies.

Other hormones control the process of normal reproduction. Lack or excess of a hormone results in disturbance to growth or health. The study of hormones has been made by doctors and chemists jointly, and many human ills have been corrected by the knowledge gained about them and their action. The use of the hormone ***insulin*** has removed the terror of diabetes.

The following steps in a study of this sort are typical of modern chemical research: (1) study of the subject in general by experimentation and observation of healthful and diseased conditions; (2) collection of the active principle (hormone in this case) from natural sources; (3) purification of the substance, analysis, and investigation of the structure (arrangement of atoms within the molecule); (4) laboratory synthesis of a compound identical with the natural one; (5) synthesis of compounds similar to the natural one in the hope of "improving on nature."

Obviously, such a study requires years of patient work and challenges the skill of many trained workers to make even the tiniest advance into the unknown.

SUMMARY

All organic acids contain the caboxyl radical  $-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$. Formic acid, the simplest organic acid, is prepared by heating oxalic acid. It decomposes when heated, forming carbon monoxide and water.

Acetic acid is formed by the oxidation of alcohol, as in vinegar making. It is also synthesized from acetylene, water, and oxygen. Acetic acid is a weak acid, that is, it dissociates slightly in water solution; it reacts with active metals, hydroxides, alcohols; it is used in the manufacture of vinegar, insecticides, and plastics.

Many other organic acids are known. Some occur in nature either as the acid itself or as salts of the acid. Included among the well-known organic acids are oxalic acid, tartaric acid, and citric acid.

All aldehydes contain the $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ group. Formaldehyde (HCHO), simplest of all aldehydes, is a gas at room temperature. It is made by the oxidation of methyl alcohol. Formaldehyde is soluble in water and is irritating to the eyes. It is used as a disinfectant and preservative and to make synthetic resins. Some aldehydes are found in nature as natural flavoring agents.

All ketones contain the $=C=O$ group. Acetone, an excellent solvent for gums and resins, is the best known compound in this class.

All ethers contain the $=O$ group. Ordinary ether is diethyl ether. It is prepared by the dehydration of alcohol. It is a low-boiling liquid, is flammable, and is an excellent solvent for waxes, gums, and grease. It is also used as an anesthetic.

Esters are made from acid and alcohol by removal of water. They are found in nature in fruits and flowers. Fats are esters, chiefly of stearic, oleic, and palmitic acids with glycerol. They may be decomposed (hydrolyzed) by steam into the corresponding fatty acid and glycerol. Fats treated with lye form soap and glycerol (saponification).

Waxes are esters of monohydroxy alcohols of high molecular weight. Carnauba wax is used for furniture and automobile polish. Beeswax has many uses.

Enzymes are catalysts, produced in living organisms, that promote definite chemical changes. Examples are as follows: Diastase in malt changes starch to sugar. Invertase in yeast changes sucrose to simple sugars. Ptyalin in saliva changes starch to sugar.

Hormones are chemical regulators of the body. The normal processes of the body are controlled by small amounts of chemical substances secreted into the blood from glands.

Hormones have been studied according to the steps characteristic of chemical research, as follows: (1) extensive, accurate observation of the problem; (2) isolating the natural material relating to the problem from impurities found with it in nature; (3) analysis of the purified natural compound; (4) synthesis of the active principle, including preparation of similar compounds.

QUESTIONS

48. Name two enzymes found in the body and one outside the body. Tell where each is produced and the purpose each serves.

49. Give an example of cooperative research between chemists and doctors of medicine.

50. Indigo dye, formerly made from plants, is now manufactured in factories. How do the five steps of chemical research apply to this example?

UNIT SEVEN - - - - - - - - - - - - CHAPTER XXXII

CELLULOSE AND PLASTICS

We start the day by rising from a bed on which cellulose in cotton is some part of the bed clothing. Our own clothing consists in part at least of cotton or rayon cellulose garments. At breakfast time we may read the news from a cellulose wood-pulp newspaper while sitting on a cellulose chair. Throughout the day paper in numerous forms—in books, letters, business blanks, wrappings—is an accepted part of life. Our vegetable food contains some cellulose. We enjoy radio programs from a radio contained in a cellulose-filled plastic case. Burning wood cellulose warms the hearth of our cellulose house.

Cellulose. The stalks of plants, wood, cotton, and linen are chiefly cellulose. From cellulose is manufactured paper, explosives, and rayon. Obviously, a large part of the vegetable world is cellulose $(C_6H_{10}O_5)_x$.

A large part of the activity of mankind is concerned with oxidation. Food is oxidized to secure energy for the body; wood, coal, and oil are burned (oxidized) for warmth and power. The vegetable world, however, reverses this process. By the process of photosynthesis carbon dioxide and water are changed to starch and cellulose in the presence of sunlight, the sun's energy thus being trapped.

Because man makes extensive demands on the vegetable world, both present and past, the problem of supply is a pressing one. Reforestation, for example, is necessary to ensure a continuous supply of paper and other cellulose products.

Properties of Cellulose $(C_6H_{10}O_5)_x$. Filter paper used in the chemical laboratory is almost pure cellulose. It burns leaving no solid remainder if pure and only a small amount of mineral matter as ash present in the original wood if impure.

A solution of zinc chloride $(ZnCl_2)$ or of copper hydroxide $[Cu(OH)_2]$ in ammonia water (NH_3 in H_2O) acts on cellulose to form a colloidal

---

New Terms

thermosetting
resin

cellulose
latex

vulcanize

dispersion.[1] When cellulose is soaked in lye ($NaOH$) and treated with carbon disulfide (CS_2), orange crumbs of cellulose xanthate form. The last two actions mentioned are the basis of manufacture of two different types of rayon.

Nitric acid (HNO_3) in the presence of concentrated sulfuric acid as a dehydrating agent adds nitrate groups ($—NO_3$) to cellulose, forming cellulose nitrate.

$$\underset{\text{cellulose}}{C_{24}H_{40}O_{20}} + \underset{\text{nitric acid}}{10HNO_3} \rightarrow \underset{\substack{\text{cellulose nitrate} \\ \text{nitrated highly (12.8 \%)}}}{C_{24}H_{30}O_{10}(NO_3)_{10}} + 10H_2O$$

The extent of nitration determines the number of nitrate groups added and the use of the product. Highly nitrated cellulose is used for explosives; less highly nitrated cellulose is used for lacquers, celluloid, and coatings for cloth that make it resemble leather.

When cooked with acid under pressure, cellulose slowly changes to starch.

$$(C_6H_{10}O_5)_x + xH_2O \xrightarrow[\text{catalyst}]{(HCl)} xC_6H_{12}O_6$$

Pulp. Pulp is made chiefly from rags or wood, although many cellulose fibers such as straw or grasses may be used. Cooking the fibrous material with steam, usually with added chemicals, produces a uniform cream of cellulose fibers.

Mechanical pulp is simply ground wood containing lignin and other materials present in the original log. Paper, such as newsprint, made from mechanical pulp can be identified because it turns yellow with a water solution of aniline ($C_6H_5NH_2$), while chemical pulp shows no color change with the same treatment.

Chemical pulp is made by cooking clean wood chips with lye ($NaOH$) or with calcium hydrogen sulfite [$Ca(HSO_3)_2$] with an excess of sulfur dioxide (SO_2). Kraft pulp is made by using sodium sulfate (Na_2SO_4) and lye. Other special pulps, such as that produced from southern pine, require additional chemical processes.

Much pulp is used in the manufacture of paper (commonly a mill makes fibers into finished paper, using its own pulp), but other uses of pulp are important. Pulp is used to manufacture rayon, to make explosives, and as a filler.

Paper. The art of papermaking consists in catching a uniform felt of fibers on a screen, removing the water, and pressing the resulting mat into a sheet. A sheet of paper so made would resemble blotting paper, unsized, unfilled, and absorbent. Binders, such as rosin soap, and fillers,

---

[1] A simplified preparation of Schweitzer's reagent A. Breslau, *Journal of Chemical Education*, vol. 19, No. 8, August, 1942.

such as clay or barite ($BaSO_4$), are added so that ink will not run. Fine papers may be coated with casein or with gelatin.

Making paper by hand can be carried out with simple equipment consisting of a fine-mesh wire screen mounted on a frame, a bucket of pulp suspension, and a warm flatiron.

Careful examination of a baker's ordinary cardboard pie plate will show the method of manufacture. Notice on one side the marks of the wire screen to which a rather irregular mat of fibers was drawn by suction.

Making sheets of paper by machine depends on doing the job continuously and rapidly. An even fall of pulp, often bleached and dyed, suspended in water is fed onto one end of a wire screen arranged as an endless belt. The water drains through the screen at first; then it is forcibly drawn through by suction. The weak, wet mat of fibers is transferred to a felt blanket arranged as another endless belt that supports it through drying and pressing rollers. After drying, the paper gains enough strength to go by itself through the rest of the machine to the calender rolls that compress the sheet. Sometimes finishes are added, or special treatment is given the surface.

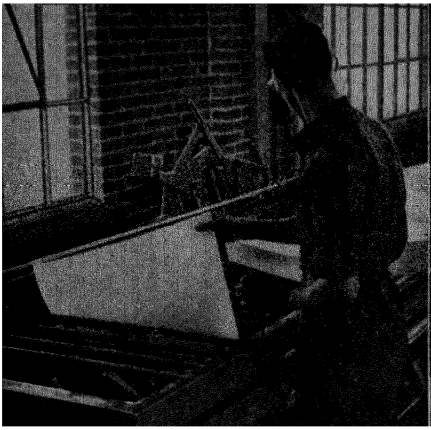
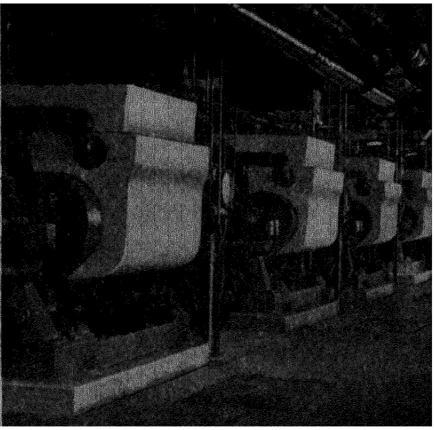
Rayon. Rayon started as an imitation of silk, but today's product has long left behind the imitation stage of development. Under the name ***rayon,*** the fiber has created a growing market for itself, second only to that for cotton. The success of this synthetic fiber is an outstanding example of the results of scientific research applied to a practical problem.

Rayon today is made by three principal processes: (1) cuprammonium, (2) acetate, and (3) viscose. The last-named method produces about four-fifths of the supply.

A Robot Silkworm. Sheets of cellulose pulp, resembling large sheets of thick blotting paper, are soaked in a solution of lye ($NaOH$). The product is treated with carbon disulfide (CS_2), forming orange-colored crumbs called cellulose xanthate (yellow cellulose). This colored material dissolves in more lye solution, forming a clear, sirupy liquid called viscose. After aging, viscose is squirted through a nozzle called a spinneret made of acid-resisting metal. Through it are drilled 10 to 150 tiny holes in a space much smaller than the surface of a dime. The number of holes depends somewhat on their size; their size, in turn, determines the diameter of the fibers produced.

On one side of the spinneret is viscose sirup under pressure. On the other is a solution containing chiefly 10 per cent sulfuric acid (H_2SO_4). During the first half second in the coagulating bath, the cellulose is reprecipitated as a strong, lustrous fiber. It is then washed, dried, and reeled. About 40 ft per sec of continuous, strong, many-stranded fibers is produced.

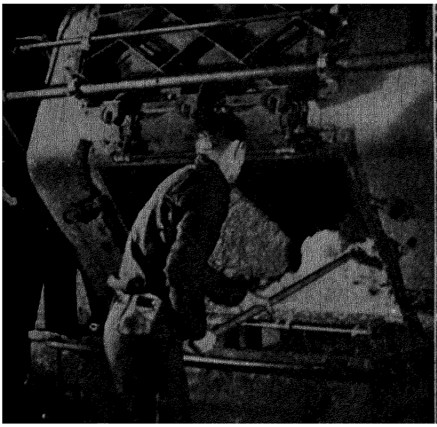
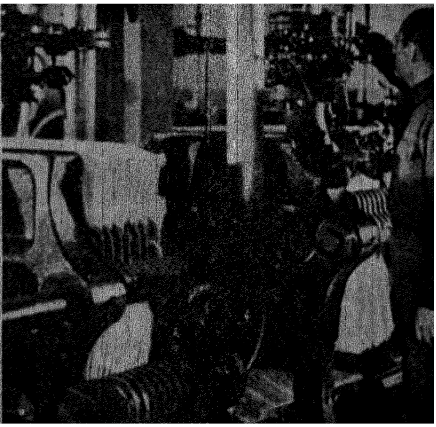
Variations on a Theme. Many variations of this process produce interesting and novel effects. Flat and ribbonlike, rayon resembles straw for hats. Flat and very thin, it appears as Cellophane. Coarse fibers can be made stiff, resembling horsehair. Much of the "horsehair" used today for forming the shoulders of suit coats never grew in a stable.

Courtesy of E. I. du Pont de Nemours & Company, Inc.

Fig. 32-1*a*.—Steeping press—sheets of cellulose.

Fig. 32-1*b*.—Shredding machines.

Courtesy of E. I. du Pont de Nemours & Company, Inc.

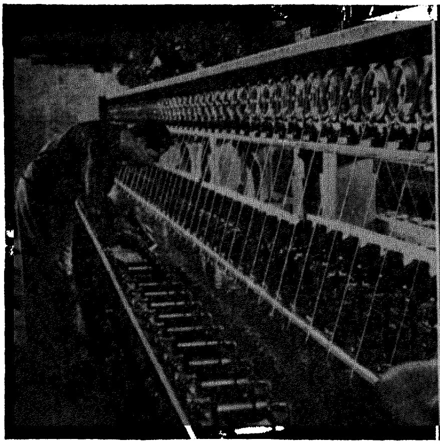
Fig. 32-1*c*.—Blending disulphide with crumbs in churn.

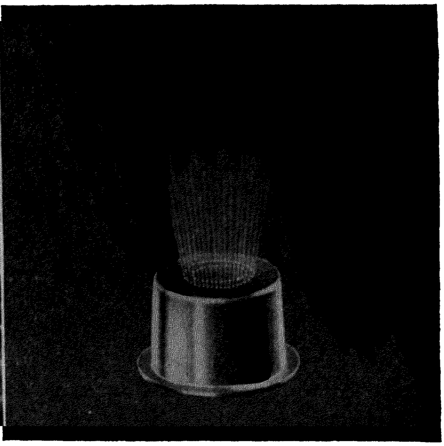
Fig. 32-1*d*.—Filtering the spinning solution.

Rayon cut into short lengths (staple fiber), carded, spun, and woven has many loose ends in the yarn. When woven or knit into cloth, this ***staple rayon*** makes a desirable fabric unlike silk or cotton with qualities all its own.

Cellulose can also be coagulated around crystals of soluble salts in such a manner that it resembles natural sponges. Cellulose sponges have the same uses as the marine product, and some advantages.

Many Farm By-products Are Available. An enormous amount of cornstalks, wheat straw, and cane as well as other cellulose-containing material is grown each year. Only a relatively small amount is used for paper and wallboard. Investigation of other uses for these farm by-products has gone forward, and much information has been gathered. But thus far only a start has been made. Many unexplored possibilities are waiting in this field of investigation.

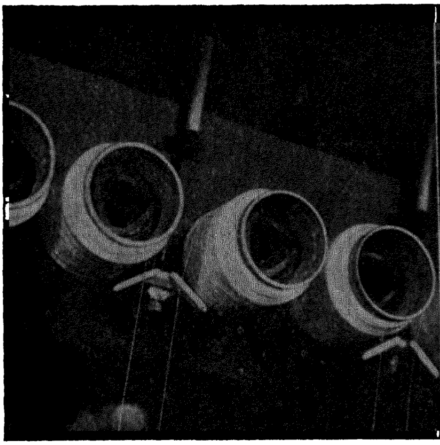


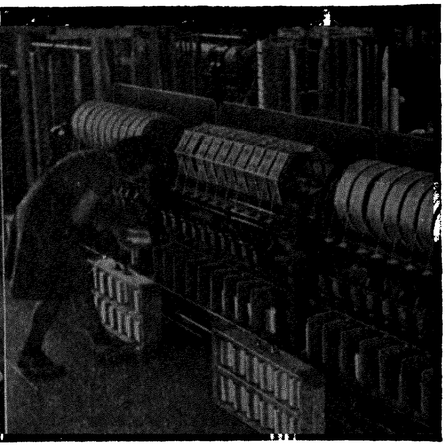


Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 32-2a.—Spinning machine.

FIG. 32-2b.—Close-up of spinneret.





Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 32-2c.—Bobbins of rayon.

FIG. 32-2d.—Winding from bobbins.

QUESTIONS

1. Answer the following questions referring to the formula for cellulose $(C_6H_{10}O_5)_x$. (*a*) What is the proportion of hydrogen to oxygen by weight? (*b*) In what other well-known compound is the same proportion found? (*c*) What is the meaning of the x? (*d*) What is the simplest formula weight?

2. Contrast the relationship of mankind to cellulose with the relationship of plants to cellulose.

3. Name five products of forests.

4. List three solvents for cellulose.

5. Write an equation for the nitration of cellulose to one-half the extent shown in the equation on page 566.

6. After cellulose has been cooked with hydrochloric acid to form starch, how can the catalyst be removed?

7. For what purpose is rag pulp used?

8. Why are knots removed before logs are made into pulp?

9. Examine the paper in a dollar bill. What is unusual about it?

10. What is the essential difference among blotting paper, writing paper, and magazine-cover paper?

11. List three uses of pulp other than the making of paper.

12. What use is made of old newspapers?

13. Find out how paper is prepared for the following uses: diplomas; butter wrapping; tissue for cold-cream removal; bread wrapping (waxed); postage stamps (reference question).

14. How is corrugated cardboard made?

15. List the principal steps in making rayon by the viscose process.

16. Why could not successful spinnerets for making rayon be made from steel? aluminum? zinc? gold? lead?

17. List three chemicals that must be shipped continuously to a viscose-process rayon factory.

18. Compare the composition of silk with that of rayon.

19. In what respect, if any, is rayon better than silk for hoisery? less desirable?

20. Describe the method for producing staple rayon fibers.

21. When rayon burns, which does it resemble most, burning cotton, silk, or wool?

22. When viewed under a microscope, which fiber does rayon resemble most closely, cotton, silk, or wool? Find out by examining samples if possible.

Plastics

What Are Plastics Like? The mud pies of childhood are plastics. Soft, yielding, and easily molded under one condition, they harden and stiffen under another, taking a more or less permanent form. More useful, dinner plates are made in a similar manner from plastic clays.

Rubber, glass, and celluloid are all plastic materials. In recent years the field has been extended to include light and transparent plastic materials of such novel design and striking uses that it has stirred the popular imagination. While the total tonnage of plastics used is low compared with the tonnage of copper, for example, the very rapid increase in the use of plastics for ornaments and electrical devices and as a substitute for metals and rubber calls particular attention to the synthetic plastic industry, chemistry's lusty youngster.

Plastics may be divided into two groups. A plastic material that behaves as clay does, hardening when heated, is called ***thermosetting.*** Others are ***thermoplastic,*** flowing when warmed.

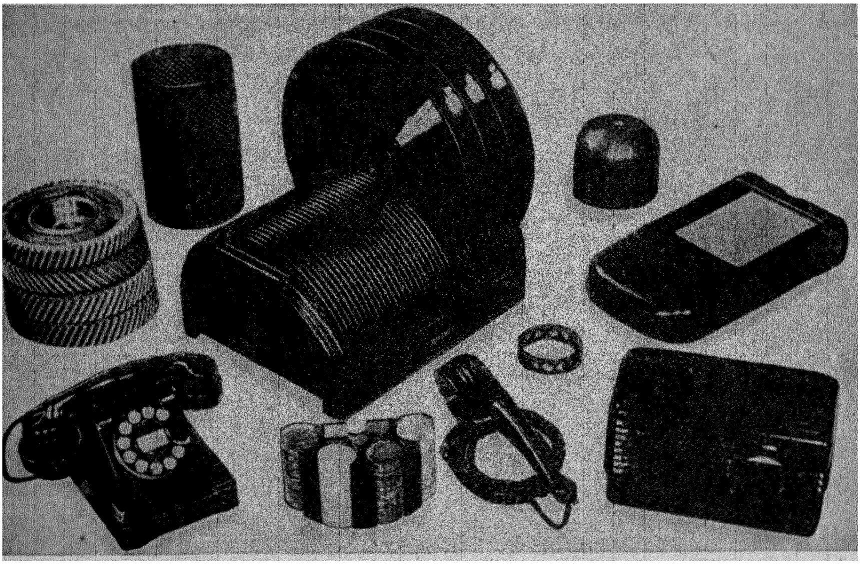
The Plastic Age. In the days of the glorious development of organic chemistry by von Bayer and Fischer in Germany, numerous new compounds were made. Series of compounds were studied and the properties of the carboxyl, aldehyde, and other groupings of elements systematically worked out. In this period of masterly development, definite compounds, liquids or crystalline solids, were sought. Whenever a combination of chemicals produced a pasty or tarry mass inside the apparatus, the fact was noted and regretted and the product put aside as an error. Progress was sought in another direction. Today's strides in the fields of plastics have, in some cases, been based on these "mistakes" of the past.

Another factor in the modern picture that did not exist 50 years ago is that organic chemicals can be prepared in carload lots, and cheaply. For example, starting with lime (CaO), coal, and water as raw materials, it is possible to operate a chemical factory that produces a 2-in. steadily flowing stream of acetic acid (CH_3COOH). Examples of carload-lot production of organic chemicals of high purity and at relatively low cost are increasing daily.

Synthetic plastics were introduced in 1855 when Alexander Parkes, in England, produced cellulose nitrate (see page 566). This was not much used until 1868, when Hyatt, in the United States, developed ***celluloid*** by adding camphor as a plasticizer to cellulose nitrate. Hyatt was seeking a substitute for ivory for making billiard balls and piano keys.

Bakelite. In 1909 Dr. Leo Hendrik Baekeland, in America, seeking a substitute for shellac, produced the first phenolic resin by putting together phenol (C_6H_5OH) and formaldehyde (HCHO). A ***resin*** is a hard gumlike substance. Cherry, pine, and other trees produce natural resins. Shellac is also a natural resin, but from an oriental insect. The ***rosin*** used on violin bows is a natural resin. ***Bakelite,*** this synthetic phenol-formaldehyde resin, may be filled or extended by adding wood flour or other inactive substances, coloring matter included; thus many varieties are produced. Many other synthetic resins have been prepared that have properties and uses not found in natural resins.

For making caps for collapsible tubes, cylinder-shaped pills composed of a mixture of resin, filler, and coloring matter are placed in a steel mold that is heated with steam under heavy pressure. After a short molding period the plastic has flowed into the form of the steel mold, producing a useful shape of a material that is hard, inactive chemically, and insoluble in water. Thus are made distributor heads for automobiles, buttons, and piccolos.



Courtesy of Koppers Company, Inc.

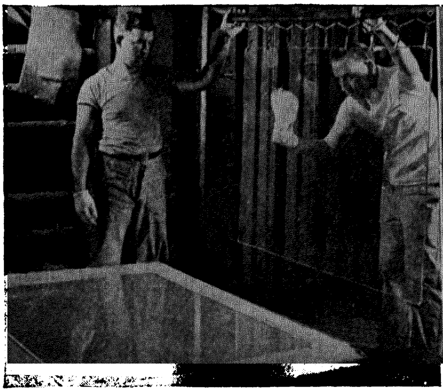
FIG. 32-3.—These phenolic plastic products came originally from coal tar. Coal tar was once thrown away as a messy nuisance.

Plastics from Natural Sources. 1. Nitrocellulose is a good example of a plastic from a natural raw material, cotton. Brush backs, combs, and still and motion-picture films are well-known articles made of cellulose nitrate, or pyroxylin. Unfortunately, the product is explosively flammable and must not be brought near flames.

2. Safety film for motion pictures at home is made with the almost nonflammable cellulose acetate. Fibers of this plastic form a type of rayon yarn called "acetate." In thin, transparent sheets, usually coated,

it is well known for wrapping merchandise. Over 10 million pounds per year of cellulose acetate is used for this purpose alone. Acetate cloth is soluble in acetone [$(CH_3)_2CO$], and spots on dresses made of it must not be removed with fingernail-polish remover.

3. Lignin, 25 per cent of wood, the natural gum that binds wood fibers together into the form of lumber, is a natural plastic. Growing interest is given to conserving and using this material, formerly wasted. Its use is limited because of its dark color, but its cost is low.



Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 32-4.

Courtesy of U.S. National Archives

FIG. 32-5.

FIG. 32-4.—Out of an inexhaustible source of raw materials—coal, air, and water—chemists in recent years have been producing new and vitally important products for modern life. Among these are textiles, dyes, antifreeze solutions, perfume bases, and plastics. Cast "Lucite," methyl methacrylate resin, shown here is an important example of this last group of chemical products.

FIG. 32-5.—The art of preserving ancient valuable documents uses modern plastic envelopes to good advantage.

4. Protein, or nitrogen-containing, plastics include those made from casein, a by-product of skimmed milk. This plastic is cheap, but it is difficult to mold. An interesting woollike fiber has been made from this raw material. Unlike the staple rayon imitation of wool, the fiber actually resembles wool in its chemical composition. Corn gluten (zein) and soybeans (soya) are also used as sources of protein plastics. Automobile steering wheels, for example, can be made from soybean plastic.

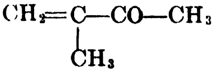
Rubber, another plastic from natural sources, will be considered separately.

Synthetic Plastics. Purely synthetic plastics are of two types: (1) the condensation type; (2) the polymerization type.

1. Condensation products are thermosetting. They involve a chemical reaction in which water is separated. Included in this classification are phenol-formaldehyde resins, phenol-furfural (from oat hulls), urea—

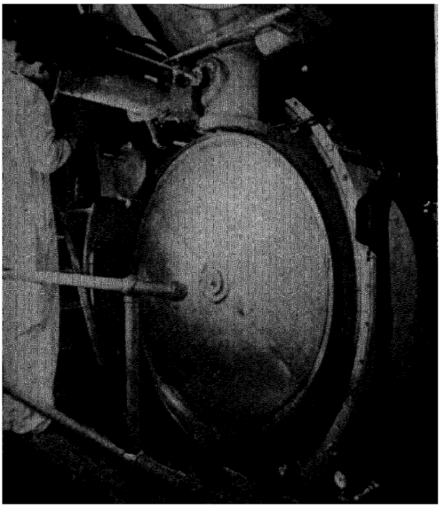
[$CO(NH_2)_2$]-formaldehyde, and "glyptal" resins, which are made from glycerol [$C_3H_5(OH)_3$] and phthalic anhydride ($C_6H_4C_2O_3$).

PLASTICS

Trade names	Uses	Chemical type	X molecules of
Lucite or Plexiglas	Light conductor for surgical instruments, nosepieces for aircraft	Methyl-methacrylate	 $CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{-}CO{-}CH_3$
Styron.....	In low-temperature safety glass	Styrene (polystyrene)	$CH_2{=}CH{-}C_6H_5$
Vinylite....	Suspenders and belts, phonograph records, Vinyon textiles	Copolymer of vinyl chloride and vinyl acetate	$CH_2{=}CHCl$ and $CH_2{=}CH{-}OOCCH_3$

Light, decorative plastics that color well are very popular for dinnerware as a substitute for or alternate to glass. These are urea-formaldehyde condensation plastics. The reaction between glycerol and phthalic anhydride, which forms the glyptal resins, corresponds to the forming of an ester (see page 559). As a coating on cloth the resin is an excellent insulator; it is therefore used in transformer windings and also, when dissolved, as gum in paints.

2. Polymerization compounds are formed mainly by the self-addition of unsaturated (see page 513) compounds into large clusters. The molecular grouping may be compared roughly to shaking fishhooks together in a box. When one is lifted out a number of others cling to it.



Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 32-6.—At Seaford, Delaware, the Nylon polymer appears first when it is extruded in ribbon form on this huge casting wheel, called "Moby Dick" by the employees. The polymer is first seen as a molten mass, but quickly solidifies and resembles ivory. In later operations it is chopped, melted, and extruded again as filaments.

Nylon. Nylon is a class name for a group of compounds known chemically as polyamides. Its origin from air, water, and coal illustrates its synthetic nature. Many chemical changes and processes are necessary between these simple raw materials and the finished product. *Nylon* resembles silk both in its lustrous appearance and in its proteinlike nature. It is a definite polymerized substance in the form of a giant molecule containing the —N=N— bond. This product was first applied to the manufacture of bristles and later to that of hosiery and other wearing apparel. It dyes readily, resists wear, and in many properties is superior to natural silk. It is thermoplastic and can be remelted and reworked. Its production, development, and marketing are examples of the triumph of American synthetic chemistry.

Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 32-7.—Winding Nylon yarn onto cones is a mechanical step in the process of making Nylon garments. The insert shows finished dyed Nylon hosiery packaged in Cellophane, a cellulose-type plastic material.

Many Plastics Have Been Developed. The number of plastics available today is well over 300 in the United States alone, and other countries have an imposing list of similar or identical products under various trade names. We should understand that each of these materials has a different set of properties, making certain plastics more or less suited to particular uses than others. In searching through the list of the properties of plastics, users can find readily those with high resistance to electric sparks, resistance to acids, resistance to water and air corrosion, and insolubility in water and in a great number of other solvents. The plastic most suited to a given need is the type with the desired properties that can be furnished at the least cost. Hence both chemical and economic knowledge are needed.

QUESTIONS

23. In general, contrast thermosetting resins with thermoplastic resins.

24. From which type of resin can the scrap trimmings be reworked?

25. A certain eyeglasses frame softens in hot water, permitting adjustments. Of which type of plastics is it made?

26. List an article made of plastic material that is used at home today but was unknown 25 years ago.

27. Some transparent acrylic resins conduct light around corners. Explain how this is possible.

28. Some transparent resins transmit light a little better than does glass. Why are they not used more extensively for eyeglasses?

29. What raw material is needed to make (*a*) Bakelite; (*b*) celluloid; (*c*) pyroxylin; (*d*) Cellophane?

30. Why should nylon garments not be pressed with a very hot flatiron?

31. What property of nylon makes it desirable for parachute shroud ropes?

32. What factors should be considered before deciding upon a certain plastic substance for manufacturing ash trays? Umbrella handles?

33. What type of plastic is suitable for making (*a*) dress-belt slides; (*b*) toothbrush handles; (*c*) men's belts; (*d*) binder in safety glass; (*e*) electrical plugs?

The Story of Rubber. When Columbus visited the New World, he noticed that the native children were playing with balls that bounced. These bouncing balls, masses of gum from the rubber tree, were so interesting and novel that he took a few back to Europe. Three hundred years later, Joseph Priestley discovered that rubber could be used to rub out pencil marks and gave the substance its name. The Scotsman, Macintosh, first daubed rubber on cloth to make a water-resisting raincoat, and Dunlop in England wrapped a rubber tube around a wheel to make the first rubber tire.

But Macintosh's raincoat was so stiff in cold weather that it would stand alone and so sticky in warm weather that it adhered to everything it touched. The overcoming of these undesirable properties of rubber was accomplished in 1839 at Woburn, Massachusetts by Charles Goodyear, who, while experimenting with a rubber-sulfur mixture, accidentally let some of it spill and become intensely heated on his kitchen stove.

From testing this sample he discovered that rubber so heated with sulfur, or ***vulcanized,*** stretches and snaps and has the desirable properties by which we recognize rubber today.

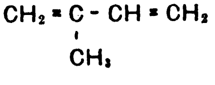
Making Rubber from Latex. Latex from the (*Hevea*) rubber tree is the chief source of rubber. Guayule, desert rabbit bush, and many other plants produce a latex juice from which a rubberlike hydrocarbon can be obtained, but in smaller amounts or mixed with unwanted plant materials. The Hevea latex is coagulated, for example, by adding acetic acid, and then the rubber is "compounded" with sulfur, zinc oxide, carbon black, and a number of other materials. These substances, when vulcanized into the rubber, produce a stable, elastic product, resistant to wear and oxidation.

Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 32-8.—This shows the final milling operation on Neoprene, a chloroprene rubber. Articles made of Neoprene not only possess similar strength, resilience, abrasion resistance, and elasticity as rubber products, but also resist the deteriorating effects of oils, heat, sunlight, chemicals, ozone, and aging.

Most of the 2 million tons of rubber per year (1939) used in the United States went into the making of tires.

Synthetic Rubber. Rubber is essentially a polymer of the simple hydrocarbon, isoprene (C_5H_8), which has double bonds.



$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2$$

This compound is closely related to butadiene ($CH_2{=}CH{-}CH{=}CH_2$), the compound that is the basis for a number of the synthetic rubbers. Butadiene can be synthesized from acetylene (C_2H_2) with sodium as a catalyst to polymerize it—hence the name ***Bu na.*** Introducing chlorine into the rubber molecule gives other properties that are useful. Unsaturated compounds from petroleum are also used as starting materials for synthetic rubber. These simple compounds are always polymerized to make the long molecules that give rubber its stretching properties.

Some types of synthetic rubber are superior to natural rubber in resistance to oxidation, especially ozonation, and for this reason are used for insulation on wires leading to spark plugs in gasoline engines. Some synthetic rubbers are also less soluble in oils and other organic solvents and swell very little in gasoline. The hose from a gasoline pump is lined with one type of synthetic rubber, Neoprene. (See Fig. 32-8.) In recent developments useful products have been obtained when synthetic rubber is polymerized with other synthetic plastics.

SUMMARY

Cellulose is the chief constituent of woody stalks of plants. It is made by photosynthesis by plants, a reduction process in the presence of sunlight. Examples of substances chiefly cellulose are cotton, wood, paper, and linen. Cellulose is soluble in zinc chloride solution, ammoniacal copper hydroxide, and sodium hydroxide solution. Cellulose burns; it is acted on by nitric acid in the presence of a strong dehydrating agent, such as concentrated sulfuric acid, and is hydrolyzed in presence of hydrochloric acid, forming starch.

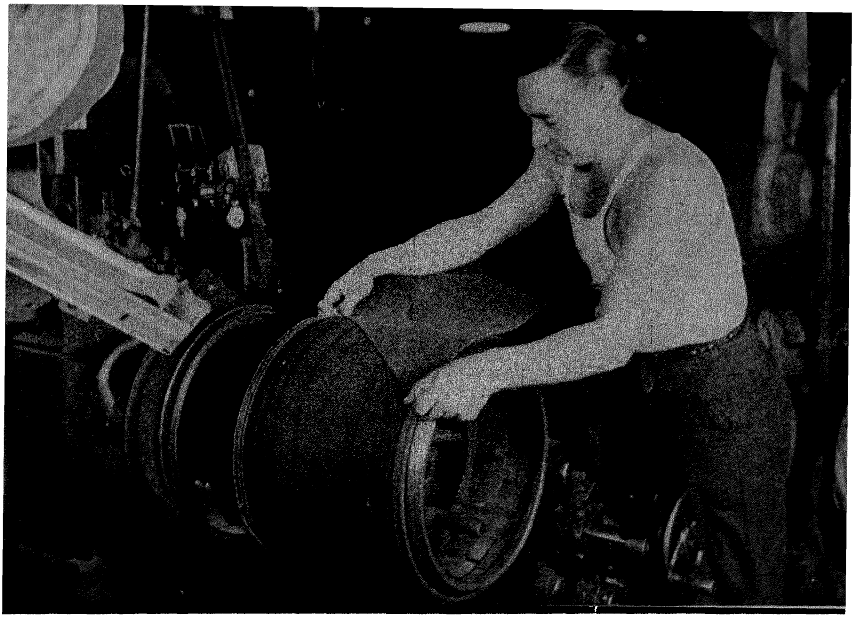
Pulp is a suspension of fibers, usually cellulose fibers. Pulp for coarse paper may be made mechanically by grinding or chemically by cooking wood chips in lye solution, sodium hydrogen sulfite solution, or sodium sulfate in the presence of lye. Pulp is used to make paper, rayon, and explosives and as a filler in plastics.

Paper is made from an even suspension of pulp, dried and pressed. Most paper is produced by a continuous mechanical process.

Most rayon is cellulose, dissolved and reprecipitated in the form of filaments. The viscose process is the most important. Rayon is the second most important fiber. The rayon-making process is versatile, permitting many variations.

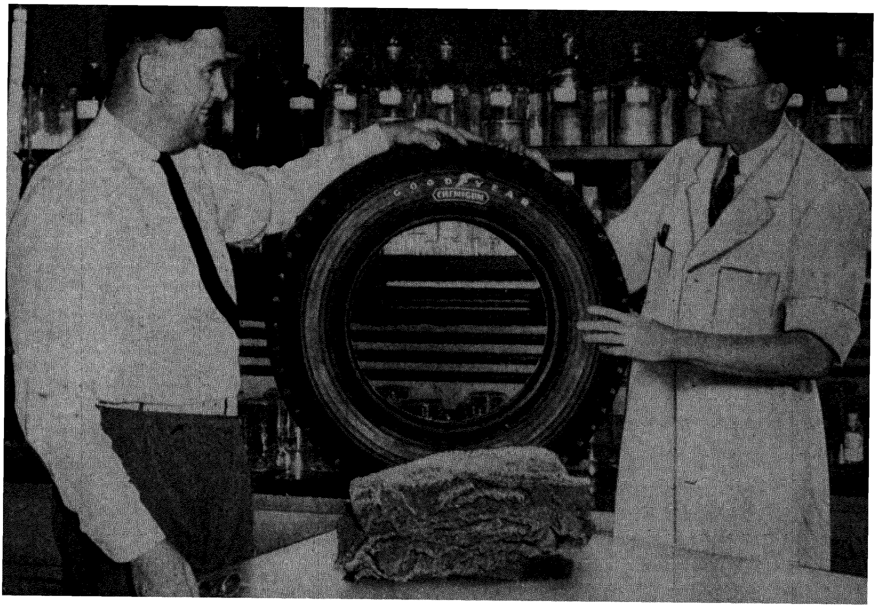
Plastics is a general term given to materials that can be made to liquefy under heat and pressure and to take some useful form in a mold. Commercially, plastics are classed as thermoplastic and thermosetting. Thermoplastic materials liquefy when heated and "set" when cooled. Thermosetting materials take final form when heated. Well-known plastics include

Celluloid—made from nitrocellulose and camphor
Bakelite—made from phenol and formaldehyde
Nitrocellulose-pyroxylin—for photographic films, brush backs, and combs
Cellulose acetate—for transparent wrapping material and safety films
Lignin plastics—raw material from wood, dark-colored
Protein plastics—made from soybeans, corn, and skimmed milk
Some synthetic plastics are transparent, brightly colored, electrical insulating



Courtesy of The Goodyear Tire & Rubber Company

FIG. 32-9.—Fabric impregnated with synthetic rubber is wound onto a drum in the first stage of making an automobile tire casing.



Courtesy of The Goodyear Tire & Rubber Company

FIG. 32-10.—This finished tire carcass is made of a synthetic rubberlike elastomer. Crude elastomer, a product of polymerization, is seen in front of the tire.

materials with a wide range of variation of properties among themselves. Prominent among them are the acrylic, styrene, and vinyl type of resins. Synthetic resins are used for impregnating cloth and wood, for making varnish, and for molding into decorative and useful devices.

Nylon is a thermoplastic resin, containing nitrogen. It is adapted to the manufacture of bristles and of strong, lustrous fabrics and is used for hosiery and clothing.

Rubber is a hydrocarbon found in several plants, but especially in the Hevea rubber tree. Rubber is vulcanized by heating it with sulfur and is compounded with carbon black, zinc white, and other fillers, including catalysts. It is used chiefly for making tires, but hundreds of other uses are important.

Synthetic rubber, made from unsaturated hydrocarbons by polymerization, has properties similar to those of natural rubber, but differing in important respects.

QUESTIONS

34. What is suggested by the following trade names: (*a*) Bu*na* rubber (catalyst); (*b*) Lan*ital* (country); (*c*) *Ameri*pol (country); (*d*) *Thio*kol rubber (element); (*e*) rayon?

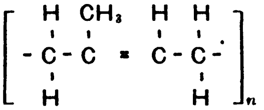
35. Write an equation for the burning of isoprene.

36. Does rubber oxidize faster when stretched? Give evidence for your answer.

37. Which is more elastic, steel or rubber?

38. Why cannot rubber be used successfully for insulation on wires leading to spark plugs on cars?

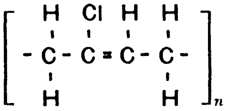
39. Point out the difference between



$$\left[-\overset{H}{\underset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-\right]_n$$

natural rubber

and



$$\left[-\overset{H}{\underset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-\right]_n$$

Neoprene

40. Name a use for which some synthetic rubbers are better adapted than natural rubber.

41. Name a use for natural rubber for which synthetic rubbers are not suitable.

42. Name three uses for reclaimed rubber.

43. (*a*) What filler in a tire notably increases the resistance of rubber to abrasion? (*b*) What filler in rubber tires produces white sidewalls? (*c*) What filler produces red rubber for inner tubes? (*d*) What is done to preserve tires not yet placed in service?

44. Is it possible for a tire to catch fire and burn while in service on the road?

UNIT SEVEN . . . . CHAPTER XXXIII

COAL-TAR CHEMISTRY

Following a suggestion of his instructor, August Wilhelm von Hofmann, William Henry Perkin, a seventeen-year-old English schoolboy, in 1856 began trying to make quinine, an important drug, the synthesis of which was accomplished 87 years later. During his experiments Perkin noticed that a colored substance was formed. The colored substance appeared when he used impure aniline ($C_6H_5NH_2$) as a starting material. Was this new substance useful as a dye? If so, he had made the first dye that did not come from a natural source.

Later, Perkin (1838–1907) showed that this compound, called ***mauve,*** was a successful dye and that others like it could be made in a similar manner. This discovery was destined to change the lives of countless people and to unlock the secret of cheap dyes, royal colors for the clothing of everyone. So extensively did this one discovery influence life that some writers call the years that first felt the effects of Perkin's discoveries the ***mauve decade.***

While Perkin sought a drug, he found a dye. The formation of the dye was partly accidental, for it involved an impurity in his chemicals. Also, without the help of von Hofmann, who solved the chemical riddle, very likely the discovery would have been delayed. Nevertheless, we honor the discoverer of this first coal-tar dye because he ***noticed*** and because he ***followed up*** his discovery.

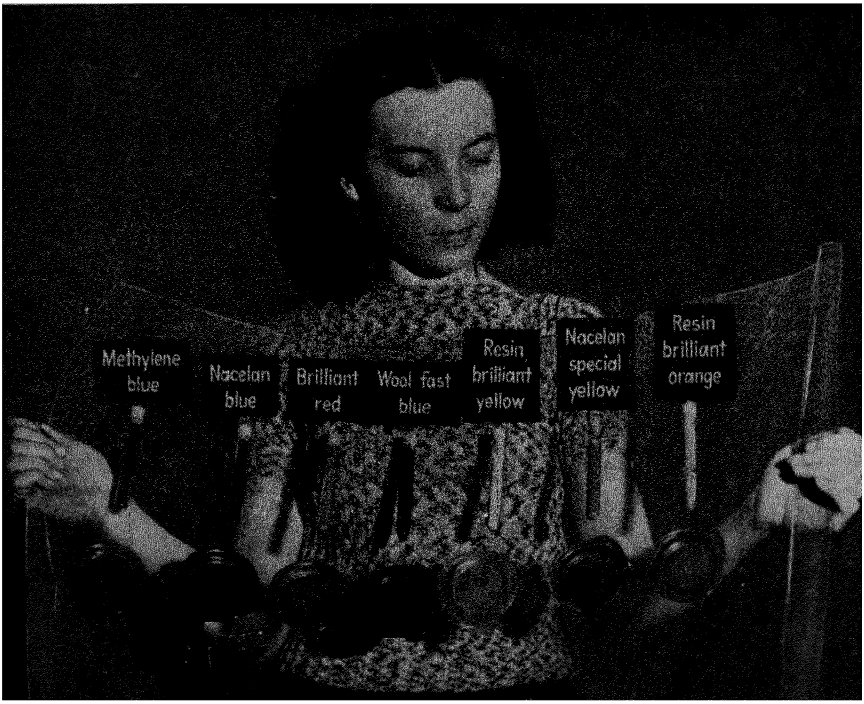
Perkin continued his work, and 10 years after the first discovery he succeeded in making alizarin, a widely used dye. It is interesting to note that this discovery was made also at the same time by two German investigators. Hundreds of chemists are employed today making dyes similar to those made by Perkin and investigating the worth of new ones.

Coal Tar. When coal is heated in a closed oven (see Figs. 33-2, 33-3) or retort, the baked coal gives off three easily separated products, namely, (1) coal gas, (2) ammonia, and (3) coal tar. Coke (4) remains in the retort.

New Terms

coal tar
benzene
toluene
phenol
naphthalene
benzene ring
TNT

Coal tar was always a trouble to the early gasmakers. There was no way to use it. The demand for road tar did not exist. Nor was anything known about coal-tar dyes or other derivatives. Consequently, much tar was allowed to flow onto near-by rivers. When the thick, black tar was discharged onto a river, the ill-smelling material was distributed down the stream, adding to the unpopularity of the gasworks. The crowning insult to nature soon followed. Tar on the water shut off the supply of oxygen. Soon the fish died, and they smelled worse than the tar, thus firmly establishing the odorous reputation of the gasworks.

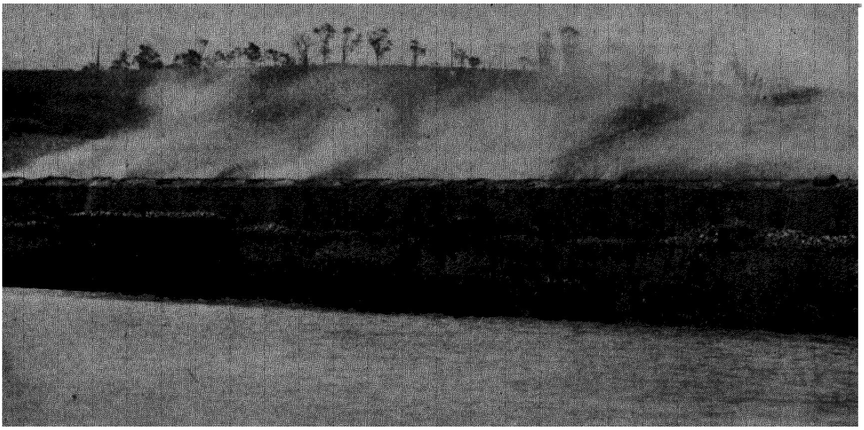


Courtesy of Westinghouse Electric Corporation

FIG. 33-1.—This young lady, a student at Girls' Commercial High School, Brooklyn, N.Y., used coal-tar dyes to color plastic materials.

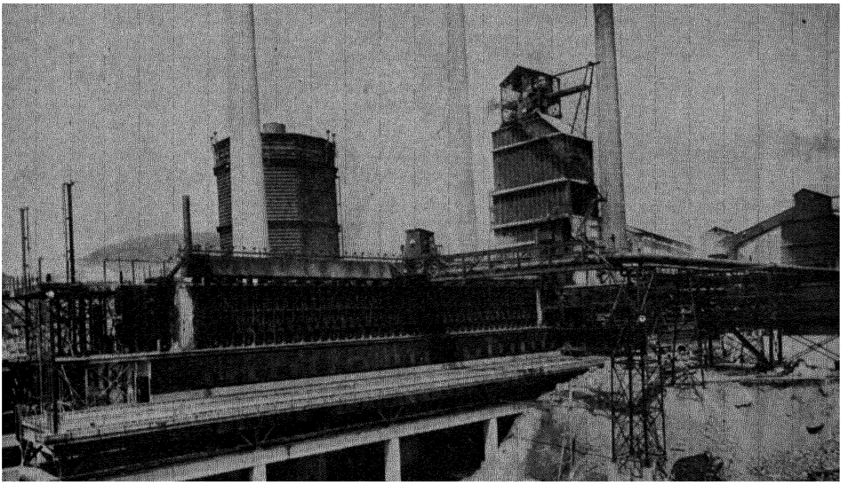
The Tar Chemist. The solution to this unhappy problem was found through chemistry. Pointed out by Perkin's experiments, the way was found to use part of the coal tar by changing it into a dye.

Today coal tar is redistilled. The material is placed in a retort and heated. As the temperature is raised, different compounds or mixtures of compounds distill out. These are separated in order of increasing boiling points. This process, as we have previously learned, is called ***fractional distillation.***



Courtesy of Koppers Company, Inc.

FIG. 33-2.—Volatile, valuable by-products go up in smoke in the old-style beehive coke ovens. These ovens are being replaced by modern by-product ovens.



Courtesy of Koppers Company, Inc.

FIG. 33-3.—This general view shows by-product coke ovens at Weirton, W. Va.

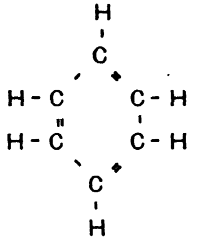
Two Hundred Thousand Products. The 10 gal of tar that come from a ton of coal yield about

3.5 lb of benzene (C_6H_6) and toluene ($C_6H_5CH_3$)
1.25 lb of phenol (C_6H_5OH)
6 lb of naphthalene ($C_{10}H_8$)
0.625 lb of anthracene ($C_{14}H_{10}$)

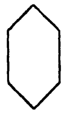
Only approximately 10 lb of products per ton of coal may seem unimportant, but two facts show otherwise: (1) Over 40 million tons of coal is made into coke each year. (2) Chemists have made over 200,000 different compounds from these five starting substances. From these, over 3000 compounds are manufactured regularly for commercial purposes. They include dyes, medicines, explosives, plastics, and photographic chemicals.

Benzene. The liquid portion of coal tar contains benzene (C_6H_6). This colorless liquid was discovered by Michael Faraday in 1825. Benzene boils at 79.6°C and is a good solvent for many organic substances. It is very flammable, burning with a smoky flame. It is a possible substitute for gasoline to a limited extent, but it is too expensive to use on a large scale. The vapors are harmful to breathe.

The Chemical Bird Cage. The formula of benzene as visualized by Friedrich August Kekulé (1829–1896) seems best explained by assuming that the carbon atoms are arranged in a ring with ***double bonds*** (two pairs of shared electrons) alternating with single bonds. This bird-cage-like structure for benzene is often abbreviated as a simple hexagon. Each angle indicates a carbon atom attached to a hydrogen atom unless another symbol is placed there.



Kekulé formula for benzene (C_6H_6)



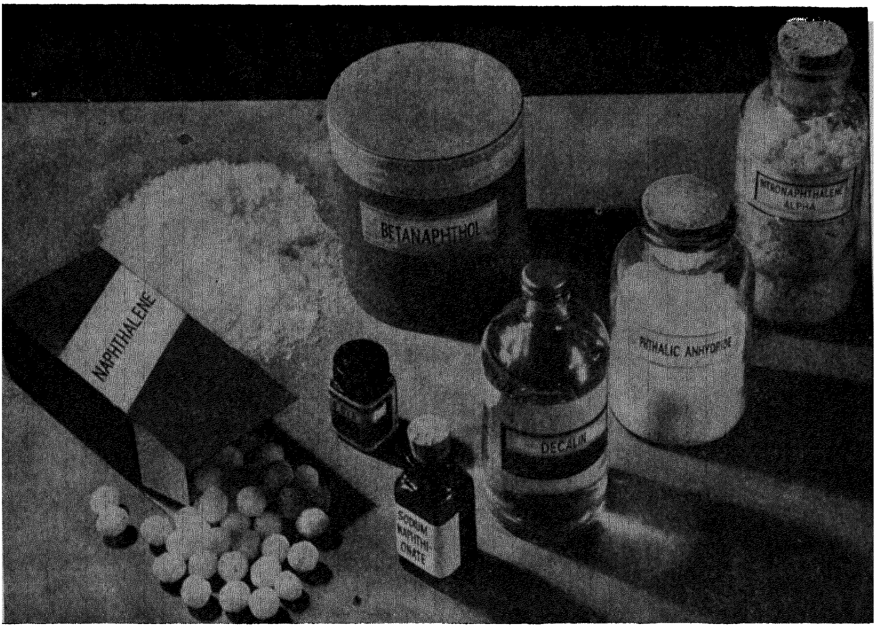
simplified formula for benzene (C_6H_6)

The lack of chemical activity of benzene suggests that the unsaturated double bonds are different in some way from those in typical unsaturated compounds like ethylene (C_2H_4). For example, benzene adds chlorine or bromine only with difficulty to form a number of products—monochlorobenzene (C_6H_5Cl), dichlorobenzene ($C_6H_4Cl_2$), and trichlorobenzene ($C_6H_3Cl_3$). More important, nitric acid with concentrated sulfuric acid forms nitrobenzene ($C_6H_5NO_2$) (page 566). By reduction with hydrogen (tin and hydrochloric acid), aniline ($C_6H_5NH_2$) is formed. Aniline is the starting point for making medicines and hundreds of dyes. For example, acetanilide ($CH_3CONHC_6H_5$), a useful but dangerous medicine, is made by combining acetic acid with aniline.

Toluene. Toluene ($C_6H_5CH_3$), a coal-tar product, is a colorless liquid that boils at 110.8°C. Chemical treatment makes toluene into benzoic acid (C_6H_5COOH), the sodium salt of which, sodium benzoate (C_6H_5COONa), is a preservative. It is used to keep cider sweet and in some brands of tomato catchup to prevent fermentation. Other useful compounds made from toluene include dyes and saccharine, a very sweet substitute for sugar in special diets.

Toluene is made from petroleum as well as from coal tar. One plant in the United States has a capacity of 10 million gallons of toluene from petroleum each year. Most of this toluene was nitrated, forming TNT.

Phenol. Phenol (C_6H_5OH), or carbolic acid, a "pink slush," has a definite pungent penetrating odor, which may be noticed in a popular brand of red-colored soap. The crystals melt at 100.5°C. The compound alone is dangerously corrosive to the flesh, but in dilute solutions it is useful as an antiseptic. The germ-killing ability of other antiseptics is rated in terms of a "phenol coefficient."



Courtesy of Koppers Company, Inc.

FIG. 33-4.—Useful products from coal tar include dyes and medicinals.

Phenol is combined with formaldehyde to make plastics (see page 573), such as Bakelite, from which telephone sets are molded. Printing inks, aspirin, medicines, and dyes are all made from this versatile compound as a starting point.

Naphthalene. Naphthalene ($C_{10}H_8$) crystals are white. They have a penetrating odor and give out a vapor that repels clothes moths. Thus this compound is used for mothballs. At 80°C the crystals melt to form a colorless liquid that boils at 218°C. Naphthalene, like anthracene

($C_{14}H_{10}$), is used as a starting substance from which many beautiful dyes are made. From naphthalene, vitamin K is synthesized.

A Long List of Coal Products. Valuable services are also available from other chemicals derived from coal tar. A solution of ammonium thiocyanate (NH_4CNS) is used in the laboratory to test for the presence of ferric ions (Fe^{+++}), for a deep-red coloration appears when they are mixed. This same compound is also used in fly sprays.

Pyridine (C_5H_5N), a compound resembling benzene in structure except that one carbon atom with its attached hydrogen is replaced by nitrogen in the ring, is a poisonous liquid usually possessing a strong disagreeable odor due to impurities. It is used often to denature alcohol. It is the starting substance for the manufacture of some of the newer drugs, waterproofing agents, and rubber-curing accelerators.

So the ugly duckling of the gas works has grown, developed, and prospered with healing in its wings and colors gayer than those of the peacock.

SUMMARY

Destructive distillation of bituminous coal yields coal gas, ammonia, coal tar, and coke. Coal tar, fractionally distilled, yields benzene, toluene, naphthalene, anthracene, phenol, and other products known as coal-tar compounds.

Benzene is a compound that structurally contains a ring of carbon atoms. It is a clear liquid that burns and is a good solvent for many organic compounds. When acted upon by concentrated nitric acid in the presence of concentrated sulfuric acid, it changes to nitrobenzene. This may be reduced to form aniline, a compound used to make dyes and medicines.

Toluene, after several chemical changes, forms TNT, benzoic acid, or dyes. In addition to being made from coal tar, toluene is also made in large quantities from petroleum.

Pure phenol is a white crystalline solid with an aromatic odor. It is used as an antiseptic and for making Bakelite, aspirin, and dyes.

Naphthalene is a white crystalline solid. It is used for moth balls and in the preparation of dyes and vitamin K.

QUESTIONS

1. What is *mauve?* (Use a dictionary.)

2. Classify the products of the destructive distillation of coal as solid, liquid, or gaseous.

3. List three uses for coal tar.

4. Describe the process of fractional distillation.

5. About how much phenol per year would be available in the United States if all were to be recovered?

6. What reason have we for representing benzene as C_6H_6 rather than by its simplest molecular formula CH?

7. Write equations for the reaction of benzene with three different substances.

8. Trace the steps from coal tar to acetanilide; to TNT.

9. Trace the steps from coal to a plastic case for a telephone hand set.

10. Write equations for the burning of (*a*) naphthalene; (*b*) anthracene; (*c*) phenol; (*d*) benzoic acid.

11. Write equations for the reaction of benzoic acid with (*a*) sodium hydroxide; (*b*) methyl alcohol; (*c*) phenol.

12. What is the percentage of carbon in naphthalene? Predict the nature of the flame from burning naphthalene. If possible, test the prediction by burning a little of the compound.

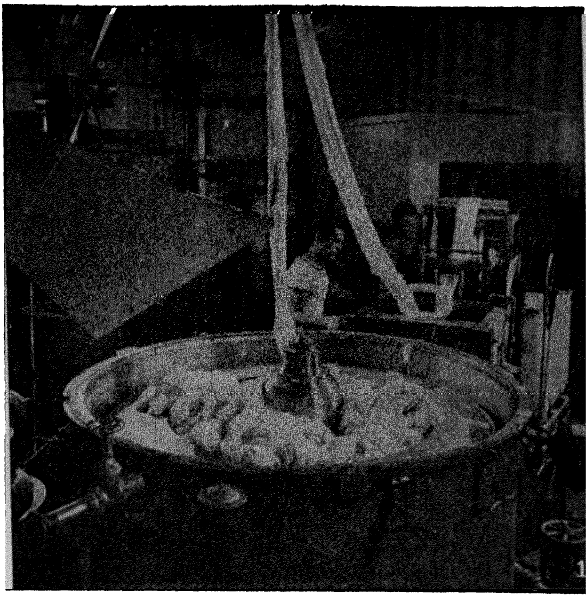
13. List five useful common substances that are derived (or one constituent that is derived) from coal tar.

14. Tell how to prove that iron is present in spinach.

15. List the names and formulas of four substances, other than water, that are sometimes put into automobile radiators.

16. Prepare a biographical account of one of the following chemists: William Henry Perkin, Johann Friedrich Wilhelm Adolf von Baeyer, Victor Meyer, Emil Fischer, Paul Ehrlich, Justus von Liebig. (Reference questions.)

UNIT EIGHT



1

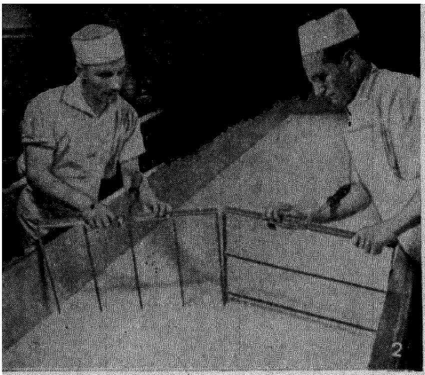
CHEMISTRY AND HUMAN PROBLEMS

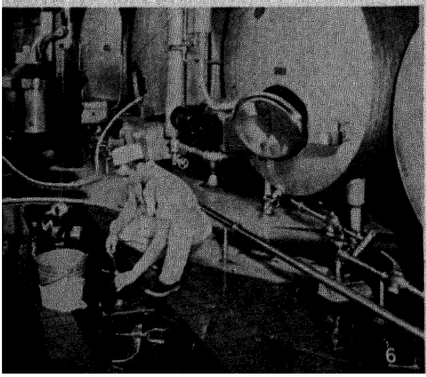
Dairy farming is one of the oldest industries. [As you read the following, see pictures (1) to (7) on this and the next page.] Picture (1) shows milk being changed into clothing. The cheese-making industry also uses milk. The milk is coagulated, usually with rennet. The coagulated casein, or curd, is gathered on wire strainers (2). The liquid that remains is called whey. The rubber-like curd (3) contains nearly all the milk's fat, casein, calcium compounds, other minerals, and vitamin A.

Dried crumbs of casein are put in trays, treated with bacteria to develop flavors, and compressed into cylinders (4). The cheese is set aside to "cure." The finished product (5) is high in protein value.

All dairy processes must be carried out with the utmost cleanliness, for bacteria multiply rapidly in milk. After use, the equipment (6) is flushed with steam and a hypochlorite solution.

Constant inspection and control are exercised in well-equipped dairies. The percentage of butterfat, the total solids, the specific gravity, and the bacteria count are investigated. This technician (7) is shown using the analytical balance.





Photos courtesy of National Dairy Council and Connecticut Dairy and Food Council

UNIT EIGHT............CHAPTER XXXIV

FOOD AND CLOTHING

In addition to improving mankind's answer to the three fundamental needs for food, clothing, and shelter, chemistry applied to natural products improves them and makes them more adapted for service. Natural drugs extracted from roots and the bark of plants are effective in many instances, but the drugs prepared synthetically, without using the plant, are still more suitable for medicines, for these compounds often comprise the active principle of the drug without undesirable impurities.

One of the most remarkable series of chemical changes is going on all the time inside the body of any living person. Food is being changed into tissues, repairs are being made to injuries, and growth is being provided to the young. Some of the food is stored, other parts are built into specialized tissue, and still other parts act as a control of the entire process.

Functions of Food. If a person lies perfectly still for a long period of time and except for shallow breathing does not move, he still needs food. The purpose of such food is to maintain the temperature of the body.

Additional food is needed to provide the energy for muscular exercise, and it is evident from experience that the amount of exercise regulates to a great measure the quantity of food required. If excess food is eaten, it may be stored as fat. Further—witness the traditional appetite of growing boys—food is needed for new growth as well as for repair in case of injury.

Today we know that food has a fourth function, namely, keeping the bŏdy in good health through the regulatory action of the vitamins and other important components. Even though satisfying food is eaten, a person may suffer from malnutrition due to lack of these important regulators.

New Terms

nutrient
vitamin
bone black

invert sugar
rayon

pasteurization
centrifuge

Nutrients. For purposes of study, food is classified as carbohydrates, proteins, and fats.

Carbohydrates are compounds of carbon, hydrogen, and oxygen, the last two elements usually being present in the proportions 2 to 1, the same as in water. They include sugars and starches. They are fuel foods only, but by conversion to fat in the body they may be stored.

Proteins are complex compounds containing carbon, hydrogen, nitrogen, and oxygen. Some proteins also contain phosphorus, sulfur, iron, manganese, and other elements. Lean meat, egg white, and milk curds are rich in protein. During the last century the brilliant studies of Emil Fischer (1852–1919), of Germany, advanced our knowledge of sugars and proteins more than the work of any other person. He was awarded the first Nobel prize in chemistry. Proteins are needed for growth and repair, but proteins are also used by the body for fuel.

Fats are well known to everyone. They are an important fuel food. We have seen that fats are esters of glycerol and fatty acids (see page 560). Oils are essentially the same as fats, but as food they are a little more easily digested.

A complete food analysis includes consideration of water, minerals, and vitamins, also. These are accessory to the three main factors in the diet.

Analysis of Food. Let us analyze milk for the presence of the various food nutrients. The scum on boiled milk is removed and treated with concentrated nitric acid (HNO_3). A yellow color is produced, which is deepened by addition of ammonia water (NH_4OH). This is a test for protein.

A sample of milk is tested with a few drops of iodine solution. The absence of a blue color indicates that no starch is present.

Another portion of the milk is boiled with an equal volume of Benedict's solution. A red precipitate of cuprous oxide (Cu_2O) indicates the presence of a kind of sugar in the milk, lactose ($C_{12}H_{22}O_{11}$).

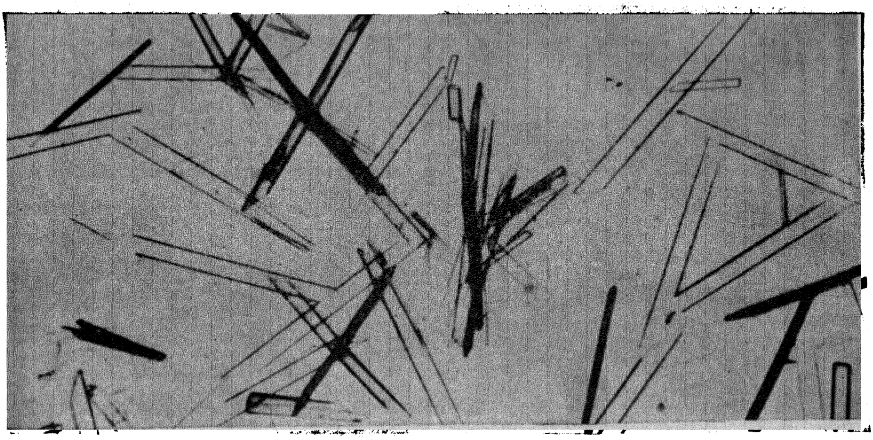
A small crucible is half filled with milk, and the contents are heated gently. After water has boiled away, the remaining solid matter when heated strongly chars and burns. Finally, after ignition over a hot flame, a white ash is left. This is the mineral matter—in this case chiefly compounds of calcium and phosphorus.

Vitamins in milk can be detected by feeding it to animals who have been fed previously on a diet entirely lacking in the particular vitamins and noting their almost immediate improvement in health if the particular vitamins are present. Other tests for vitamins are available, but the techniques are too elaborate for an elementary discussion.

Food Measurements. Experiments have proved that the heat produced by food is the same whether the food is burned in the body or in a calorimeter. The unit of heat used in food measurement is the Calorie (large calorie, Cal), or kilocalorie (Kcal), 1000 times the small calorie (see page 102). Carbohydrates and proteins produce about 4 Cal per g or 1800 Cal per lb. Fats yield about 9 Cal per g or 4100 Cal per lb.

Food Requirements. The average grown person needs about 1 g of protein per kilogram of body weight per day. This amount increases gradually down the age scale to 3.5 g per kg of body weight for children three years old.

The total calorie value of food required by the average adult is about 2400 per day. This amount varies considerably with age, occupation, state of health, climate, and other factors. Many persons seem to thrive on a diet lower in protein and less in amount than the figures given here. These values were suggested by a committee of food specialists.



Courtesy of Merck and Company, Inc.

FIG. 34-1.—This picture would have been impossible to take one generation ago. The crystals are vitamin B_1, thiamin hydrochloride. No vitamin has gained such widespread adoption as a pure compound as B_1.

Vitamins. Before definite information was known about vitamins, seafaring men knew that long voyages without fresh vegetables would produce scurvy among the crew. The British Navy discovered that a small ration of tomato or lime juice would prevent or cure this disease. Doctors discovered that cod-liver oil would greatly help cure or prevent rickets, a disease that weakens the bones in children. These and other facts were gradually accumulated, but about 1907 feeding experiments definitely proved that certain substances, other than the main nutrients and mineral substances, were essential in a complete diet. These substances, necessary in only the tiniest amounts, were called vitamins, and are designated by letters.

Vitamin A is made in the body from the yellow coloring matter in carrots (carotene) and in leafy vegetables, by hydrolysis. Dairy products and fish-liver oils are rich sources. It is fat-soluble but not water-soluble.

Courtesy of Merck and Company, Inc.

FIG. 34-2.—The sick rat shown at the top is suffering from a diet lacking in vitamin B_1. Lack of food containing B_1 caused this polyneuritic condition. Below we see the same rat completely and speedily cured by adding vitamin B_1 to his diet.

Vitamin A promotes normal growth in children, prevents eye diseases and "night blindness," and helps the body resist infections.

Vitamin B is now known to be composed of several vitamins. We have isolated and identified B_1 from the B complex. (See Fig. 34-1.) This is called ***thiamin;*** it is found in vegetables and in the coarser parts of the germs of grains. These rougher parts of grains are removed in the processing of foods, as, for example, in making white wheat flour. Knowledge of nutrition has increased a demand for whole-grain cereal products and for adding vitamin B_1 to bread. This was done on a nation-wide scale in England during World War II and also extensively in America. This vitamin is not stored in the body, and a sufficient amount should be taken in with the food each day. Without vitamin B_1, beriberi results. (See Fig. 34-2.)

Vitamin B_2 or ***riboflavin,*** was formerly known as vitamin G. It promotes growth and a healthy condition of the skin.

Vitamin B_5 or ***niacin, nicotinic acid,*** is a preventive for pellagra, a disease that has for symptoms nervous disorders, skin eruptions, and upset digestion. B_5 is found in meat, milk, and yeast.

Included in the B complex are pyridoxin (B_6), pantothenic acid (B_3), and adenylic acids (B_8) and other substances that are now being investigated.

Vitamin C, ascorbic or ***cevitamic acid,*** is present in abundance in the juices of citrus fruits, in tomatoes, in green peppers, and in less amounts in many other foods. It is easily destroyed by heating and air. Vitamin C prevents scurvy or its beginnings, among the symptoms of which are bleeding gums and loosening of the teeth. Some experimental animals, such as rats, can manufacture their own vitamin C from other materials in their food. Human beings evidently cannot do this but must rely on fresh fruits and vegetables for their supply of vitamin C.

Vitamin D, the sunshine vitamin, is also known to consist of at least

10 separate compounds, all of which may be considered together for our purposes. Lack of this vitamin causes rickets, a bone disease. The sun shining on the skin develops vitamin D in the body. Likewise, the sun shining on small plants and animals in the sea causes them to develop this compound. They in turn become food for fish who store vitamin D in their livers. Fish-liver oils are rich sources of this vitamin.

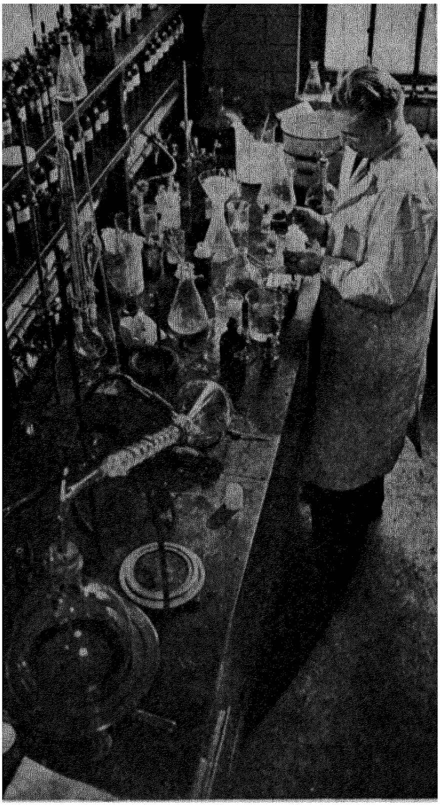
Passing some materials under artificial sunshine, rich in ultraviolet light, produces in them the equivalent of vitamin D. This treatment produces irradiated food. ***Viosterol,*** a vitamin D concentrate, is made by artificially irradiating ***ergosterol,*** a substance extracted from yeast. This process parallels the production of vitamin D in the human body.

Vitamin E is found in wheat germs, lettuce, lean meat, milk, egg yolks, and other foods. This vitamin is known to be important for the process of normal reproduction in rats, but its place in human nutrition is not established. Without a sufficient supply of this vitamin in the diet of the mother, the young rats may be born dead and usually in advance of normal schedule. Apparently no general lack of this vitamin exists in human beings.

Vitamin K, now known to consist of K_1 and K_2, is important because it hastens the clotting of blood. This has been a great help after surgical operations, and already it is standard practice in hospitals to give a small amount of it to newborn infants, who cannot make it for themselves during the first few days of their life. The result has been the saving of many infants from death by internal bleeding and giving others a better start.

The Vitamin Search. The story of the vitamins is not merely a listing of the vitamins by letters and recording their sources and purposes, important as this knowledge is to everyone preparing meals. Behind each story is a drama of intensive and exhaustive search: rooms full of rats and other experimental animals, each being fed specialized diets, and the results being recorded accurately and painstakingly; chemists working with 2 tons of rice bran to isolate a sample of 0.005 gram (454 g in each pound and 2000 lb in each ton); the complex structure of the organic compound being accurately determined by using so skillfull a technique that a sample scarcely visible is large enough; finally, the identical vitamin being synthesized in the laboratory. Later comes commercial production of the vitamin, even by the ton. These or similar chapters are part of the story of each vitamin. The entire knowledge of vitamins is scarcely 30 years old, and the field is rapidly developing. Eight vitamins have already been synthesized, and six of them are available as pure chemical compounds, commercially manufactured.

Good Health with a Balanced Diet. With so much knowledge available about vitamins, how can we maintain good health without using expensive vitamin concentrates? The best answer seems to be to eat a ***balanced diet.*** This means a diet containing the proper amounts of carbohydrates, proteins, fats, and mineral matter. If we include in this diet fresh fruits and vegetables, some dairy products, whole grains, and, if possible, although not necessary, some meat or fish, we need not fear any of the so-called "deficiency" diseases that come from lack of vitamins.



Courtesy of Merck and Company, Inc.

FIG. 34-3.—This chemist is isolating vitamin B_1.

Sugar. One of the most important carbohydrate foods is common table sugar, or sucrose ($C_{12}H_{22}O_{11}$). The chief sources of this compound are sugar cane and sugar beets. Each contains about 18 per cent by weight of sugar, but about twice as much tonnage of sugar is obtained from cane as from beet. Let us follow sugar from the cane until it appears on our table in the form of pure white crystals.

The cane is trimmed to the stalk only and crushed to remove the juice. The remaining pulp, or ***bagasse,*** is used to make Celotex wallboard. The juice is partly purified by adding lime, which precipitates some impurities, and then it is filtered. The filtrate is evaporated by boiling it at a reduced temperature in vacuum pans. The resulting slush of crystals is freed from the mother liquor, or molasses, by centrifuging. The crystals, known as raw sugar, are brown with an unpleasant taste and a slight odor.

The second stage in the preparation of white sugar for the table is accomplished at a refinery. The raw sugar is dissolved and passed through activated charcoal or ***bone black.*** This process removes the color and odor from the sugar. The solution is again evaporated under reduced pressure, and the crystals are separated. This time they are glistening, white, uniform crystals.

Inverting Sugar. When some forms of soft candy are made, a little vinegar is added to cane sugar and the mixture heated. In the presence of acid the sucrose combines with water and forms two simpler sugars, isomers (see page 535), not as sweet as sucrose and not crystallizing so readily. They therefore make a smooth, noncrystalline candy.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{(H^+)} \underbrace{\underset{\substack{\text{glucose, or}\\\text{grape sugar}}}{C_6H_{12}O_6} + \underset{\substack{\text{fructose, or}\\\text{fruit sugar}}}{C_6H_{12}O_6}}_{\text{invert sugar}}$$

The mixture is called invert sugar. Cane sugar does not reduce Benedict's solution, but invert sugar does.

When sugar is heated slowly, caramel, a popular flavoring material, forms.

Other Sugars. Milk sugar, or lactose ($C_{12}H_{22}O_{11}$), is the natural sweetening agent in milk, in which it occurs to the extent of about 5 per cent. When milk sours, lactose changes to lactic acid by bacterial action.

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{lactic acid}}{4C_3H_6O_3} \quad (CH_3CHOHCOOH)$$

The acid coagulates the colloidal casein into a curd. The souring of milk can be greatly delayed by pasteurization, that is, by heating and maintaining it at a temperature of 143°F for 33 minutes or, in the new process, at 160°F for 15 seconds. Lactose reduces Benedict's solution.

Maple sugar is sucrose plus certain flavoring materials that are present in the sap of the sugar maple tree.

Corn sugar, or corn sirup, is glucose ($C_6H_{12}O_6$) made from starch. It is used in candy- and jam making because it does not crystallize easily. Honey contains this sugar, and many of its commercial uses depend upon its slow crystallization property.

Starch ($C_6H_{10}O_5$)$_x$. Let us shred a small potato into water, using a kitchen grater, and then strain the mixture through a piece of cotton cloth to remove fibrous material, collecting the cloudy filtrate in a transparent vessel. In a short time, a white deposit settles at the bottom. Now let us pour, or decant, the liquid above the white material into a test tube and add a drop of iodine solution to the residue. The iodine produces a dark-blue color, showing that the white material is starch.

Potatoes contain only 15 per cent starch, but corn contains 65 per cent. Different sorts of starch can be distinguished from each other by comparing under a microscope the tiny grains or flakes of starch with samples from a known source. Each kind has its characteristic appearance. Starch is used for laundry purposes to stiffen cloths and to give a luster to ironed articles; to make glucose, alcohol, and dextrin; and as a food. Dextrin, which is familiar to all in the form of the gum on envelope flaps and postage stamps, is made by heating starch slowly.

Glucose is made from starch by boiling it in a sealed vessel with acid,

$$\underset{\text{starch}}{(C_6H_{10}O_5)_x} + xH_2O \xrightarrow{(HCl)} \underset{\text{glucose}}{xC_6H_{12}O_6}$$

and neutralizing the excess acid. Commercial glucose made in this manner contains also some dextrin and maltose ($C_{12}H_{22}O_{11}$) (see page 597).

Preserving Foods. One of the most inconspicuous, yet important, contributions to the art of living comfortably is our ability to preserve foods. Sealing sterile food in an airtight container is widely practiced at home and in factories. Refrigerated food is transported by steamship, railroad, and truck from producing centers to markets. Quick-frozen foods have such tiny ice crystals that the cell walls of the food are not broken. This preserves freshness and flavor until the food is prepared for serving. Jams keep well because of the high sugar content. Drying, salting, pickling, smoking, and similar methods of preserving foods are among the older means that were developed before refrigeration and are still used extensively today.

Chemical preservatives may be used in some cases. Sodium benzoate, a compound derived from coal tar, is used for this purpose, but in a limited amount. Foods containing preservatives are so marked on the label, a provision of the Pure Food and Drug Act.

QUESTIONS

1. Suggest some foods that a person should eat if he wishes to gain weight quickly.

2. Suggest some foods that a person should eat if she wishes to lose weight.

3. A knowledge of food chemistry is important to persons in what occupations?

4. What is wrong with a diet consisting of purified fats, purified carbohydrates, and purified proteins?

5. Distinguish a hydrocarbon from a carbohydrate.

6. What element is always present in protein foods that is not present in carbohydrate or fats?

7. What function of protein food cannot be duplicated by carbohydrates or fats?

8. Trace the course of a nitrogen atom from Chile saltpeter to muscle tissue in an animal.

9. Trace the course of a carbon atom from carbon dioxide in the air to fat tissue in the human body.

10. How can you prove that an apple contains (*a*) water; (*b*) sugar; (*c*) minerals?

11. Assuming that you need 1.5 grams of protein per kilogram (2.2 pounds) of body weight, what is your daily protein requirement?

12. Which in general of the following is richer in vitamins: (*a*) white (unfortified) or dark bread; (*b*) white or yellow turnips; (*c*) bleached or green celery; (*d*) green-leaf or head lettuce?

13. What proof have we that vitamins are necessary supplementary foods?

14. Name three occupations in which a knowledge of vitamins is important.

15. Aviators defending the coast of England at night were supplied with carrots and urged to eat them. How do carrots help aviators?

16. In processing grains most of the coarse bran is removed, the vitamin content of the resulting flour being low. People seem to like white bread, but they should not be deprived of vitamins normally present in grain. How has the baking industry met this problem?

17. Do the conclusions reached from experiments carried out on diets for animals always hold true for diets for human beings?

18. How may a person be sure that his diet is adequate in respect to vitamins?

19. Explain how the diet of a person depends upon climate. Give examples.

20. What special food value has each of the following: (*a*) fish livers; (*b*) calf liver; (*c*) sea food in general; (*d*) citrus fruits; (*e*) spinach; (*f*) bananas; (*g*) beans; (*h*) coffee; (*i*) soybeans?

21. Give the names and formulas for four carbohydrates.

22. Describe a test to determine the presence of sugar in a body fluid.

23. Why is toast more digestible than bread?

24. Why is pasteurization of beverage milk desirable?

25. What change is brought about in candymaking when sugar is heated with vinegar?

26. What change is brought about in the final product by "pulling" molasses taffy (with buttered fingers)?

27. A 100-gram sample of milk contains 1.6 per cent lactose. What weight of lactic acid is present in the sample when all the sugar has fermented?

28. Corn products for sweetening are on the market. Among them are Dyno sugar and Karo sirup, both light and dark. (*a*) From what part of the corn are these sugars made? (*b*) What is the composition of Dyno (see box)? (*c*) What is the difference in composition between dark and light Karo sirup? (*d*) Name a purpose for which Karo sirup is better adapted than sucrose.

29. What purpose does lactose in milk serve?

30. Why are men's shirt collars starched? What use is made of the starch in corn flakes?

31. Some children hide crusts under their plates. What makes crusts different from the rest of the bread? How do crusts compare in taste with the rest of the bread? Why do some children dislike them? What is zwiebach?

32. In home canning, what precaution should be taken before sealing the jars to prevent spoilage?

33. Which is probably the better product of each of the following: (*a*) tomato catchup with or without preservative; (*b*) frozen or chilled imported beef; (*c*) pasteurized or raw milk; (*d*) oleomargarine or butter; (*e*) sprayed or unsprayed apples? In answering the question tell "better for what" and "why."

Clothing

Let us take a mass of cotton fibers, such as absorbent cotton or a boll from the cotton plant. By combing, the fibers can be laid parallel, and by twisting and drawing them out a thread can be spun. The thread can then be knitted or woven into cloth.

This simple experiment illustrates the mechanical processes necessary in making cloth. Chemical processes consist in bleaching, dyeing, and finishing the cloth and testing the fabric in the various stages of its manufacture.

Cotton. Cotton is by far the most important fiber. In chemical composition it is chiefly cellulose, like wood. When viewed under the microscope, cotton fibers appear similar to flat, twisted ribbons. They burn somewhat like paper, and are unaffected by most dilute chemicals. Cotton is used chemically for the manufacture of nitrocellulose. The seeds of the plant yield meal for cattle food and cottonseed oil.

Rayon. Although the production of rayon is only a fraction of that of cotton, the industry is growing rapidly. Rayon is regenerated cellulose, made by dissolving cellulose and reprecipitating it in the form of smooth, continuous fibers. This has already been described (see page 567). Rayon fibers can be distinguished from cotton fibers by viewing them under the microscope, where they appear as round tubes or rods. Viscose rayon, the most common type, burns like paper. Acetate rayon (cellulose acetate) can readily be distinguished from the viscose type in that acetate dissolves readily in acetone [$(CH_3)_2CO$] and viscose does not.

Wool. Animal hair is protein in nature, containing the elements carbon, hydrogen, oxygen, nitrogen, and sulfur. Wool viewed under magnification shows overlapping scales similar to miniature shingles on each rodlike fiber. This is an identifying characteristic. Wool burns like hair, with an unpleasant odor. Dilute alkalies dissolve it, and concentrated nitric acid turns it yellow.

Synthetic Wool. Protein matter in the casein of milk, in fish, and in soybean meal has been used successfully to produce synthetic wool. The process of manufacture is quite similar to the making of rayon. The regenerated protein is kinky, like wool, and an excellent heat insulator. Some of it is called Lanital.

Silk. Silk, the wrapping of the cocoon of the silkworm, is also a protein product. It resembles rayon when viewed under the microscope but differs from it in chemical nature. In fact, silk responds to chemical tests in almost the same way as wool, but its general smooth, lustrous appearance when magnified readily distinguishes it from wool.

SUMMARY

The functions of food are to supply heat, to give energy for muscular movement, to provide for growth and repair of tissues, and to control general health.

The nutrients are carbohydrates, proteins, and fats. Carbohydrates include starches and sugars. They are compounds of carbon, hydrogen, and oxygen, the latter two in the proportion of two hydrogen atoms to one oxygen. Proteins are organic nitrogen-containing compounds. Fats are esters of glycerol with fatty acids. Minerals, vitamins, and water are also essential in a balanced diet.

Nutrients are identified by the following laboratory tests: (1) Starches turn iodine solution blue. (2) Some sugars form a brick-red precipitate of cuprous oxide when boiled with Benedict's solution. (3) Proteins form a yellow color with the addition of concentrated nitric acid. The color turns darker orange when moistened with ammonia water. (4) Fats make a grease spot on unglazed paper. (5) Minerals remain as ash when the food is ignited.

Food measurement is similar to fuel measurement, for food heat values are measured in calories. Food requirements of persons differ, depending upon many factors.

Vitamins are compounds that are essential in small amounts for the maintaining of good health. Lack of a sufficient supply causes a "deficiency" disease, such as scurvy, rickets, or beriberi. Although the amount required is small, the supply may be insufficient unless the diet is correct. The human body can manufacture some vitamin D in sunlight. Several of the vitamins are now identified as definite chemical compounds and are manufactured synthetically.

Sucrose, or common table sugar, is found in plants, especially sugar cane, sugar beet, and (the sap of) the sugar maple tree. Sugar cane is crushed and the extracted juice evaporated under vacuum, forming raw sugar, which is separated from molasses in centrifugal machines. Refining sugar consists in dissolving raw sugar and passing the solution through adsorbing agents, including carbon char. The resulting clear liquid is evaporated under reduced pressure, and the crystals are dried by whirling them in the perforated basket of a centrifugal machine.

Sucrose boiled with a little acid forms glucose and fructose, two isomers that do not crystallize readily. Heating sucrose gently forms caramel.

Lactose, milk sugar, is found in milk. It changes into lactic acid when milk sours.

Starch, found in many plants, may be identified by its characteristic tiny grains or flakes. It is used for laundry purposes and food. It is also used to make alcohol, glucose by hydrolysis, and gum dextrin by gentle heating.

Cotton is a plant fiber, chiefly cellulose. Rayon is regenerated cellulose. Wool is a protein animal fiber. Synthetic wool, made from skimmed milk and other materials, resembles wool in both general appearance and protein nature. Silk is animal fiber of high strength and pleasing luster.

QUESTIONS

34. Define *warp; woof.*

35. Name a type of fabric that has threads woven in three different directions at right angles to each other.

36. Which fibers when burning smell like burning paper? Which like burning hair?

SPECIAL REPORTS

1. Prepare a report on the process of obtaining sugar from beets.

2. What is a polariscope? What are its uses?

3. What difference in vulcanization causes the differences between hard rubber and elastic rubber? Which lasts longer? Is there a chemical reason for this?

4. Types of synthetic rubber produced commerically in the United States are Buna S (GRS), Buna N, Neoprene, Butyl rubber, and Thiokol. Write an account of the development and manufacture of one or more of these.

5. Prepare a report on the obtaining, preserving, coagulating, compounding, and vulcanizing of natural rubber.

UNIT EIGHT - - - - - - - - - - - CHAPTER XXXV

CHEMISTRY FOR CLEANLINESS, HEALTH, AND BEAUTY

Two centuries ago a householder who wished to make soap had to save waste kitchen fats and wood ashes. The wood ashes were soaked in water and strained. The more or less clean solution of potash was then boiled with the fat and a rather soft soap obtained.

Today's soap is hard, pleasantly scented, and in soft water an effective cleansing agent. It keeps well, dissolves at a moderate rate, and provides an alkaline colloidal suspension of suds. This condition is excellent for emulsifying grease and hence for cleansing.

Soap. Ordinary soap is a sodium salt of a fatty acid of higher formula weight, such as sodium stearate ($C_{17}H_{35}COONa$). Mixed also with this compound are the more soluble sodium oleate and palmitate, for no natural fat is derived entirely from one fatty acid. Potassium soaps are in general more soluble than sodium soaps. They are made by using some potassium hydroxide (KOH) in place of the corresponding sodium hydroxide. Such a product would be used for a shaving soap.

Soapmaking. Soap for the market is made in huge kettles, which in some instances are capable of holding as much as several carloads of finished soap in a single batch. (See Fig. 35-1.) First the kettle is filled with a mixture of fat and lye solution. Steam is bubbled through the contents for about 4 hours, which cooks and stirs the mixture. The following reaction, called ***saponification,*** takes place:

$$\underset{\substack{\text{fat}\\[4pt] \text{glyceryl ester of}\\ \text{stearic acid}}}{(C_{17}H_{35}COO)_3C_3H_5} + \underset{\substack{\text{lye}\\[4pt] \text{sodium}\\ \text{hydroxide}}}{3NaOH} \rightarrow \underset{\substack{\text{soap}\\[4pt] \text{sodium}\\ \text{stearate}}}{3C_{17}H_{35}COONa} + \underset{\substack{\text{glycerin}\\[4pt] \text{glycerol}}}{C_3H_5(OH)_3}$$

The soap formed floats in the kettle like a huge curd. It is coagulated from the colloidal condition by adding common salt. Then, after removal

---

New Terms

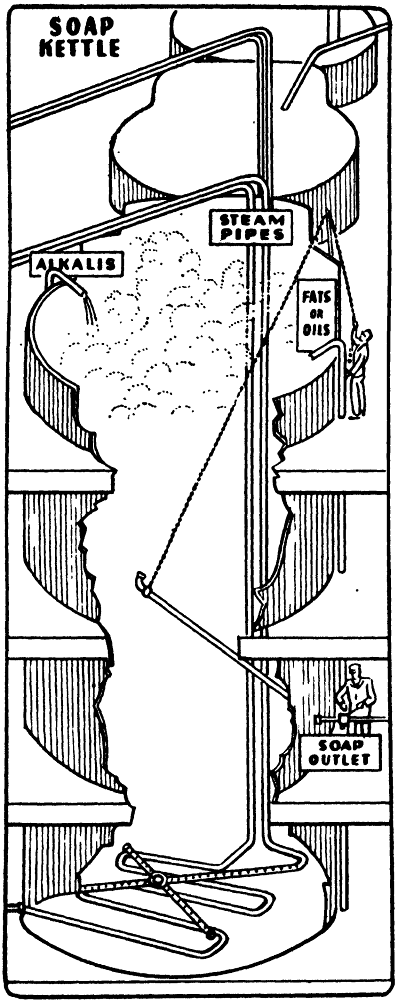
soft water
hard water
saponify
insulin
adrenalin
hydrolysis
antiseptic

from the kettle and hardening, it is mixed in a crutching machine, molded into blocks, and cut into slabs and cakes.

The glycerol is recovered by fractionally distilling it from the liquid mixture that remains.

Millions of pounds of soap are used each year in processing Buna S synthetic rubber. The soap acts as an emulsifying agent in the formation of a synthetic latex.

Kinds of Soap. Fundamentally all soaps are made by treating fats and oils with a base. The product may be varied, however, by using different raw materials and finishing processes and additional materials. Soap will float if tiny air bubbles are beaten into it during the finishing processes. When the materials are dissolved in alcohol, transparent soap is obtained. Castile soap is a variety of soap that is made from olive oil. Scouring soaps have finely ground abrasives incorporated in the cake, while scouring powders have some soap included with the scouring agent together with sodium carbonate and trisodium phosphate, which serve as builders, or agents to make the soap act more rapidly. A great variety of perfumes and antiseptics are included with different sorts of soaps. Rosin is usually added to the fat in the making of laundry soap. The rosin reacts with the lye in the same manner as the fat does. The sodium rosinate formed is fairly soluble and aids in suds making.



Courtesy of Colgate-Palmolive-Peet Company

FIG. 35-1.—This commercial soap-making kettle extends through three floors of the building.

Soap chips can be made by running a thin sheet of liquid soap onto a refrigerated cylinder, or drum, and scraping off the soap in small broken pieces as a continuous process. Soap granules are dried, thick, miniature soap bubbles. Soap powder is made by spraying soap and sodium carbonate solution into a drying room. The soap powder, bound together by the sal soda crystals ($Na_2CO_3 \cdot 10H_2O$), collects on the floor of the drier.

Chemical Actions with Soap. Soap is an ionized salt with an organic radical ion and a sodium ion. At one end of the organic radical is a long chain of nonpolar carbon atoms; at the other, a polar carboxyl radical. The positive sodium ion is largely free in the solution, as in all sodium salts. The solubility of soap in both organic and inorganic compounds is explained in part by its dual nature.

Soap in acid solutions forms a curdy precipitate of a fatty acid, a very weak acid.

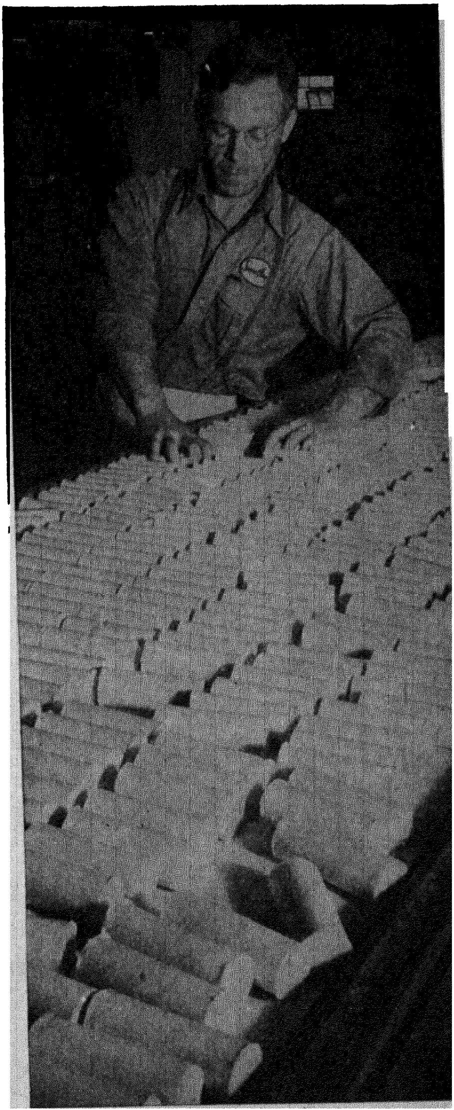
$$\underset{\text{soap}}{C_{17}H_{35}CO\overset{-}{O}\overset{+}{Na}} + HCl \rightarrow$$

$$\overset{+}{Na}\overset{-}{Cl} + \underset{\text{stearic acid}}{C_{17}H_{35}COOH} \downarrow$$

Metallic ions other than sodium or potassium form a curdy precipitate of the soap and of metal that separates as a scum. This happens with the calcium and magnesium ions that are present in hard water.

$$2\underset{\text{soap}}{C_{17}H_{35}\overset{-}{COO}\overset{+}{Na}} + \overset{++}{Ca}\overset{-}{Cl_2} \rightarrow$$

$$2\overset{+}{Na}\overset{-}{Cl} + \underset{\text{insoluble calcium soap}}{(C_{17}H_{35}\overset{-}{COO})_2\overset{++}{Ca}} \downarrow$$



Courtesy of Manhattan Soap Company

FIG. 35-2.—This scene in a soap factory shows a stage in the preparation of soap into bars for retail trade.

These "metallic soaps" are useless for cleaning. In fact, they are a decided hindrance to good washing. They precipitate and collect in the fiber of the cloth, shedding water and forming a gummy mass. Cloth washed in hard water does not take dye evenly, and hair washed in hard water looks dull unless rinsed free of this precipitate. A scum of precipitate together with the attached dirt forms an unpleasant-looking ring around the washbasin when hard water is used for washing.

Metallic Soaps. Calcium soap, although undesirable in washing, is suitable as a lubricant for some purposes. Other metallic soaps have special uses. Zinc stearate is used in antichafing powder, and copper oleate impregnated in marine ropes makes them resistant to fouling by marine growth.

QUESTIONS

1. Describe how soap aids in removing particles of solids from hands; from clothes.

2. How can soap be tested to determine whether sodium hydroxide or potassium hydroxide was used in its manufacture?

3. How can soap be tested for excess lye?

4. What type of fat is used in making (*a*) sodium stearate; (*b*) sodium oleate; (*c*) sodium palmitate?

5. Write the equations for (*a*) the hydrolysis of glyceryl palmitate $(C_{15}H_{31}COO)_3C_3H_5$; (*b*) for its saponification. Write similar equations for the hydrolysis and saponification of glyceryl oleate $(C_{17}H_{33}COO)_3C_3H_5$.

6. Some soap manufacturers claim that their products contain olive and palm oils. In what sense is this true?

7. From what is "tar" soap made?

8. What is the purpose of adding "builders" to soap powder? How do they act?

9. Describe from start to finish the process of making a cake of white floating soap.

10. In wartime, housewives are urged to turn in waste kitchen fats. To what use are these fats put?

11. Write the formula equation for the saponification of glyceryl stearate with lye.

12. Write the formula equation for the interaction of soap solution (use sodium stearate) with solutions of (*a*) $Ca(HCO_3)_2$; (*b*) Na_2SO_4; (*c*) HCl; (*d*) $MgSO_4$; (*e*) $FeCl_3$; (*f*) alum.

Soft and Hard Water. Soap lathers readily in rain water or other ***soft water*** where no metallic ions are present to react with the soap. ***Hard water,*** on the other hand, reacts with soap and wastes it, interferes seriously with cleansing, and forms a deposit or scale in boilers. (See Fig. 35-3.) Hard water contains the ions of calcium or magnesium. If hard water can be softened by simple boiling, the hardness is said to be ***temporary.*** Otherwise, the hardness is called ***permanent,*** and chemical treatment is needed to soften it.

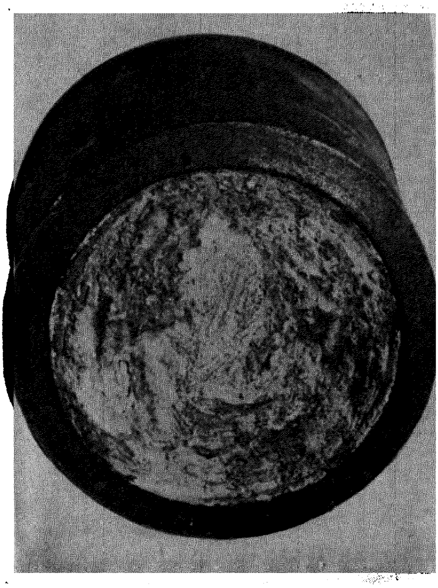
Temporary Hardness. A certain family uses water from a well. Hot water for domestic use is obtained by heating the well water in a large kettle. Every few days, a collar-shaped ring of white solid crust is taken out of the kettle. This crust effervesces when acid is added, and the gas liberated turns clear limewater milky. Here is a typical case in which temporary hard water is used. Let us assume that calcium bicarbonate was dissolved in the well water. This compound decomposes when heated.

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

This method of softening temporary hard water is too expensive for city-wide scale usage. For urban use a carefully controlled amount of slaked lime is added to the water.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

This precipitate is allowed to settle in huge basins, and the clear softened water is run off and after being filtered is piped to the consumer.



Courtesy of The Travelers Insurance Company

FIG. 35-3.—This steel boiler tube was completely filled with hard scale from hard water.

Permanent Hardness. Permanent hardness is usually due to the presence of calcium and magnesium salts other than the hydrogen carbonates. Many methods are used for softening permanent hard water. Most of them depend on the exchanging of calcium ions in the water for sodium ions from the softening agent. The sodium ions in the water do not react with soap, which is itself a sodium compound. For example, washing soda is a widely used water softener in water purification installations.

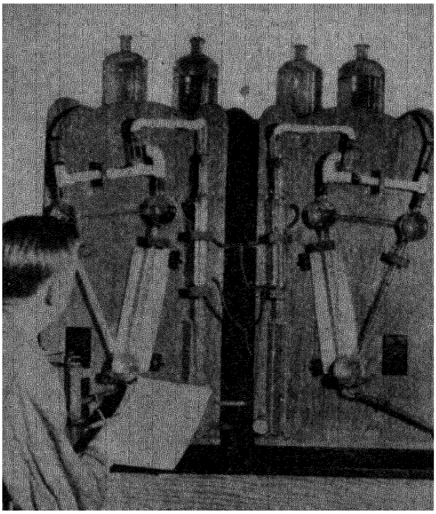
$$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3\downarrow$$

Borax ($Na_2B_4O_7{\cdot}10H_2O$), trisodium phosphate (Na_3PO_4), and ammonia water (NH_4OH) are all used for the same purpose. Soap, too, is a water softener, but an expensive one.

In another type of water-softening process, zeolite clay may be used or, better, commercially manufactured artificial clays, such as Permutit, that resemble the natural sodium aluminum silicates. We shall represent the complex zeolite radical by *Ze* in the equation.

$$Na_2Ze + MgCl_2 \rightleftarrows MgZe\downarrow + 2NaCl$$

The hard water is run into a tank containing the zeolite grains. Here the water exchanges its calcium and magnesium ions for sodium ions by reaction with the clay, which retains its granular form. After a period of service, the clay is reactivated by soaking it in 10 per cent salt water. This causes the reverse action to occur. The resulting magnesium and calcium compounds are flushed out, and the softener is ready for further service.



The Travelers Insurance Company

FIG. 35-4.—After a correct water softener is determined, its actual performance in a boiler is studied in these model boilers. The heating is done electrically by a wire coiled around the tube that is backed by a sheet of asbestos.

Sodium "metaphosphate," marketed under the trade name of Calgon, and sodium tetraphosphate in solution have the ability to lock calcium or magnesium ions in the form of a complex ion so tightly that they will not react with soap. These compounds are marketed widely for washing dishes in machines without leaving streaks and for washing clothes without leaving gray patches.

Ion-exchange Resins. A way to render water almost chemically pure without distillation has been found and put into practical service in industries that formerly required the more expensive distilled water. In this process the raw water is slowly run successively through two tanks of synthetic resins. In the first tank the metallic ions, such as calcium and magnesium, are exchanged for hydrogen ions, rendering the water acid. In the second tank the acid is absorbed, removing not only the hydrogen ions but sulfate, chloride, and nitrate ions as well. The resin in the first tank is regenerated by an acid, and that in the second tank by soda ash (Na_2CO_3) solution. The treated water, since it contains neither positive nor negative ions, compares favorably with once-distilled water in purity.

Suds in Hard Cold Water. Salt-water soap contains much of the soluble potassium salts of the fatty acids. It is derived chiefly from coconut oil. In spite of the fact that such soap can make suds in very hard water because it is very soluble, an unwanted scum forms.

Newer ***detergents*** make suds in any sort of water, regardless of dissolved mineral compounds. One that is widely used and marketed under the name of Dreft or in solution for shampoo as Drene is essentially the sodium salt of a sulfonated alcohol of high formula weight, sodium lauryl sulfate, with a chain of 12 carbon atoms ($nC_{12}H_{20}O\cdot SO_2\cdot ONa$). Though expensive compared with soap, these compounds serve as wetting agents in cleansing cloth preparatory to dyeing, in cleaning metals preparatory to drawing or plating, and in numerous special cases where their cost is easily justified. Dreft solution, for example, gives a tough film of foamy suds even in ice-cold, hard water.

Hydrolysis. A certain school cafeteria has the problem of washing greasy dishes. The manager would like to change the grease on the dishes to soap, that is, wishes to ***saponify*** it and use the soap formed in this manner for cleaning the dishes. He selects trisodium phosphate as a compound that will do this. The pH value (see page 225) of a molar solution of trisodium phosphate (13.8) is almost that of a molar solution of sodium hydroxide (13.9), and it is much easier to handle. The explanation of the action of this compound as a base is found in its reaction with very hot water in the washing machine.

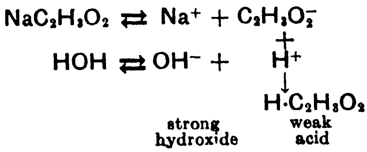
$$Na_3PO_4 + HOH \rightarrow Na_2HPO_4 + NaOH \quad \text{(formula equation)}$$
$$PO_4^{---} + HOH \rightarrow HPO_4^{--} + OH^- \quad \text{(ionic equation)}$$

Such an action of a dissolved salt on the ions of water is called ***hydrolysis*** (see page 232). Sodium carbonate can also be used for the same purpose.

$$Na_2CO_3 + HOH \rightarrow NaHCO_3 + NaOH \quad \text{(formula equation)}$$
$$CO_3^{--} + HOH \rightarrow HCO_3^- + OH^- \quad \text{(ionic equation)}$$

The explanation of hydrolysis involves reactions between ions and water. Let us consider a solution of sodium acetate ($NaC_2H_3O_2$), a salt that may be considered to have been formed by interaction of the strong base, sodium hydroxide ($NaOH$), and the weak acid, acetic acid ($H\cdot C_2H_3O_2$). Four ions are present in the solution, namely, Na^+, $C_2H_3O_2^-$, H^+, and OH^-. The latter two are originally present in small amount from the water that dissociates very slightly. The Na^+ and OH^- ions do not tend to join together, but the H^+ and $C_2H_3O_2^-$ ions do join to form the slightly dissociated molecule called acetic acid ($H\cdot C_2H_3O_2$). This leaves effectively Na^+ and OH^- ions in solution. When we test a solution of sodium acetate with litmus paper, we find that its solution turns the red color to blue.

These actions may be summarized as follow:



$$\begin{array}{ccccc} NaC_2H_3O_2 & \rightleftarrows & Na^+ & + & C_2H_3O_2^- \\ & & & & + \\ HOH & \rightleftarrows & OH^- & + & H^+ \\ & & & & \downarrow \\ & & & & H\cdot C_2H_3O_2 \\ & & \text{strong hydroxide} & & \text{weak acid} \end{array}$$

More simply,

$$C_2H_3O_2^- + H_2O \rightarrow HC_2H_3O_2 + OH^-$$

Salts like copper sulfate ($CuSO_4$) and zinc chloride ($ZnCl_2$) in solution hydrolyze and produce solutions containing excess hydrogen ions. Again this is due to the action of water on the dissolved ions. Each of these compounds may be considered to be derived from a weakly dissociated hydroxide and a strong acid.

$$Cu^{++} + HOH \rightarrow (CuOH)^+ + H^+$$

Compounds like aluminum sulfide (Al_2S_3) that may be considered derived from both a weak hydroxide and a weak acid hydrolyze vigorously. In this case hydrogen sulfide gas is liberated.

$$Al_2S_3 + 6HOH \rightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow$$

In solutions of compounds like common salt (NaCl) and potassium nitrate (KNO_3), none of the ions change the pH of the solution. They act neutral to litmus. The pH value of sodium chloride solution, for example, is the same as that for pure water, namely, 7.

Dry Cleaning. Everyone knows that woolen suits cannot be washed satisfactorily in water. Cleaning greasy overalls and woolen garments is accomplished by "dry cleaning," in which a fluid is used but the fluid does not mat down the cloth as water does. The cleaning fluid is a fraction from petroleum resembling gasoline or some chlorinated organic compound. The fluid, to which a special soap is added, is passed through the garments, removing grease and dirt, until it comes through clear. The garments are then ventilated and pressed. The fluid is recovered, passed through a bed of adsorbing material like activated charcoal, and then rectified, or distilled, for re-use.

Cleaning Metals. Let us recall that metals can be cleansed of oxide films by acids, by fluxing with zinc chloride ($ZnCl_2$) or ammonium chloride (NH_4Cl), or by fluxing in such a fashion that the oxide forms a slag (see page 279). Clean metal surfaces are necessary for many operations that are performed on metals, such as plating, etching, photo-engraving, and drawing into wire. When a hot alkali solution is used for washing a metal free from grease, the addition of a small amount of one of the newer detergents for a wetting agent is often helpful.

QUESTIONS

13. What is the effect of treating hard water with sodium hexametaphosphate (in slight excess) and then adding soap solution?

14. Write equations for softening temporary hard water (*a*) by boiling; (*b*) by adding sodium carbonate; (*c*) by adding hydrated lime.

15. Write equations for softening two sorts of permanent hard water by adding sodium carbonate.

16. How can all the salts in hard water be removed without resorting to distillation?

17. What methods for obtaining drinking water are available to shipwrecked sailors afloat on a rubber raft?

18. How can suds be produced in hard water without removal of the dissolved salts?

19. From what materials are such commercial products as Dreft and Drene compounded?

20. What would be the most effective way of softening hard well water for a country home?

21. Define and illustrate hydrolysis of a salt.

22. Woolen clothes cannot be washed successfully with hot soapy water. How may they be cleansed?

23. Visit a dry-cleaning establishment, and write a report on the procedure for cleaning one's school clothes and recovery of the cleaning fluids. What compounds are used in the process?

24. Why is glycerol considered to be an alcohol? How is it obtained commercially?

25. Why do solutions of washing powders have an alkaline reaction?

26. How does the process of removing a grease spot with soap and water differ from that of removing it with gasoline?

27. What substances are formed when fats are hydrolyzed?

28. From what is silver polish made, and how does it accomplish the cleaning?

29. How can silver be cleaned "electrolytically"?

30. Why is rosin sometimes used as a flux in soldering copper wire?

31. Compile a list of soldering fluxes and the metals on which they are used.

Health

Antiseptics. A number of chemical compounds are used for killing germs. If the surface of the skin is washed with a little 70 per cent grain alcohol (ethanol, C_2H_5OH), the region is perfectly sterile. Surgical instruments may be sterilized by steaming them under pressure. Mercury (mercuric, valence II) chloride ($HgCl_2$) in solution with ammonium chloride (NH_4Cl) is a powerful antiseptic; but since it is very poisonous, care must be exercised in its use. Tincture of iodine (I_2), hydrogen peroxide (H_2O_2), and boric acid (H_3BO_3) are all well-known antiseptic agents. Each has its special uses. Phenol (carbolic acid, C_6H_5OH) is a useful germ killer.

In addition to general antiseptics, special compounds are available to attack fungus growths or infections of the body. Gentian-violet dye is used to combat impetigo, and ammoniated mercury ointment subdues infections. Copper naphthenate is a recently discovered remedy for ringworm and "athlete's foot." It is also used to prevent mildew on tents.

Medicines. No internal antiseptic has yet been found. Any compound strong enough to kill bacteria will also kill the corpuscles in the blood or injure tissue. Recently, however, certain compounds called the "sulfa compounds" as a group have been found to be most useful in medicine. They seem to attack germs in the body in such a fashion that the white corpuscles can kill them rapidly. Almost daily we hear about seemingly impossible cures from pneumonia and meningitis by use of sulfathiazol, sulfanilamide, sulfapyridine, or a related compound. Sulfadiazene is useful in intestinal disorders. The use of these compounds in powder form has gone far in the prevention of gangrene infections in wounds and overcoming other infections in the body caused by dangerous streptococcus bacteria.

Penicillin, an extract obtained from the mold *Penicillium notatum,* is another modern medicine that has produced remarkable cures for infections of the blood stream. The material was first described by Dr. Alexander Fleming in 1929. Today many difficulties connected with its production on a large scale have been overcome, and this important medicine has been added to the lifesaving resources available to the doctor.

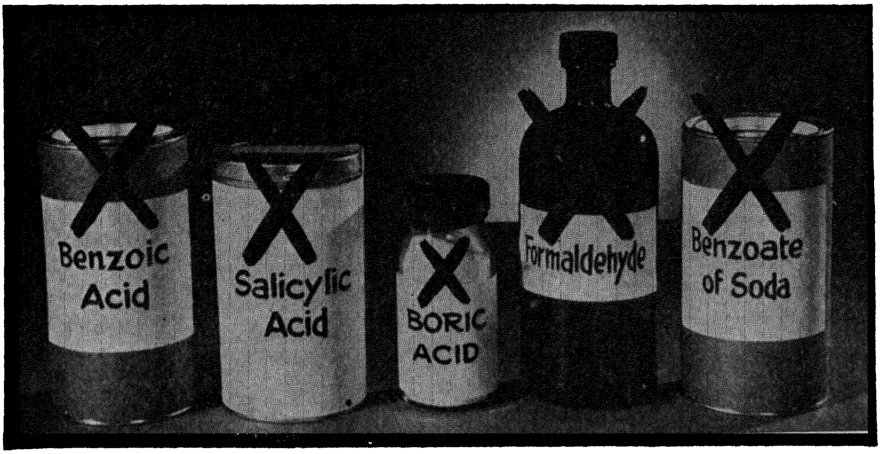
In addition, certain chemical agents are specific for definite ills. Ehrlich's six hundred and sixth experiment in the preparation of arsenical medicines resulted in ***salvarsan,*** which destroys the bacterial cause of the dread disease syphilis. Tetrachloroethane is used to "worm" dogs.

Experiments with the digestion of carbohydrates and the function of the pancreas in this connection led Banting and Macleod to the discovery of ***insulin,*** a hormone required in digestion produced by the pancreas. When this substance was purified and isolated, a specific remedy for diabetes was obtained. Diabetes is now listed among those diseases which are almost conquered, and this by the application of chemistry.

Space does not permit more than a suggestion or two to bear out the point that both organic compounds, such as aspirin, and inorganic compounds, such as sodium hydrogen carbonate (bicarbonate of soda, $NaHCO_3$) and magnesium hydroxide [milk of magnesia, $Mg(OH)_2$], play an important part as medicines that help us maintain or regain health.

Physiological Chemistry. A great number of experiments are in progress that deal with the application of chemistry to the functioning of the human body both in sickness and in health. The processes of digestion, respiration, growth, and recovery from disease are all studied with the greatest care. The effects of various medicines are watched in ***clinical*** chemistry, starting with animal experimentation.

One method of proceeding is to extract some of the active principle. This process is often a long, expensive one, for some substances like hormones and vitamins are present in the body in only the tiniest amounts. Dr. John J. Abel, an American investigator, prepared ***adrenalin,*** an extract obtained from tiny glands that are located on top of the kidneys. He was the first to obtain a hormone in crystalline form as a pure substance. This compound, manufactured synthetically, is now available to doctors as a medicine, epinephrine, and as such has been the means of saving many lives. It has the combination of properties of stopping bleeding and being a heart stimulant at the same time.



Courtesy of H. J. Heinz Company

FIG. 35-5.—These compounds are undesirable when used as preservatives in food.

Beauty

History of Cosmetics. Studies of Egyptian mummies reveal that the art of using cosmetics was well advanced as early as 4000 B.C. We have positive evidence that Roman ladies used stibnite (antimony black, Sb_2S_3) to darken lashes. Perfumes were first used to cover objectionable odors by their overpowering fragrance, but modern usage of perfumes in most cases is more delicate and subtle. In Elizabethan times a masculine parliament of England passed a decree making it unlawful for women to use cosmetics for the purpose of concealing their true age. Today beauty aids are available to men and women in all walks of life at moderate prices, due in part to modern methods of machine production.

The cosmetic business today grosses over 2 billion dollars a year, and reputable manufacturers employ chemists to check the quality of raw materials as well as to supervise their manufacture.

Powder. Talcum powder is chiefly ground rock talc ($Mg_3Si_4O_{11}\cdot H_2O$) with a suitable scent added. Face powder contains zinc white (ZnO) or titanium dioxide (TiO_2) for covering, kaolin clay for adhesion to the skin, precipitated chalk ($CaCO_3$) for absorbing perspiration, and talc for a slippery texture. In addition, more or less coloring matter and perfumes are added. Many variations of these ingredients are available.

Face Creams. Tests show that as a skin cleanser no superior substitute has been found for soap and water. In fact, frequent washing with soap and water is one of our best and simplest ways to keep well and aid in personal attractiveness. Soap has a slight antiseptic action. For most satisfactory results, users of face creams are advised to wash the face first. Creams cleanse and lubricate the skin.

Cold creams are a stable emulsion of (1) an oil (olive, mineral) and (2) a waxy material (beeswax, lanolin) in (3) water stabilized by (4) an emulsifier (borax, $Na_2B_4O_7$); (5) a perfume is added. These ingredients are simple and inexpensive. Indeed, a most satisfactory face cream can be made at home by using no more complicated apparatus than an ordinary double boiler and an eggbeater (see Appendix).

Vanishing creams are chiefly emulsions of potassium soaps. They correspond very closely to brushless shaving-cream preparations.

The variations possible in face creams are countless. Hence many varieties are on the market. None, however, will feed the body through the skin, which is an organ of excretion. Some creams are represented as bleaching, while others are alleged to remove freckles. Some of these preparations, especially bleaching creams, may contain mercury compounds. These should be used with the greatest caution, if at all; for mercury compounds are poisonous, and their use may result in disfiguring the face and marring beauty.

Lipstick. The basis of lipstick is a thick, waxy face cream, perfumed and colored. The fire-engine red color is obtained by the use of dyes. Irritation of the lips may develop if poisonous dyes, such as certain aniline dyes, are used.

Nail Polish. The original nail polish consisted of a mildly abrasive powder like talcum powder. Fingernails buffed on a chamois pad using this powder take on a smooth, satinlike polish. This method of polishing nails is still effective.

Many persons today prefer to coat the nails with a quick-drying lacquer, which dries with shiny surface and which has the added feature of the choice of a great variety of colors. The result of such paint jobs depends largely on the skill of the artist. Lacquer solvent or acetone [$(CH_3)_2CO$] will remove lacquer polish from the fingernails.

Dentifrices. Most dentifrices consist of a mild abrasive like precipitated chalk ($CaCO_3$), a little soap or soaplike material, such as the sodium salt of a sulfonated higher alcohol, and a pleasant flavoring. Other than convenience, no particular advantage can be claimed for the dentifrice in either the powder or the paste form. The purpose of a dentifrice is to clean and polish the teeth. A preparation that aids in doing this without injury to the teeth has fulfilled its purpose. Clean teeth are more attractive to look at than discolored or dirty ones. No relationship between the brushing of teeth and absence of tooth decay has been proved.

A dentifrice containing an abrasive as hard as pumice, which is harder than some of the exposed parts of the teeth, should be avoided. Sodium peroxyborate (perborate, $NaBO_3 \cdot 4H_2O$) in tooth powder may produce gingivitis, an irritated condition of the gums. Such inexpensive materials as salt, bicarbonate of soda, and precipitated chalk, plus a little flavoring, make a satisfactory, yet very inexpensive, homemade dentifrice. If the user prefers to froth at the mouth, he adds powdered soap.

Composition of Cosmetic Products. The composition of typical lotions, mascaras, rouges, toilet waters, perfumes, after-shave astringents, hair tonics, bleaches, depilatories, and styptic pencils can readily be found in standard reference books. There is no mystery about their ingredients. None can do anything more helpful for the user than to cause him or her to think of the impression being made on others by his or her personal appearance.

It is interesting to note that the use of cosmetics is, to a measure, to imitate the glow and natural radiant beauty of youth reflecting wholesome living. Those who possess these characteristics have little need for artificial aid.

SUMMARY

Soap is an important emulsifying agent for cleansing. It may be made at home by boiling fats with alkali and also may be made commercially in huge kettles from various fats and oils by reaction with either sodium or potassium hydroxides. An important by-product is glycerol (glycerin). Soap, which contains builders to make it a better cleansing agent, is packaged as cakes, flakes, or powder. Chemically, soap is a salt of a fatty acid; sodium and potassium soaps are soluble, but calcium and magnesium soaps are insoluble.

Mineral salts in "hard water" precipitate calcium and magnesium compounds by reaction with soap. "Soft water" lathers freely. Temporary hard water is softened by boiling. Permanent hard water must be treated chemically to remove minerals that react with soap to form a precipitate.

The newer detergents are not like soap; they are important in the processing of fabrics and metals, but they serve as cleansing agents even in hard water.

Hydrolysis is the reaction of ions of dissolved salts with water.

Salts of a strong base and a weak acid form alkaline solutions as a result of hydrolysis; and salts of a strong acid and a weak base form acid solutions. Salts of a strong acid and a strong base are neutral in solution. For example, Na_3PO_4 produces an alkaline solution in water by hydrolysis and aids in the removal of grease.

Dry cleaning involves the use of grease solvents like carbon tetrachloride and certain hydrocarbons, with various special soaps added to aid removal of solid particles.

Cleansing metals involves the removal of oxide or sulfide films. Fluxing forms a slag and cleans metals in a furnace.

Antiseptics are compounds that kill bacteria with little damage to their host. Many antiseptics are produced by chemists.

Like the newly discovered sulfa drugs, some compounds are given to persons for their specific effects; most medicines, however, produce a general, not a specific, effect; that is, they aid the body in overcoming the invading bacteria. Some are hormones, like insulin or adrenalin. Some are organic compounds, like morphine or aspirin, which reduce pain.

Physiological chemistry is the study of the chemical reactions of body functions.

Cosmetics are mixtures and compounds for aiding personal attractiveness. Included among cosmetics are talcum powder, face creams, lipsticks, and nail polish lacquers.

Dentifrices serve to clean and polish the teeth. Most dentifrices consist of a mild abrasive, a little soap or soaplike material, and a pleasant flavoring.

QUESTIONS

32. What antiseptics are usually found in the household medicine cabinet?

33. Write a theme on the history of chemotherapy, mentioning *Dr. Ehrlich's Magic Bullet.*

34. Are hormones drugs? What is insulin? Adrenalin?

35. Compile a list of safe household remedies for stocking a medicine cabinet.

36. What compounds are used as pigments in lipstick? Are lipstick pigments ever a source of irritation to the user?

37. What are the usual ingredients of tooth powders? Face powders? Talcum powders? Foot powders? Dusting powders?

38. In what way are fingernail lacquers and high explosives similar?

39. Why should one not remove stains from an acetate rayon garment with fingernail-lacquer solvent?

UNIT EIGHT . . . . CHAPTER XXXVI

CHEMISTRY FOR SAFETY, PEACE, AND WAR

The twentieth century has been marked by a steady increase in the insurance business, especially in the United States. This business has a peculiar interest in keeping people alive and well. Investigators for insurance companies study the causes of accidents and deaths at home and in industry. Facts are gathered about deaths from disease, also. For example, when a disease, such as cancer or heart disease, is one of the leading causes of death, public attention is drawn to it through advertising. Equal enthusiasm is devoted to the study of the cause and prevention of accidents. Safety engineers find out about safe and unsafe practices and materials.

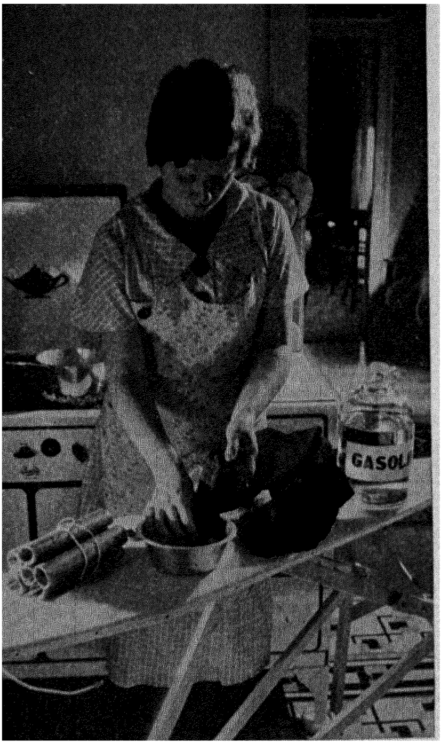
Courtesy of The Travelers Insurance Company

FIG. 36-1.—In this gas-air explosion at Oakland, California, the newspapers estimated damage of $50,000.

New Terms

detonation
cordite
allergy
vesicant
projectile

Gas-air Mixtures. In a hospital, the tense atmosphere of a certain busy operating room has relaxed. The operation has been concluded successfully, and the instruments are being put away. The air is still full of the gas used as an anesthetic. A nurse disconnects a light by pulling out an electric plug at a convenience socket. A spark is caused, and the entire room explodes.



Courtesy of The Travelers Insurance Company

FIG. 36-2.—This lady is far safer with dynamite on her ironing board than with an open pan and jug of gasoline and a flame at the stove.

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

People are hurt, possibly killed, and property destroyed.

A mechanic is working on a car. The guard has slipped off his portable electric light bulb with which he lights his work. The bulb swings against the motor, breaks, and exposes the white-hot tungsten wire to a mixture of air and gasoline vapor. A blinding flash of burning gasoline sears the mechanic and destroys the car.

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

These are all too frequent happenings. Mixtures of flammable gas and air (see page 527) have been known to flash back 600 ft and ignite the source. (See Fig. 36-1.)

Household fuel gas explodes when mixed with air in an oven. Gasoline, ether, some dry-cleaning fluids, turpentine, fingernail polish and other paints, and many similar liquids give off heavy vapors that mix with air and explode. It cannot be emphasized too often that the surest way to prevent accidents from such volatile flammable liquids as these is knowledge of their danger.

The carrying of gasoline into a home is dangerous. (See Fig. 36-2.) Most people do not understand that the vapors formed when gasoline is used constitute the chief hazard and that it is only a matter of chance whether or not these vapors will find some source of ignition, such as a pilot light in a kitchen stove or a glowing ember in the fireplace from yesterday's fire.

Colored Flames. When a truck stops by the roadside for repairs, a kerosene-burning, bomb-shaped lamp with an open flame is frequently used to warn travelers of the danger. This light will burn even in a rainstorm and will not be blown out in a high wind—hence its use around excavations.

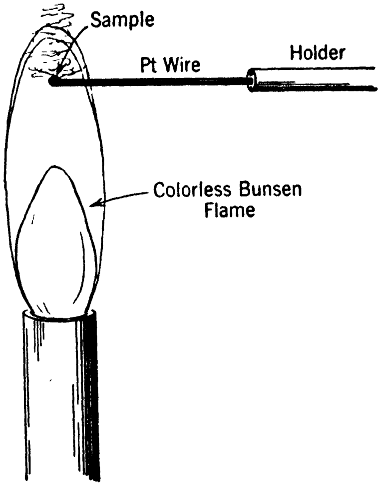


FIG. 36-3.—A sample of a strontium compound heated in a Bunsen flame colors the flame red.

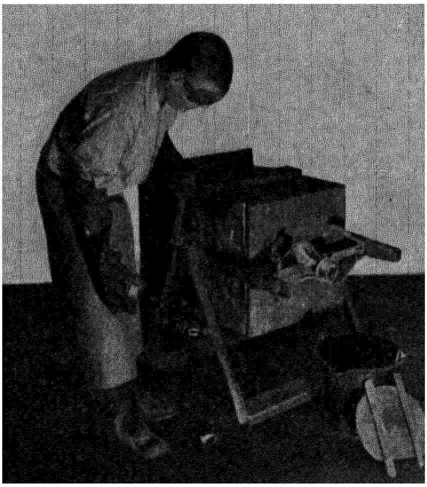
If the truck must be stopped on the highway itself, red flares are used. The burning material contains fuel, a supporter of combustion, such as potassium perchlorate ($KClO_4$) and some compound of strontium, for example strontium nitrate [$Sr(NO_3)_2$]. These red flames are used in celebrations as well as for danger signals on railroads and highways. The red-colored flame from all vaporized strontium compounds is characteristic and is a means of identifying them in the laboratory. The method of performing the test is illustrated in the diagram. (See Fig. 36-3.)

Lithium flames are scarlet and those from sodium compounds yellow. When held on a clean metal in a colorless flame, barium compounds produce a green color. Copper chloride gives a blue-green flame.

Curiously, no one yet has made candles suitable for home decorative lighting that burn with a colored flame. Many patents have been granted on this subject, but no satisfactory candles have been produced thus far. Colored smokes, however, are used successfully in warfare.

Safe at Home. Many accidents at home, such as a fall from a stepladder, are purely mechanical, but chemical knowledge will help prevent many other types. Chemistry cannot keep soap from being slippery, but chemists have helped develop nonskid mats for the bathroom.

All fires should have a proper draft to prevent the deadly carbon monoxide gas from entering the home. All furnaces and hot-water heaters should be connected to a chimney with sheet-metal pipes to remove all the carbon monoxide. This is especially true in the case of gas hot-water heaters, for the gas flame striking against a water-cooled surface is chilled below its ignition point, permitting some of the carbon monoxide to escape.



Courtesy of The Travelers Insurance Company

FIG. 36-4.—This is a safe method of pouring corrosive acid from a carboy.

Toilet articles, such as combs, brushes, and ornaments, made of celluloid or other flammable plastic material should be kept from hot-air driers. Photographic films, lacquers, and some toys are made of cellulose nitrate, which is violently flammable; they should therefore be kept away from open flames.

Modern technical chemistry applied to glass furnishes stronger, clearer glass, more free from strains than the product of a generation ago. The milk bottle of today makes five times as many trips as did the now-broken milk bottle of twenty years ago. The gas, Freon (CF_2Cl_2), used in a modern mechanical refrigerator is nontoxic, noncorrosive, and nonflammable, thanks to chemistry. Freon, however, does form poisonous hydrogen fluoride and hydrogen chloride in an open flame.

Other Safety Devices. The treads of stairways, especially in public buildings, are nonskid even when wet by virtue of the presence of some form of ground abrasive aluminum oxide (Al_2O_3) in the wearing surface. Today's steel is more uniform, stronger, and less subject to fatigue and corrosion than the metal of our father's day.

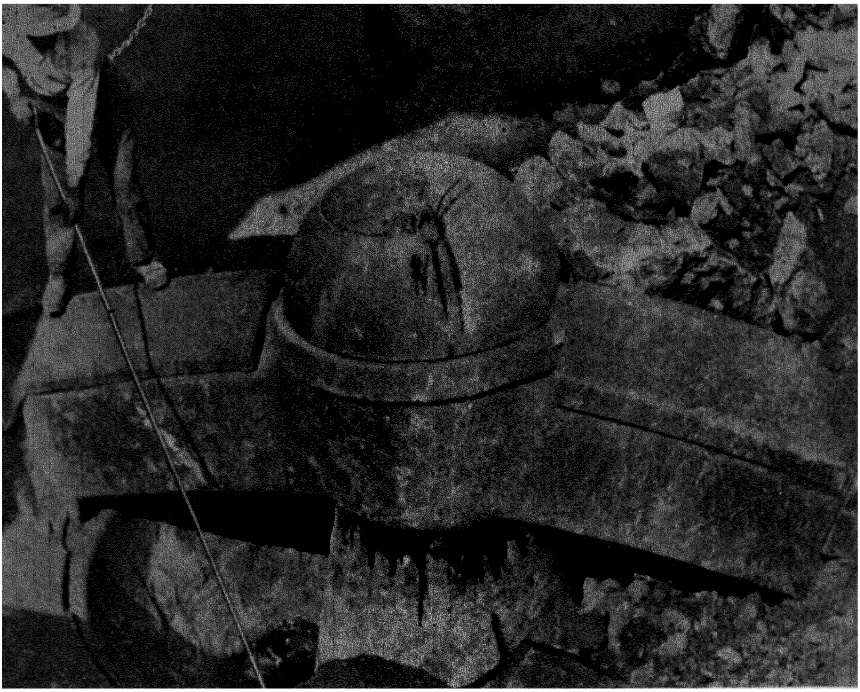
Spring steel, which failed after 3 million flexings in a corrosive atmosphere, is now replaced by beryllium-copper alloy, good for at least 1 billion flexings. The part that this alloy plays in making airplanes safe can be seen from the fact that more than 100 small but important parts of a modern transport plane are made of it.

Courtesy of The Travelers Insurance Company

FIG. 36-5.—These boys are trying a dangerous experiment—they were not forewarned. The bottle contains Dry Ice. Dry Ice in a bottle with the top screwed on has caused serious and painful wounds. What might happen?

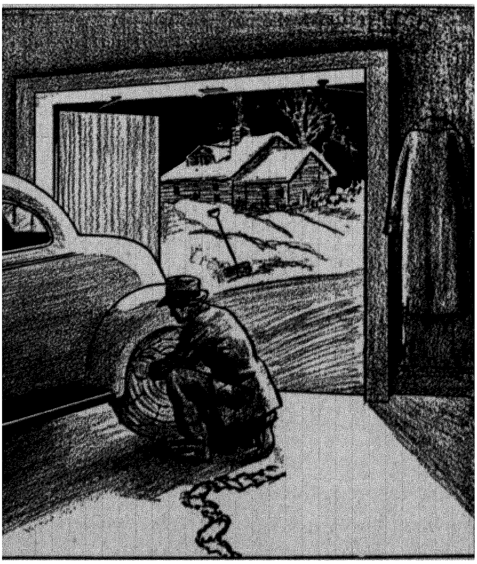
Irritating Dust. A great deal of rock wool and similar substances is used for home insulation purposes, and this is often installed by the homeowner. The dust produced during installation, although not dangerous, is irritating to the nostrils, and it is desirable that a filter type of respirator be worn. The dust is needlelike in form and, being alkaline, is likely to produce skin irritations, especially should a person perspire. For this reason, it is recommended that sleeves be kept rolled down and gloves be worn.

Allergies. Skin irritations, dermatitis, and allergies cause more losses from an occupational-disease standpoint than all other occupational diseases—silicosis, lead poisoning, benzol poisoning, and the like. Poison ivy is the classic example. Protective clothing against known irritants is helpful. Protective ointments, such as hand creams, are being prepared



Courtesy of Portland Cement Association

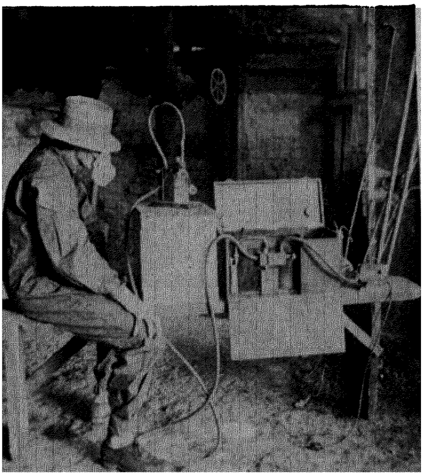
Fig. 36-6.—The crunching hard steel jaws of a gyratory crusher engulf a whole carload of rock. Observe the safety chain on the worker's belt.



Courtesy of The Travelers Insurance Company

Fig. 36-7.—The correct way to avoid carbon monoxide poisoning.

and used as a protection against irritants and solvents. Less irritating soaps or detergents are being recommended, especially where dyes or grease must be removed from the hands.



Courtesy of United States Metals Refining Company

FIG. 36-8.—This chemical engineer is obtaining a sample of air suspected of containing poisonous fumes.

Courtesy of The Travelers Insurance Company

FIG. 36-9.—A flour-dust explosion at Omaha, Nebraska, caused this disaster.

Thus we see that, as a result of applying the facts learned through chemistry, living is made safer and more secure. The careful observer will be able to extend this list almost indefinitely.

QUESTIONS

1. What gas was in the operating room in which the explosion described on page 618 occurred? Name two other anesthetics that produce explosive mixtures.

2. Name three possible sources of ignition of a gas-air mixture.

3. An electric light bulb smashed in gasoline vapor continues to glow during the explosion and for a short time afterward. Then it "burns out" quickly. Explain.

4. Suggest four safety rules for marking and handling cans of gasoline.

5. A painter, who has just finished mixing a quantity of paint, pauses to light a cigarette. A cigar lighter is struck in the dust-laden air of an attic that has just been "housecleaned." Explosions result in both cases. Explain. Give another example of an explosion that might take place at home.

6. List four flame colors and the elements that cause them.

7. Write formula equations for the following reactions: (*a*) barium chloride solution and sulfuric acid; (*b*) barium nitrate solution and sodium sulfate solution; (*c*) barium peroxide and sulfuric acid; (*d*) strontium nitrate heated.

8. Statistics show that persons are far safer riding in a train than at home. Explain how this is possible.

9. Why should all gas heaters be vented?

10. What danger exists in having no ventilation in a room containing a fire burning in a coal or wood stove?

11. Some rooms are heated by gas-fired radiant-heating devices. What danger accompanies their use?

12. Is it possible for combs in a lady's hair to catch fire?

13. Why are "starred" or chipped beverage bottles dangerous?

14. In a school building what measures are taken for (*a*) fire protection; (*b*) public safety? Do these involve chemistry directly?

15. How do workmen handling coal protect themselves from dust?

16. What dangerous condition develops when a tunnel is driven through granite? Does the same condition exist if the rock tunneled is limestone? What protective measures should be taken?

17. How can one avoid ivy poisoning while working near poison ivy vines? What first-aid measures are advisable to relieve ivy poisoning?

18. What is a safe manner of keeping and handling the following poisonous materials sometimes found at home: (*a*) arsenical flypapers; (*b*) arsenical ant baits; (*c*) insect sirup containing lead arsenate; (*d*) barium-containing rat poisons; (*e*) insect powder containing sodium fluoride; (*f*) bichloride of mercury tablets for making strong antiseptic solutions; (*g*) poison jars containing cyanides for killing insect specimens; (*h*) garden poisons containing calcium or lead arsenate?

19. What type of paint should be used on children's toys and play-pens? What type should not be used?

20. Give a new example of "better things for better living through chemistry."

Chemistry in War

Smoke Screens. Smoke screens for hiding ships as well as land targets are well known in naval and military strategy. (See Fig. 36-10.) On the water a destroyer cuts down the air supply to its oil-burning boilers and provides more oil than can be completely burned. A dense black smoke billows from its stacks, screening the convoyed merchantmen or battleships.

On land, white phosphorus is an effective material for creating smoke. When dry, the element ignites spontaneously and burns, forming a dense white cloud.

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

Other smokes depend on the presence of moisture in the air. Tin tetrachloride ($SnCl_4$), titanium tetrachloride ($TiCl_4$), or sulfur trioxide (SO_3) dissolved in concentrated sulfuric acid when released into the air forms dense clouds of acid smoke.

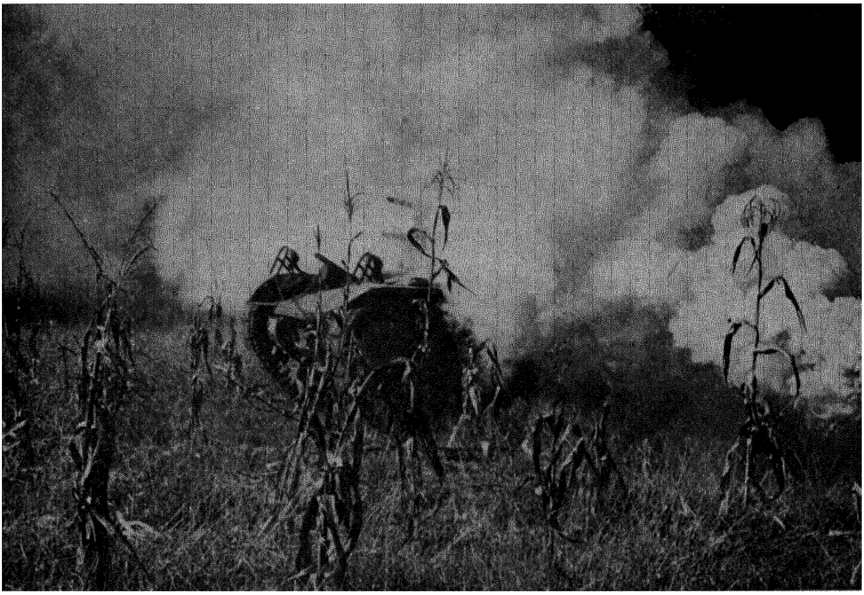
$$SnCl_4 + 4HOH \rightarrow 4HCl + Sn(OH)_4\downarrow$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

Peacetime uses of this practice are seen in skywriting and spraying or dusting growing plants from an airplane. Colored smokes are available.

Odds for Death—Gas 1 to Steel 12. Almost everyone thinks that, given the choice of being overcome by gas in warfare or stopping flying fragments of lead or steel, the second is the better choice. Death or wounds from being struck is more understandable to the average person.

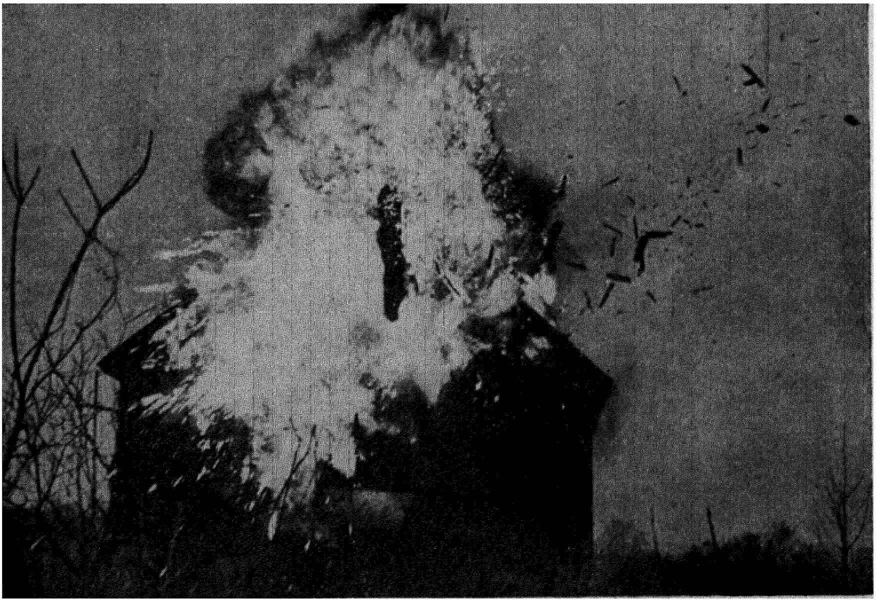
Let us take a look at the facts as revealed by World War I. The Surgeon General of the United States Army reported that 27.3 per cent of all disablements then were due to gas. Of these, 98 per cent recovered. Of those wounded by other means, 25 per cent failed to recover. A permanent or fatal injury from steel had 12 to 1 odds over injury from gas.

That is, gas from a military standpoint was more effective in that it disabled the enemy and put his men in the hospital, but as a whole it was more humane than steel or disease. There are relatively few aftereffects of gas if the soldier is in good health. Also, gas drives defenders out of dug-in positions more effectively and humanely than any other known method—that is, if war can be considered humane in any respect.



Courtesy of U.S. Army Signal Corps

FIG. 36-10.—A tank battalion in training maneuvers rolls through a smoke screen.



Courtesy of Chemical Warfare Service, U.S. Army

FIG. 36-11.—This explosion of a gasoline-filled incendiary bomb was carried out to test the destructiveness of such a device.

Gas Warfare. The first use of gas warfare goes back to nature herself. The effective use of stinking mercaptans as a weapon of offense and of defense is distinctly remembered by those who have molested a skunk. The smoke and stench of burning sulfur and pitch were used in the siege of some cities in ancient times.

Modern gas warfare started in April, 1915, when the Germans used chlorine gas at Ypres, France. The gas was dense and hence was carried by wind and gravity. Its successful use depended on surprise. Although the Allied intelligence had informed the authorities of the planned attack, no serious effort was made to combat it.

Later phosgene ($COCl_2$) was used. This irritates the eyes and causes vomiting, as well as being extremely poisonous. It was used in an attempt to make soldiers remove their gas masks. This gas was successful from a military standpoint because the effects are often delayed, giving the victim a short period of false security when he should be taking treatment to counteract the poison.

In 1917 the Germans used the famous mustard gas [$(CH_2Cl{\cdot}CH_2)_2S$]. This is really a liquid that evaporates in the heat of the sun. It irritates the lungs, burns the skin, and disables men for a long time. It is classed as a vesicant, and it is one of the most persistent of the war gases.

Just at the close of World War I, lewisite ($CHCl{:}CHAsCl_2$) was developed. This deadly liquid irritates the eyes and has all the poisonous qualities of the other gases combined. Fortunately, lewisite was never used for military purposes, and all that had been manufactured was dumped into the sea shortly after hostilities stopped. No general use of poison gas was reported in World War II.

The term ***poison gases*** includes both poison fogs and smokes. Their purpose is to render an area untenable. If a persistent type of gas or liquid is used, an area is forbidden to any occupation, enemy or friendly, for several days, possibly a week.

To be effective for military use, a substance must either be a gas or become a gas at ordinary air temperatures. It must not act chemically on the steel tanks that hold it or on their metal fittings. It must be cheap and simple to prepare. Mild heating should not decompose it, and it must withstand compression. Moreover, when diluted by a relatively large amount of air, it must still be intolerable to the human body. Only a few substances are known that meet all these requirements, even after an intensive search has been made. No great fear for new disastrous war gases need be felt although the nitrogen-mustard gases are reported as being extremely deadly. Also, protection against all sorts of war gases is keeping pace with their production and use.

Defensive Gas Warfare. Along with offensive gas warfare, the protection of soldiers and animals from the effects of gas is equally important.

The canister type of gas mask is generally used for this purpose. (See Figs. 36-12, 36-13.) The canister contains activated charcoal (see page 549), soda lime [(NaOH—CaO) mixture especially prepared], other chemicals, and layers of absorbent cotton and other filtering substances. The breathed air passes in through the canister, which effectively filters out poisonous fogs and smokes and absorbs poisonous gases. After a limited time the canister must be replaced. No effective protection against mustard gas had been devised at the end of World War I. Today gas masks and a complete suit of protective clothing are available to protect soldiers against various gases.

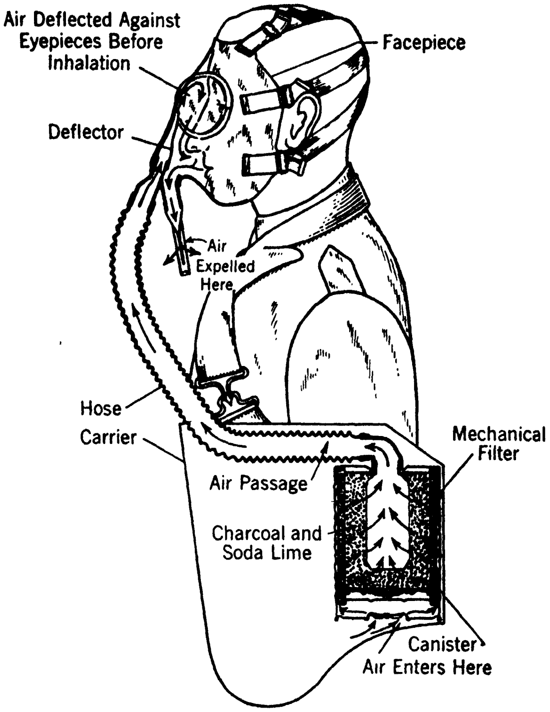
Courtesy of Chemical Warfare Service, U.S. Army

FIG. 36-12.—Three soldiers show how standard service, diaphragm (for shouting orders), and optical gas masks are worn.

Experience gained in gas warfare has helped in developing effective gas masks for protection in case of fire, industrial, or mining hazards. Firemen, repair men, and rescue squads can be properly equipped to save life, stop the spread of disaster, or remove the cause of trouble.

Explosives—Gunpowder. Black gunpowder was invented by the Chinese and used for firecrackers. Later, it was adapted to military uses by the Europeans. It contains saltpeter (KNO_3), carbon, and sulfur. The more effective sodium nitrate, although hydroscopic, may be substituted for potassium nitrate if the powder is kept in an airtight container. When exploded, black gunpowder makes much smoke. It is too weak for modern military demands, but it is extensively used for blasting.

Detonation. In order to start a large explosion, an electric spark or the mechanical shock of a small explosion is used. Such a preliminary explosion shock, or detonation, may be caused by igniting mercury fulminate $[Hg(ONC)_2]$ or lead azide $[Pb(N_3)_2]$. The extensive use of mercury fulminate as a detonator in military explosives boosts the wartime price of mercury.



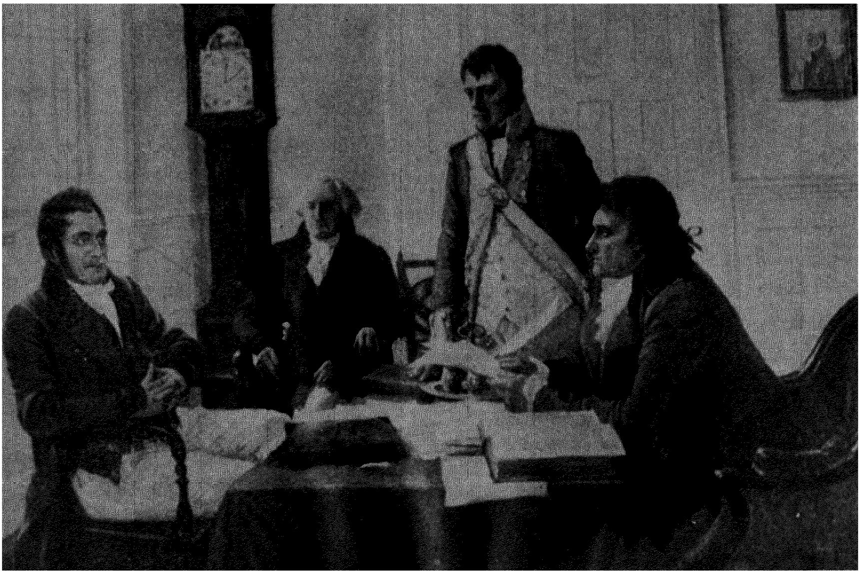
Courtesy Chemical Warfare Service, U.S. Army

FIG. 36-13.—The passage of air through the canister and the gas mask (service type).

Preparation of High-power Explosives. A nitrating mixture of nitric and concentrated sulfuric acids is used in the preparation of the so-called "nitro" explosives. The concentrated sulfuric acid serves to remove water.

$$\underset{\text{glycerol}}{C_3H_5(OH)_3} + \underset{\text{nitric acid}}{3HNO_3} \xrightarrow{\text{conc } H_2SO_4} \underset{\text{glyceryl nitrate}}{C_3H_5(NO_3)_3} + 3H_2O$$

Glyceryl nitrate is a colorless oily liquid. It is commonly called nitroglycerin and is known as "soup" among "yeggs" according to the detective stories. In medicine it is used as a heart stimulant, but it should not be handled by the fainthearted, for it is a very sensitive explosive and resents all kinds of rough treatment. We have seen how Alfred Bernhard Nobel tamed this explosive by absorbing it in wood flour to make dynamite (see page 364).



Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 36-14.—American history and chemical history are tied together in this picture. Here we see E. I. du Pont de Nemours, Esq., discussing the location of the first American powder mill with President Thomas Jefferson.

Nitrocellulose, or guncotton, is made in a similar manner, except that cotton instead of glycerol is the raw material. After nitration, the guncotton is dissolved in ether and alcohol to form a jellylike mixture. This is extruded into "grains," or cylinder-shaped rods of the explosive, ready for use. The propellant charge for a projectile used frequently is ***cordite,*** a mixture of 65 per cent guncotton, 30 per cent nitroglycerin, and 5 per cent petroleum jelly.

Nitro Compounds. When the same nitrating mixture of acids mentioned in the previous paragraph is put on phenol, a chemical change takes place, resulting in tri-nitro-phenol, or picric acid, a beautiful yellow crystalline substance that is an excellent dye for silk as well as an explosive compound when detonated.

$$\underset{\text{phenol}}{C_6H_5(OH)} + 3HNO_3 \xrightarrow{\text{conc } H_2SO_4} \underset{\text{picric acid}}{C_6H_2(OH)(NO_2)_3} + 3H_2O$$

Starting with toluene, a similar compound, except that the methyl

(CH_3) group is present in place of the hydroxyl (OH) radical, a similar result is obtained upon nitration; *t*ri-*n*itro-*t*oluene.

$$\underset{\text{toluene}}{C_6H_5(CH_3)} + 3HNO_3 \xrightarrow{\text{conc } H_2SO_4} \underset{\text{TNT}}{C_6H_2(CH_3)(NO_2)_3} + 3H_2O$$

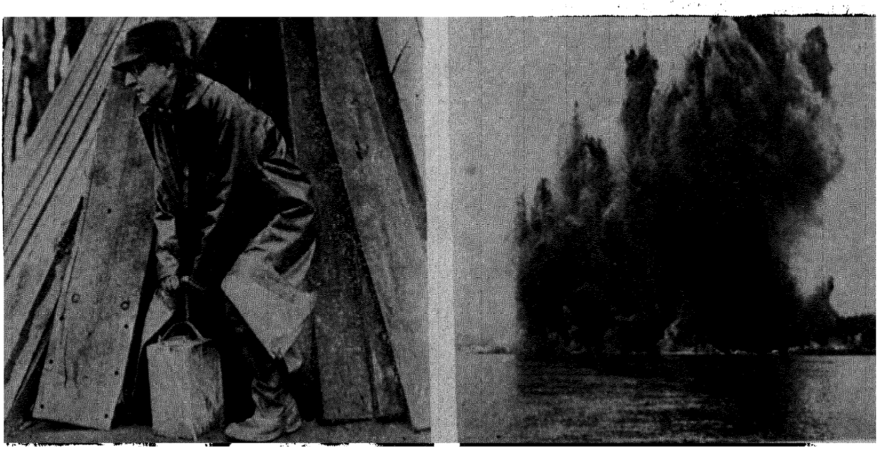
The bursting charge in a projectile, the explosive that is to shatter the steel into bits and send them flying on their destructive errands either on impact or on firing by a previously set fuse arrangement, is frequently

(*a*) (*b*)

Courtesy of E. I. du Pont de Nemours & Company, Inc.

FIG. 36-15.—(*a*) Shows cases of 60 per cent gelatin dynamite unloaded and (*b*) put into tubes to blast a trench for the "Big Inch" oil pipe line in the bottom of the Susquehanna River. (*c*) The charge of 16,000 pounds is ignited and (*d*) a powerful blast follows in part of an eight-foot-deep trench, 2000 feet long. In all, 60,000 pounds of dynamite were used.

(*d*)



called amatol. (See Fig. 36-16.) This explosive is a mixture of TNT and ammonium nitrate (NH_4NO_3).

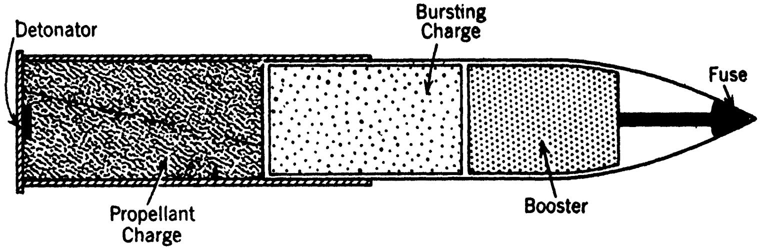


FIG. 36-16.—A military projectile, simplified, consists of several types of explosives.

Dyes and Explosives. Before the start of World War I, Germany was the only country in the world that specialized in manufactured synthetic dyes from coal tar. As we have just seen, the methods of making dyes and the methods of making explosives are much alike; similar materials are used, and the same sort of manufacturing experience is needed. In fact, picric acid is one example of a compound that can be used for either purpose (see page 630). Thus Germany had a military advantage over the allied countries opposing her through her knowledge of chemistry.

When the war was in progress and Germany was shut off from trading with the rest of the world, dyes became scarce, and explosives more so. Forced by this situation to manufacture these products for her own use, the United States developed a vigorous chemical industry. After a period of learning, dyes were eventually produced that equaled and surpassed those formerly obtained from Germany.

Chemistry in Peace

Causes of War. Some of the wars of the past have been fought over principles or religion, but many others have been wars of conquest for land. Among the fundamental causes of war and mass movements of people seeking new land, we must include hunger or fear of hunger. Their own land limited or unproductive, people have started out in search for better land, sometimes taking it from its former owners by force.

As related in the ancient Hebrew story in the book of Genesis (3: 19, 4: 12) in the Bible, among the punishments laid upon Adam for eating forbidden fruit and upon his son Cain for murdering his brother Abel was that the earth would yield crops only after a hard struggle. The apparent unwillingness of the earth to produce food in abundance is evident. Once a garden is used, its productivity drops off sharply unless it is fertilized. After a few years' use the earth becomes well worked and in good condition for farming, but the crop is not worth the effort to raise it. This discouraging situation is explained and given a moral meaning in the Bible stories.

We know now that the productivity of the land can be renewed by the use of fertilizers (see page 290), but such knowledge came slowly. The rivers, such as the Nile, that overflowed their banks each year and brought fertility to the soil were the centers of early civilizations. In such regions, where people were free from the fear of lack of food and of the necessity of working hard all day long for enough food merely to live, the arts flourished and a measure of culture developed.

Today, also, the growing of food does not occupy all the time of the human race. Thanks to chemical fertilizers we have some time to spare. We see, then, that applied chemistry offers a solution to the everpresent food problem. The answer in the past has been war in many cases. If nations that are growing rapidly in population can be freed from the fear of lack of food, then time need not be spent in military activity in preparation for conquest.

The Trade Route to Chile. What has been said about lack of food holds true in less measure of other raw materials.

In the country of Chile in southwest South America lies an extensive deposit of nitrates. This mineral deposit is unique; in no other place are there such resources. Nitrates are needed for two important purposes—for making explosives and for fertilizers. These two uses are important in peacetime and indispensable in war. A nation that was cut off from a trade route to Chile would feel handicapped, especially if that nation was ambitious, energetic, and highly industrial in its activities. Such was the situation of Germany before World War I. Stores of nitrates had been accumulated, but the supply melted away when wartime demands were added to normal needs. We have seen that, when nitrates are added to sulfuric acid and warmed, nitric acid is produced. Nitric acid is needed for manufacturing explosives, such as glyceryl nitrate (nitroglycerin) and smokeless powder, or guncotton. The connection between Chilean nitrates and explosives is therefore direct. Without nitrates no large amounts of explosives could be made. Also, without a trade route to Chile there was danger of starvation.

Nitrates for All. Chemical work by Fritz Haber in Germany, by the United States Fixed Nitrogen Laboratory, and by others has shown clearly that nitrogen from the air, together with hydrogen from water, could in the presence of catalysts be made into ammonia (see page 386). The ammonia can be oxidized to nitric acid by oxygen from the air by the catalytic method of Ostwald (see page 362).

No nation is lacking in air and water. Hence all can produce nitrates, and a supply of the most easily exhausted fertilizing material is now assured, depending only on power resources.

Stakes of War. Military objectives in World War II included sources of raw materials, such as coal, iron ore, rubber, manganese, tungsten, and other metals and especially petroleum. A steady supply of all these materials is demanded industrially, especially in wartime. Without them, industries must shut down or find a suitable substitute; and if factories shut down, people face starvation. Nature has distributed these raw materials on the earth without the slightest regard to national boundary lines or man's convenience in obtaining them. What help has chemistry to offer in supplying these needed raw materials?

Assume that we had to get along with a smaller supply of iron ore. Could we use wood, aluminum alloys, or plastics as substitutes? The results of such substitution have not always been satisfactory, but sometimes interesting and valuable progress has resulted. In fact, for years the timing gears of automobiles have been made of layers of cloth impregnated with plastic material (phenolic resin, for example) instead of steel.

Among the possibilities of alternate materials must be mentioned the following: (1) aluminum—or copper; (2) gasoline—or alcohol or similar liquid fuel obtained from an annual crop; (3) white lead—or titanium oxide; (4) tin—aluminum or, for foil, waxed paper; (5) tungsten—or molybdenum; (6) rubber—or synthetic chlorinated rubberlike material.

Thus a knowledge of chemistry points out the possibility of a satisfactory or even a superior substitute for many substances. Chemistry points the way to an improved use of our power resources. Chemistry offers a solution to the ever-present problem of food supply. In these ways chemistry becomes a force for peace.

SUMMARY

A knowledge of chemistry promotes our safety in many respects.

Flammable gas-air mixtures are among the most common causes of explosions. Carbon monoxide poisoning may result from household fuel gas, from any fire not properly vented, and from the tail-pipe exhaust gases of gasoline engines. Celluloid and other nitrocellulose products burn rapidly. Dusts may produce irritation if sharpedged or silica-containing. Some plants, such as poison ivy, irritate the skin.

Steps to avoid accidents include the use of safety motion-picture film at home, the use of nontoxic refrigerants, stronger glass, and more reliable metals, and careful handling of poisons.

Colored flames warn of danger. Luminous flames from kerosene contain glowing unburned carbon. Green flames contain barium compounds, sometimes copper. Red flames contain strontium compounds. The color imparted to a flame by lithium is crimson; by sodium, yellow; by potassium, violet.

Chemistry plays its part in war and in maintaining peace.

Smoke screens may be formed from clouds of sooty smoke, phosphorus pentoxide from burning white phosphorus, or hydrogen chloride mist formed by hydrolysis of certain chlorides. Gas warfare in World War I proved less disastrous than other forms of destruction.

Chlorine was the first gas used in offensive gas warfare. Phosgene, used later, caused extensive casualties. "Mustard gas," a volatile liquid, is a persistent vesicant. Lewisite, an arsenic-containing vesicant, is available. Only a few substances have the properties needed for offensive gas warfare.

Gas masks are used in defensive gas warfare. In the canister type of gas mask, the canister contains filters for smoke and fog and activated carbon, soda-lime, and other chemicals to absorb poisonous gases. A complete suit of gas-resisting clothing is needed to protect against vesicant gases. Improved masks are now available to meet industrial hazards.

Gunpowder, a mixture of sulfur, saltpeter, and charcoal, was the first military explosive. Detonators are explosives that set off other explosives. Mercury fulminate is used extensively as a detonator. High explosives are made by nitrating, that is, by using a mixture of concentrated sulfuric and nitric acids.

Nitrating glycerin produces glyceryl nitrate. Nitrating cotton produces guncotton. Nitrating phenol produces picric acid. Nitrating toluene produces TNT. Military explosives are usually mixtures of the foregoing materials, including ammonium nitrate in some cases.

In World War I the chemical industry of Germany gave that country an advantage over the Allies. World War II found the United Nations with chemical resources matching those of the Axis nations.

Chemistry has aided in removing the causes of war by providing chemical fertilizers. The trade route to Chile saltpeter is now less coveted. Chemical resources, especially petroleum, rubber, tin, manganese, iron ore, and tungsten, were important factors in World War II. Applications of chemistry are sought more and more by nations to provide many needed substances or suitable substitutes.

QUESTIONS

21. How are smoke screens made (*a*) at sea; (*b*) by land troops; (*c*) by airplanes?

22. Is it possible to (*a*) sow seeds; (*b*) spread insecticides by airplane?

23. Write an essay supporting the use of poison gas in warfare.

24. Present the case against the use of poison gas in warfare.

25. When pitch and burning sulfur are mixed, what two ill-smelling gases are formed?

26. Name a marine creature that uses a "smoke screen" for protection.

27. In event of a gas attack on a city we are told that civilians are reasonably safe in a closed room on the second floor. Account for this.

28. Make a list of the specifications of a gas suitable for offensive warfare.

29. Outline the specifications for a gas mask and canister suitable for protection of soldiers.

30. Will a military gas mask give protection (*a*) against carbon monoxide; (*b*) against sulfur trioxide mist; (*c*) in a room where the oxygen content is low; (*d*) indefinitely?

31. Point out the similarity in the manufacture of TNT, "nitroglycerin," picric acid, and guncotton.

32. A 100-pound lot of gunpowder contains 75 pounds of potassium nitrate. What weight of sodium nitrate will supply an equivalent amount of oxygen?

33. For what purpose can wet gunpowder be used?

34. Under what conditions may sodium nitrate be substituted for potassium nitrate in gunpowder?

35. What is the composition of (*a*) dynamite; (*b*) cordite; (*c*) amatol; (*d*) guncotton; (*e*) gunpowder?

36. During World War II, government advertising displayed in grocery stores and newspapers urged housewives to "Save Fat for Gunpowder." What was the intended meaning?

37. A large projectile contains two detonators, two booster charges, a propellant, and a bursting charge. State the purpose of each explosive.

38. Point out three chemical advantages that Germany possessed at the beginning of World War I.

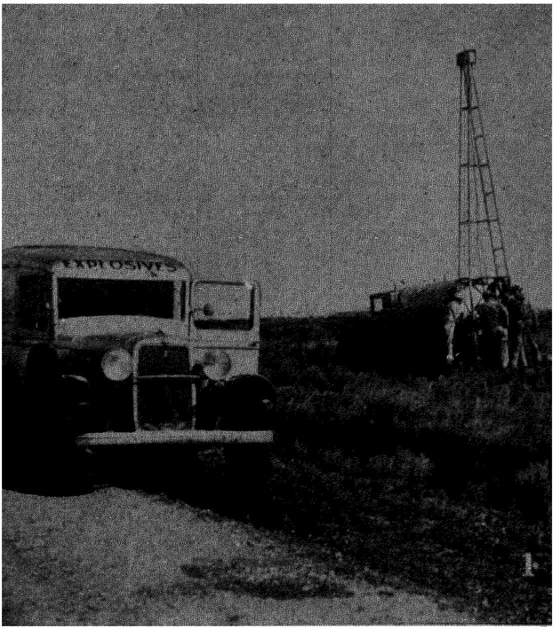
39. World War I started soon after the development of the Haber process of nitrogen fixation in Germany. World War II started soon after the development of synthetic high-octane gasoline in Germany? How are these chemical facts connected with the starting time of hostilities?

40. In what respects may World War I be called the Nitrogen War?

41. Point out ways in which chemical progress may act as a force for (*a*) war; (*b*) peace.

42. What effect have the sulfa drugs made upon the death rate from wounds in World War II?

UNIT NINE



ADDITIONAL TOPICS

THE petroleum industry deserves considerable study. Petroleum is our principal liquid fuel. From it are derived many products, many of them pure compounds.

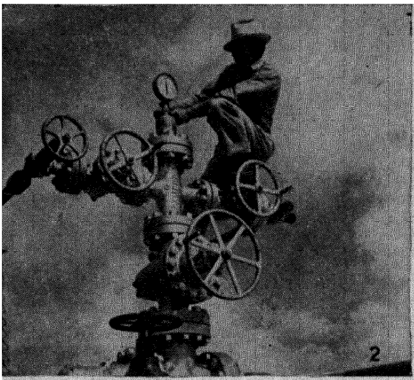
Explosives are used to explore for oil fields. Sound waves, set up by a small dynamite explosion (1), are recorded by a seismograph (vibration-indicating instrument), indicating the presence of structures favorable to petroleum discovery.

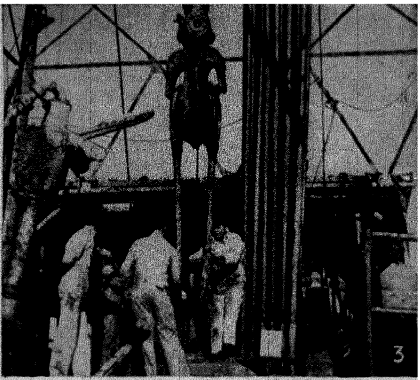
Picture (2) shows a worker who has climbed onto the "Christmas tree," one of the many devices used to control the flow of oil and gas and to prevent wasteful "gushers."

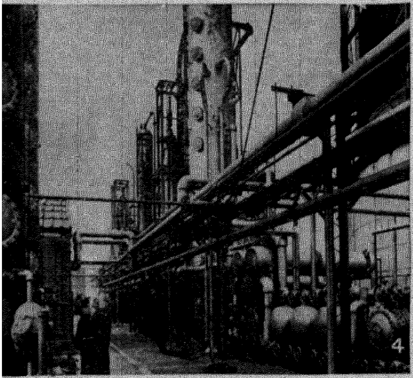
Drilling for oil is a rugged task. It calls for heavy equipment, a trained crew, and technical skill. Picture (3) shows a rotary-drill rig good for a 15,000-ft crunch into the rock below.

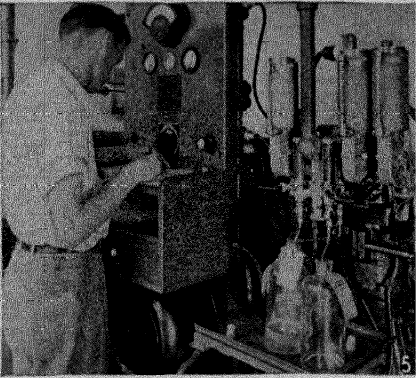
A refinery is a complicated maze of pipes and towers. While some may look like the product of futuristic artists or crazy plumbers, they are, on the contrary, carefully designed and engineered. In these towers (4) oil absorbs gases to aid in yielding gasoline. Each run of gasoline must be tested in the laboratory for performance.

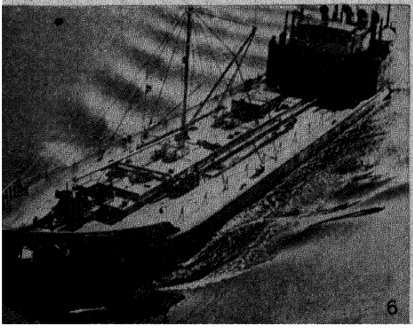
The testing engine (5) has an adjustable compression ratio and interchangeable carburetors. Volatile flammable petroleum products are shipped by steamer (6), tank cars, or pipe lines, and stored in spheroid tanks (7).











Photos courtesy of American Petroleum Industries and Free-Lance Photographers Guild

UNIT NINE - - - - - - - - - - - - CHAPTER XXXVII

RADIOACTIVITY

The sight of a beautiful wild mustang stirs something in the heart of a stalwart cowboy. He wants to saddle and ride the spirited animal. The same challenge of the untamed is felt in the element radium by scientists. No one has tamed radium. It goes its own way unaltered by man's most extreme efforts.

Where Radium Is Found. The element radium is widely distributed, but it is by no means abundant. One of the most interesting sources of this element is the ore from a region almost on the Arctic Circle, near Great Bear Lake in northern Canada. Besides radium, silver and uranium are present in the ore. From the northern mine the ore is transported partly by airplane to extraction plants, where it is treated by a method which resembles that first used by Mme Curie.

The Discovery of Radium. Marie Sklodowska, later Mme Marie Curie (1867–1934), the leading woman scientist, the greatest woman of her generation, and the first person to receive a Nobel prize twice, started her career unimpressively. Driven by intolerable political oppression from her home town of Warsaw, Poland, she studied at Cracow and later went to Paris. There she lived in very poor circumstances, but happily, doing laboratory drudgery while studying at the Sorbonne. It was here that she met Pierre Curie, a young physics professor. Romance entered the laboratory. The two married and continued their careers with scientific fervor. When in 1906 Pierre Curie was killed in a traffic accident, Marie bravely carried on her researches alone, comforted by her two children and encouraged by scientists all over the world. (See Fig. 37-1.)

Antoine Henri Becquerel (1852–1908), a French physicist, had previously made a study of a radiation resembling X rays that is emitted from certain minerals. He found that uranium, an element of

---

New Terms

radium
alpha particles
beta particles
gamma rays
transmutation
uranium
fission
subatomic energy
fractional crystallization
mother liquor
atomic bomb

high atomic weight, has the ability to act on a piece of photographic film although the film is covered and not exposed to light. This element, he found, is apparently a source of X rays. It scatters rays that affect photographic paper and makes the air near it a conductor of electricity. These rays are produced continuously, can penetrate solid objects, and are easily detected. This spontaneous production of radiations he termed ***radioactivity.***

FIG. 37-1.—This French commemorative postage stamp honors the discoverers of radium. The premium above postage goes for cancer research. See stamp, 1*f* 75 for postage plus 50*c* for cancer research.

Marie Curie investigated this new property, radioactivity. She found it exhibited by all compounds of uranium, and in intensity proportional to the amount of uranium. Then she investigated all other known elements to find out whether any were radioactive. Thorium proved to be the only other one. Both uranium and thorium are elements of very high atomic weight.

Marie Curie wrote,

> In my general examination of so many chemical products I had taken not only the pure elements and their compounds, but also natural products, ores, and minerals, and it is then that I came face to face with unexpected facts. I expected, of course, that all minerals containing uranium and thorium—very often the same minerals contain both elements—would be radioactive, but it seemed also, from my point of view, that none of them ought to have as much radioactivity as pure uranium or thorium oxide. But what I found was quite different! I found several minerals that had stronger radioactivity than the oxides of thorium and uranium, the ratio being as high as 4 in the case of one sample of pitchblende. In order to explain this abnormal behavior of minerals, I admitted that in those minerals was contained some new element with an atomic radioactivity much stronger than that of uranium and thorium, and which could be present in the minerals only in a very small proportion, because they were not detected in the analysis of the mineral. This particular hypothesis has been verified by the discovery of polonium and radium by Prof. Curie and me.[1]

A ton of pitchblende ore residues was given to these courageous experimenters by the Austrian government. In this ton there was contained only about $\frac{1}{5}$ g of radium. Finding a needle in a haystack would have been a much simpler problem. The pitchblende had distributed in it both radium and barium compounds. Radium is almost identical in its behavior with barium. After chemical treatment of the pitchblende, the resulting solution was heated a certain time: barium bromide was thus

---

[1] *Chemical and Metallurgical Engineering*, vol. 24, p. 1138, 1920.

crystallized, and radium bromide crystallized with it. But when the two compounds had partly crystallized, the Curies discovered that a little more of one compound was in the crystals and a little more of the other was in the ***mother liquor*** from which the crystals were forming. This was the greatest difference between radium and barium compounds which they were able to find and by which they could separate the two. With this slight difference as their only key, they set about the laborious task of isolating the radium compound from the barium. The process involved ***fractional crystallization.*** A set of radium bromide crystals was allowed to form; the mother liquor was poured off and saved, and the crystals were redissolved and recrystallized. The liquids of the same radium concentration were combined, evaporated, and recrystallized. After this process was repeated hundreds of times, a liquid finally resulted that contained almost pure radium bromide, only $\frac{1}{10}$g, but the first in the world to be obtained.

A small sample was enough to find out the atomic weight of the new element, 226, and to allow its spectrum picture to be taken in a spectrograph (page 48).

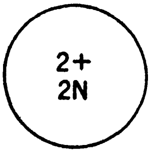


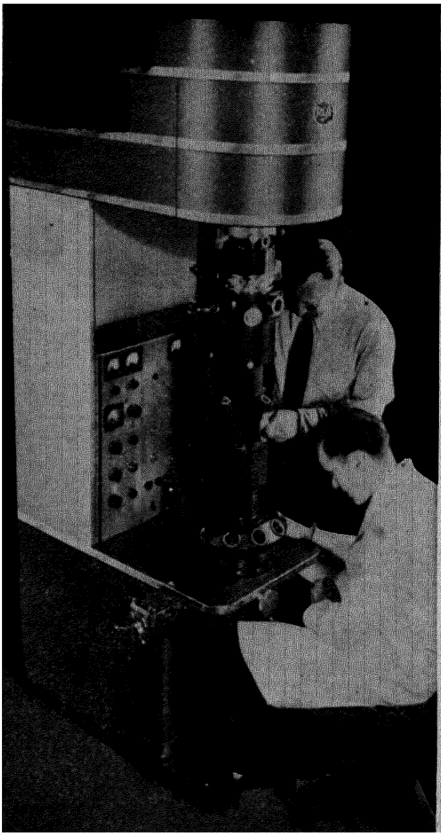
FIG. 37-2.—The nucleus of a helium atom is called an alpha particle when it is ejected.

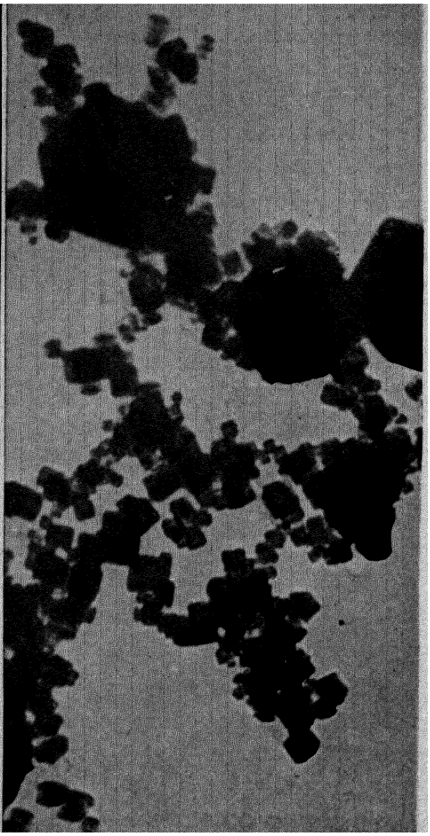
Radium's Projectiles. The chemistry of radium, being similar to that of barium, is not startling. Its atomic properties, however, are amazing. We find that radium or its decomposition products, as well as other naturally occurring radioactive elements, give off three sorts of radiations, named for the first three letters of the Greek alphabet.

The ***alpha particles*** are positively charged helium atoms. They are the nuclei of the helium atoms (see Fig. 37-2), consisting of two protons and two neutrons. The outer shell pair of electrons is missing. Hence the alpha particle has a net positive charge of two units. These alpha particles are shot out over 300,000 times faster than a car traveling at 100 miles per hour. They may drive through as much as 8 cm of air at ordinary pressure, knocking a few million electrons off "air" molecules on their way. When an alpha particle gathers in two electrons, it becomes an ordinary helium atom. The tiny trace of helium found in the air has its source in the minerals of the earth that contain traces of radioactive compounds that are continually shooting out alpha particles.

The ***beta particles*** are electrons moving with almost the speed of light. Just like electrons moving in a long glass tube, they can be deflected from their path by a magnet or by an electric charge (see page 180). They are attracted toward any positively charged object. Hence they must carry negative electric charges. These particles or rays have more penetrating power than alpha particles.

The ***gamma rays*** correspond to the splash created by the escape of the alpha or beta particles and are energy radiations. Gamma rays are shorter in wave length than visible, ultraviolet, or even X-ray light waves, although of the same nature. They have high ability to penetrate solids. The gamma rays from radium cause it to act on a photographic film. They travel in a straight line at the speed of light and are not affected by a magnet or an electric charge. They are shut off only by collision with heavy atoms, for example, lead nuclei in sheets of lead about 4 in. thick.





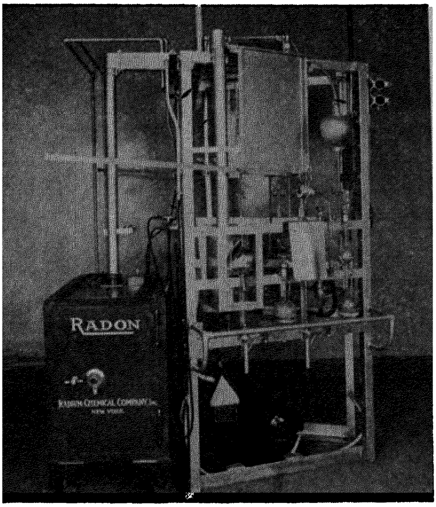
Courtesy of Victor Division of Radio Corporation of America

FIG. 37-3.—The electron microscope, shown above, has revealed to mankind a new realm of the ultra-small.

FIG. 37-4.—Magnesium oxide magnified 44,000 times by a stream of electrons in the electron microscope reveals its crystalline nature.

An Element Changes. In radium we have an entirely new sort of property. Unlike elements of low atomic weight, this element changes spontaneously into something else. In fact, radium is produced from uranium and changes successively into nine other elements. Finally, after the loss of five alpha particles and four beta particles, in the process of changing from one element to another, an isotope of lead with atomic weight 206 is produced. Ordinary lead has atomic weight 207.2 and is a mixture of several isotopes.

Even more interesting is the fact that radium itself came originally from uranium, which has in the process of producing radium already lost three alpha and two beta particles. That is, radium is just one stopping place in a long series of radioactive ***transmutations*** (the conversion of one element into another).



Courtesy of Radium Chemical Company, Inc.

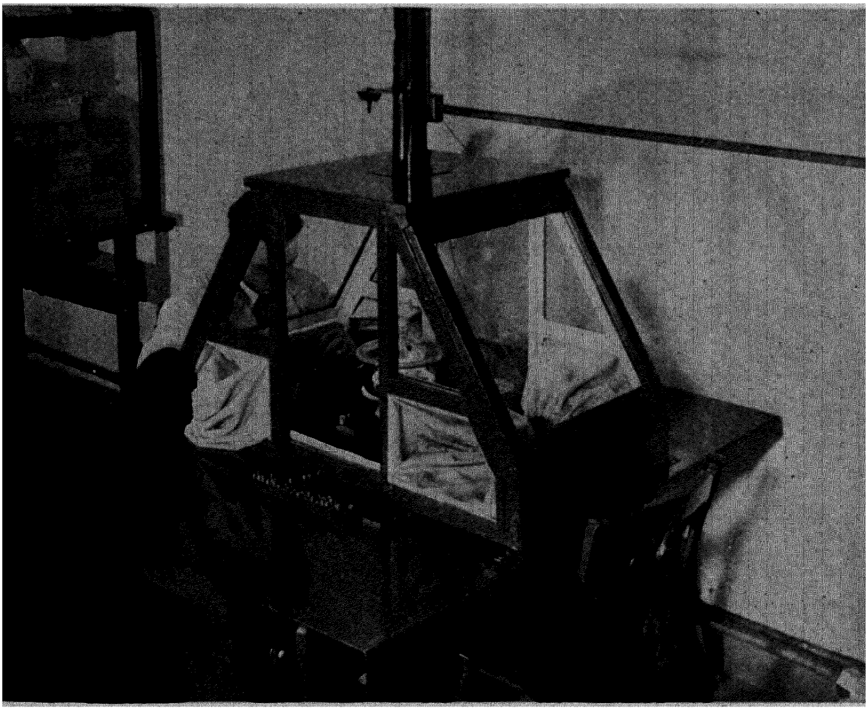
FIG. 37-5.—The safe holds radium. Every day a supply of its decomposition product, gaseous radon, can be pumped off and used for industrial or hospital uses.

We must think of an element, then, not as a simple substance that cannot be changed into a different simple substance, but rather as a simple substance that cannot be changed into a new substance ***by ordinary chemical means.***

The decomposition of radium is curious from another standpoint. In 1690 years, half of any given sample of radium will have disappeared by radioactive decomposition and started down the atomic-weight scale toward lead. In another 1690 years half of the remainder will have disappeared, and so on. By calculation toward the opposite direction, scientists have estimated the age of the earth's crust. The number of years estimated by this chemical means agrees well with the number estimated by geologists from a study of rocks and the amount of salt in the sea. It is about 2000 million years. The earth itself is much older.

The Uranium Nucleus. The atomic weight of the most common isotope of uranium is 238. Its atomic number is 92, near the bottom of the list. By subtraction of the atomic number from the atomic weight (page 186), we find that the nucleus of an uranium atom contains 146 neutrons as well as 92 protons. In the outer shells 92 electrons occupy places in various orbits. The outer electrons of uranium that show no special properties are not as important as the nucleus that is erupting.

This heavy nucleus apparently is unstable. Its group of neutrons and protons can be pictured as quarreling among themselves. The quarrel is continual and violent. Neither the low temperature of liquid helium nor the high temperature of an electric arc slows or hastens the turmoil within the nucleus. Occasionally an atom of uranium disrupts. In the fray a fragment of the nucleus is expelled, two neutrons and two protons together, or an alpha particle. An atom of a new heavy element remains, but this is also unstable. Following this disturbance a neutron within the nucleus is broken up, and its electron, a beta particle, is thrown out. The melee rages, continuing to discharge both alpha and beta particles from the nucleus until a lead nucleus is formed. Then a peaceable arrangement is reached, one that is stable and does not lose projectiles.



Courtesy of Radium Chemical Company, Inc.

FIG. 37-6.—Filling radium salt into platinum containers requires a special handling technique.

In each 4 billion years half of the quantity of uranium on the earth has disappeared and started down the path toward lead. Which atom will be next to disrupt cannot be predicted, but the exact number of atoms that will disrupt each year *can* be told. This is quite like the statistics used in life-insurance companies. They cannot predict who will die, but they can predict accurately how many policyholders will die within a year.

New Energy. All the while this nuclear rearrangement is proceeding, large amounts of energy are being given off. Any sample of radium is warmer than its surroundings because of the energy constantly being emitted. Measurements of the force that is required to shoot out alpha and beta particles with such enormous speeds show that here mankind has discovered another source of energy, ***subatomic energy.*** This new source of energy fascinates us because of its possibilities, for what shall we do when all the cheaply-reached coal, oil, and gas have been burned?

The Sun. Our earth receives only a tiny fraction of the energy given out by the sun. Yet that small amount is enough to move the winds, evaporate and lift all the water of the rains, keep the earth at a livable temperature, and grow all green plants; and, through the course of past eons, it has provided the earth with a supply of fossil fuels.

What is the source of the sun's tremendous amount of energy? It is probable that, under the terrific conditions of temperature on the sun, new elements are being formed from protons and electrons, releasing energy at the same time.

The Transmutation of Elements. The scientific attack on the nucleus of atoms, using the cyclotron and other high-powered tools, gives a partial answer to the fundamental puzzle of science: What is matter?

The changing of the atom of an element into the atom of another element is accomplished by changing its nucleus. The number of outer electrons seems to change rapidly whenever necessary, either going out to or coming in from the neighborhood.

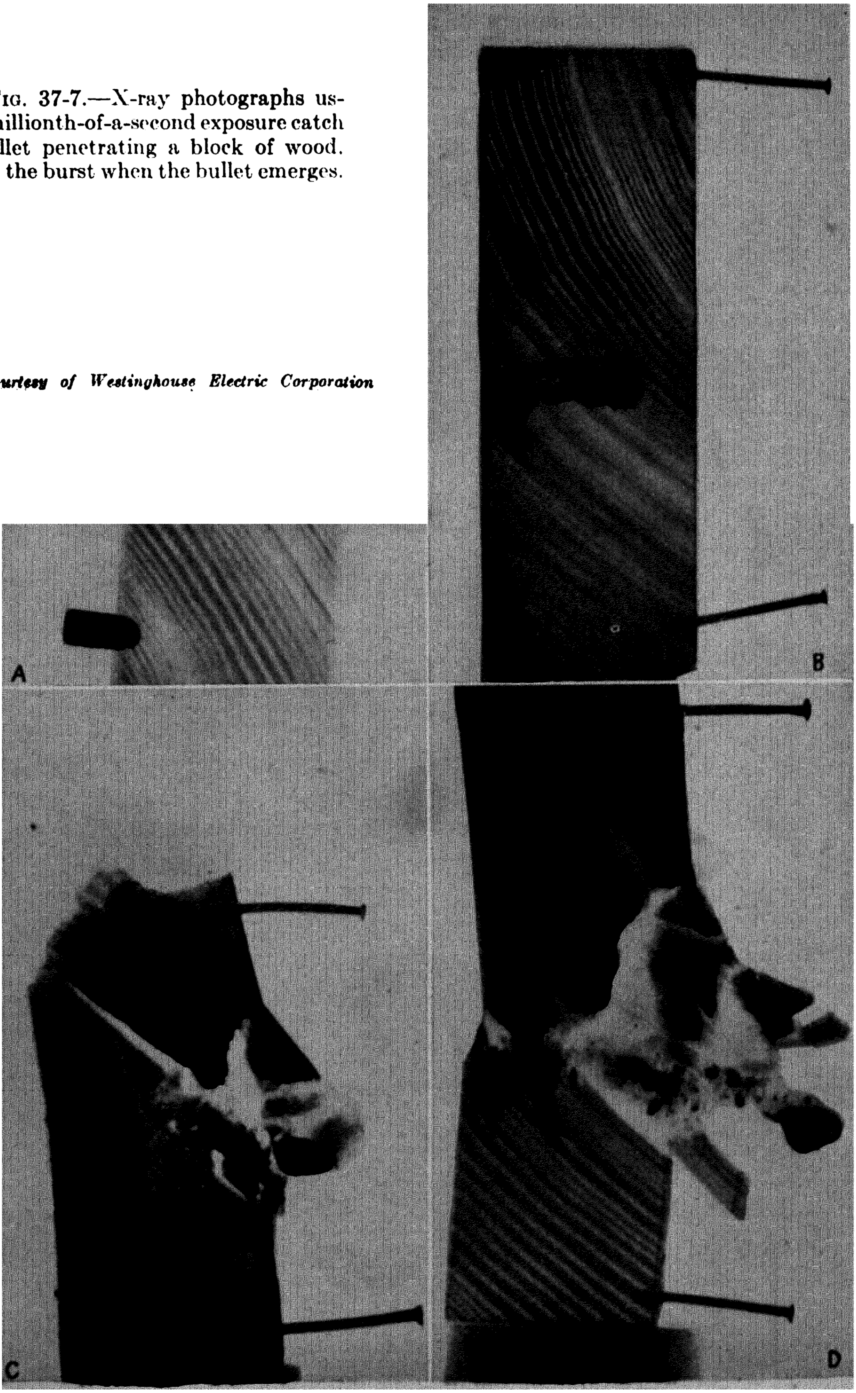
The actual changing of one element to another was first accomplished in 1919 by a British physicist, Sir Ernest Rutherford (1871–1937). He used alpha particles for bullets and shot these at nitrogen atoms, hoping to hit their nuclei. He ***succeeded in knocking a proton out of a few nitrogen atoms,*** changing them to oxygen atoms of atomic weight 17.

$$ {}^{14}_{7}\mathrm{N} + \underset{\substack{\text{alpha}\\ \text{particle}}}{{}^{4}_{2}\mathrm{He}} \rightarrow \underset{\text{proton}}{{}^{1}_{1}\mathrm{H}} + {}^{17}_{8}\mathrm{O} \qquad {}^{\text{at. wt.}}_{\text{at. no.}}(\text{symbol}) $$

His hits were only one out of half a million. Very much more energy was spent shooting, therefore, than was released by the change in the few atom nuclei. His experiment, however, was extremely important

Fig. 37-7.—X-ray photographs us-
g millionth-of-a-second exposure catch
bullet penetrating a block of wood.
ote the burst when the bullet emerges.

Courtesy of Westinghouse Electric Corporation



in proving that one element could be changed into another and in pointing the way to our present ideas of the structure of an atom.

Since these first experiments neutrons and positrons have been discovered. Neutrons have no electric charge; thus they make a better bullet than an alpha particle for entering through the electron shell and approaching the positively charged nucleus. Once they are moving rapidly, with the impetus of a cyclotron behind them, they accomplish changes in atomic nuclei readily. ***Lead has been made into gold,*** the dream of the alchemist. Lithium has been knocked apart to become two atoms of helium, and other changes have been accomplished.

$$\underset{\text{lithium}}{{}^{7}_{3}\mathrm{Li}} + \underset{\text{deuterium}}{{}^{2}_{1}\mathrm{D}} \rightarrow \underset{\substack{\text{2 helium}\\\text{atoms}}}{2\,{}^{4}_{2}\mathrm{He}} + \underset{\text{neutron}}{{}^{1}_{0}\mathrm{n}}$$

But none of these changes is on a large scale, and all are expensive. The trace of gold made by this method is so small that it cannot be found by careful examination with the spectroscope, nor can it be seen with the most powerful microscope. It can be detected only because when so made it is radioactive. We know that gold can be made in this way, but the way is obviously not practical at present.

Induced Radioactivity. Careful examination of the products of transmutation shows that they are often radioactive; that is, they give out particles and decompose into elements of different atomic numbers. This discovery was first announced in 1934, by Frédéric and Irene Curie Joliot, son-in-law and daughter of the famous Mme Curie. Since then, Prof. Enrico Fermi at the University of Rome and later at Columbia University and Prof. E. O. Lawrence at Berkeley, California, and many others have focused attention on this field of physics by producing other artificial radioactivity. Radio-isotopes of all the elements have been synthesized, including those which have not been found occurring naturally. Thus, it has been found possible to investigate the chemical reactions of as yet undiscovered elements!

Uses of radioactive isotopes of common elements made by the cyclotron have been found. Radioactive sodium in salt is used in medicine. Its effects last for a limited time before the compound becomes ordinary salt. A trace of a radioactive element put into the sprayed finish on cars or refrigerators serves as the basis for a method of determining how thick a coating of finish has been applied. The intricate course of phosphorus from the time sodium phosphate is eaten until the phosphate is incorporated in bones can be followed by adding a trace of radio-phosphorus to the sample. Using radio-iron, the digestion of iron salts by normal and anemic animals can be studied. Radio-iodine has given information about the functioning of diseased and healthy thyroid glands.

In addition to their use in medicine in attacking cancerous body tissues, radium compounds are used industrially for nondestructive testing. A container of radioactive material (radium sulfate) is supported on one side of a piece of metal, often a casting, under investigation. A photographic plate is fastened on the other side. The gamma radiations from the decomposing radium cause a shadowgraph on the film just as X rays do. Faults and flaws, if present in the metal, are readily detected by studying these shadow pictures.

The Atomic Bomb. In August, 1945, atomic bombs were exploded over Nagasaki and Hiroshima. Both these Japanese cities were almost completely destroyed. Although the explosions were small compared with some volcanic eruptions that have taken place in past eras, each nevertheless was of an enormous size never before achieved in the controlled explosion of a single bomb. They were accomplished by changing a small amount of matter into energy. The two explosions brought World War II to an abrupt end and ushered in a new era of possibilities for mankind—possibilities of harnessing subatomic power or possibilities of self-destruction.

Isotopes of Uranium. The success of the atomic-bomb project was due to many factors. Important among them was a painstaking study of the properties of uranium. Natural uranium is found to consist of three isotopes, 99.3 per cent of U-238 (92 protons, 146 neutrons), 0.7 per cent of U-235 (92 protons, 143 neutrons), and a trace of U-234 (U-II).

Neutron Bombardment. The two important isotopes of uranium show an astonishing difference in their products when bombarded by neutrons. U-238 is converted into two new synthetic elements, not known in nature, elements 93 and 94, named neptunium and plutonium, respectively.

U-235, on the other hand, when bombarded with neutrons, undergoes fission. In this process it splits into two parts, radioactive isotopes of elements such as barium and krypton, and emits additional neutrons. The products of fission weigh less than the original U-235 that underwent the change, and the destruction of matter is accompanied by a release of a tremendous quantity of energy. This change is the basis of the atomic explosion of U-235.

A Chain Reaction. If the neutrons emitted by U-235 during fission can be directed toward additional U-235 atoms and they in turn undergo fission and emit more neutrons, and so on, a chain reaction will be established. In a U-235 atomic bomb practically all the atoms undergo fission simultaneously. The amount of energy from this action in a small bomb of less than 200 lb. in weight is equivalent to that released by 20,000 tons of TNT in exploding.

Production of Plutonium. Plutonium is a synthetic element that undergoes fission and hence is capable of producing an atomic explosion. Neutrons acting on U-238 may produce this synthetic element.

$$^{1}_{0}\mathrm{n} + ^{238}_{92}\mathrm{U} \rightarrow (^{239}_{92}\mathrm{U}) \rightarrow ^{239}_{93}\mathrm{Np} + ^{0}_{-1}e \rightarrow ^{239}_{94}\mathrm{Pu} + ^{0}_{-1}e$$

or, more simply,

$$\mathrm{n} + \mathrm{U\text{-}238} \rightarrow (\mathrm{U\text{-}239}) \rightarrow \mathrm{Np\text{-}239} + e^{-} \rightarrow \mathrm{Pu\text{-}239} + e^{-}$$

The device for accomplishing this transformation is called a pile. (See Fig. 37-8.) Slugs of uranium are sealed in aluminum cans and placed within a block of highly purified graphite. Stray neutrons (from cosmic rays) start the reaction. Some neutrons are absorbed by the surroundings; others hit U-235 nuclei and keep the chain reaction going, evolving energy and using up U-235; and the remainder hit U-238 nuclei, producing neptunium and plutonium.

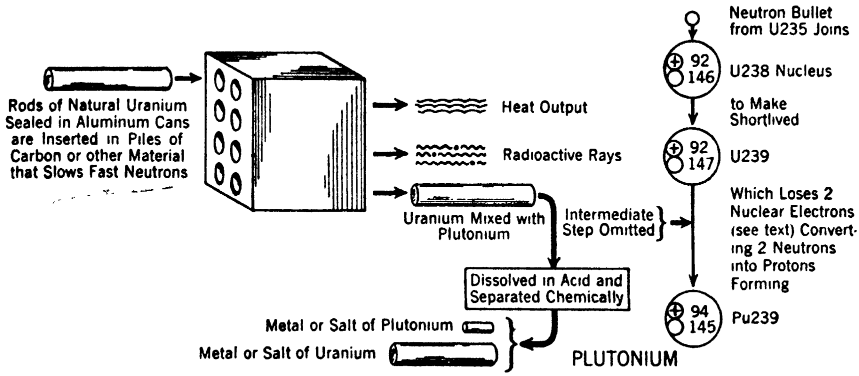


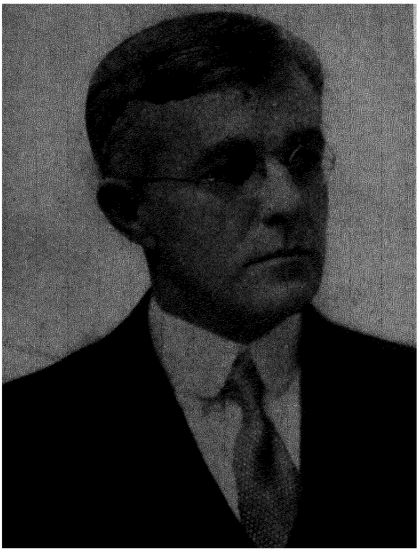
FIG. 37-8.—Man-made plutonium—U-235 substitute.

The slugs are removed (by remote control) from the pile and dissolved. The plutonium is separated chemically from the unchanged uranium and from the fission products. While the production of plutonium is very expensive, it is a cheaper way of producing an atomic bomb than separating U-235 from U-238. Both these processes were developed for war purposes by the Manhattan Project between the years 1942 and 1945 at a cost of approximately 2 billion dollars.

Synthesis of Elements 95 and 96. Bombardment of U-238 and Pu-239 with very high energy helium ions in a cyclotron results in the formation of radioactive isotopes of two new elements of atomic numbers 95 americium and 96 curium. Even though these are produced in very small amounts only, their chemical properties have been studied, and it has been shown that they belong in the third group of the periodic table.

The Atomic Era. Uranium piles will have peacetime uses. They are the cheapest source of neutrons, and they can be used to convert many of the ordinary elements into radioactive isotopes that are useful in all fields of science, particularly in medicine. Investigations concerning these and other developments are under way.

Not the least important among the by-products of atomic bombs is the fact that they have made people think about the futility of war and about the place that chemical laboratories and scientists in general occupy in a normal, healthy society.



Courtesy of General Electric Company.

FIG. 37-9.—Dr. Irving Langmuir, Associate Director, Research Laboratory, General Electric Company, Schenectady, New York, the inventor of the gas-filled electric lamp and pioneer in many branches of electrical engineering. Millions of persons throughout the civilized world depend on artificial light, and almost all of it comes from lamps made on the Langmuir principle. He has also made important contributions to the study of atomic structure.

SUMMARY

Radioactivity is the spontaneous emission of radiations from certain chemical elements found in a number of minerals. These radiations resemble X rays in that they have great penetrating power and travel at enormous speeds. Radiations were discovered by Becquerel from uranium. The Curies, investigating radioactivity, discovered the radioactive element radium in pitchblende and isolated radium bromide by the process of fractional crystallization. Fractional crystallization is the process by which a solvent is partly evaporated and the less soluble substance crystallized and removed by filtration, leaving the more soluble compound in solution.

Radioactive elements are continually emitting alpha or beta rays and frequently gamma rays. Alpha rays are positively charged helium nuclei, He^{++}; they travel at approximately 30 million miles per hour, or about one-fifteenth the speed of light, and have the least penetrating power of the three types. Beta rays are negatively charged electrons, e^-; they travel in a crooked path at approximately nine-tenths the speed of light and have greater penetrating power than the alpha rays. Gamma rays are energy radiations; they are very short, highly penetrating light rays similar to X rays. They travel in a straight line at the speed of light. Radium forms compounds similar to those of barium. It is produced spontaneously from uranium and disintegrates successively through nine other elements in turn until finally lead is formed. The disintegration proceeds at a constant rate; half of any sample transmutes in 1690 years. Transmutation is the conversion of one element into another.

The nucleus of uranium disintegrates to form other elements, radium being among this series. Subatomic energy in tremendous quantities is continually liberated when unstable nuclei, such as those of uranium and radium, disintegrate. Uranium (U-235) has been split by neutron bombardment; atoms of lightweight elements are produced. The amount of energy liberated in nuclear fission is much greater than in any other known process, equal weights being considered.

It is believed that new elements are being formed on the sun from protons and electrons, releasing energy at the same time.

The transmutation of atoms involves the changing of their nuclei. The first artificial transmutation was accomplished by Rutherford, who bombarded nitrogen gas atoms with alpha particles, producing protons and atoms of oxygen. Other transmutations have been accomplished with the aid of cyclotrons and similar devices. Often, the isotopes produced artificially are themselves radioactive; radioactive isotopes of all the elements have now been synthesized.

Atomic energy has been used for military purposes. Using the action of neutrons on either U-235 or plutonium, a chain reaction can be started that consumes matter and releases enormous quantities of energy. This discovery has profoundly influenced human thinking.

QUESTIONS

1. List the properties of the radiations from uranium ores.

2. Review the reasoning of Mme Curie that led to her discovery of radium.

3. Why was the Curies' task in isolating radium bromide not a simple one?

4. Describe each of the three radiations from radioactive substances.

5. How do modern transmutations (*a*) differ from and (*b*) resemble those sought by the alchemists?

6. Define *chemical element*.

7. State two facts about the nucleus of the uranium atom.

8. A thermometer placed in a sample of radium registers a few degrees higher than the temperature of the surroundings. From what source does the energy come?

9. What is the meaning of $^{16}_{8}O$; $^{1}_{1}H$; $^{12}_{6}C$; $^{35}_{17}Cl$; $^{23}_{11}Na$?

10. List two uses for compounds made radioactive by a cyclotron.

MORE CHALLENGING QUESTIONS

Reference Questions

11. What is a spinthariscope? Tell how it operates.

12. Describe Millikan's oil-drop experiment.

13. What is the composition of the luminous paint used on watch dials? Account for its giving light in darkness.

14. What is the missing product of transmutation in the nuclear reaction. (*Do not write in this book.*)

$$^{10}_{5}Be + ^{4}_{2}He \rightarrow ^{1}_{0}n + \cdots$$

15. Write a book report on *Madame Curie*, Eve Curie (translated by Vincent Sheean), Doubleday, Doran & Company, Inc., Garden City, New York, 1938; *The Men Who Make the Future*, Chap. X, Bruce Bliven, Duell, Sloan & Pearce, Inc., New York, 1942; *The Advance of Science* (edited by Watson Davis), Doubleday, Doran & Company, Inc., Garden City, New York; *Atomic Energy for Military Purposes*, H. D. Smyth, Princeton University Press, Princeton, New Jersey, 1945.

16. Tell how a uraniun pile operates and what it produces. How might an uranium pile be adapted to serve as a power plant?

UNIT NINE .... CHAPTER XXXVIII

CHEMISTRY AND RADIANT ENERGY (LIGHT)

The conditions under which mankind exists are so delicately balanced that, if only slight changes should occur, life as we know it would cease. Should the properties of substances be slightly altered—for example, if ice became denser than water—the effects over a long period of time would make life utterly impossible. If the sunlight contained just a little more or less ultraviolet light, our doom would be sealed. In this chapter we shall see how some chemical actions of light affect our very existence.

Action of Sunlight on the Upper Atmosphere. The temperature of the sun is now thought to be maintained by the conversion of hydrogen into helium, a process of transmutation. As a result, a great amount of energy is released, and the temperature of the surface of the sun is at least 6000°C. A tremendous amount of energy is radiated, as light and heat, and our comfortable climate is maintained by the small fraction that reaches the earth continuously. The light that reaches the outer atmosphere is comprised of nearly all wave lengths from short ultraviolet rays to long infrared. If light of all of these wave lengths penetrated very far into the atmosphere, life at the earth's surface would be destroyed. Fortunately, most of the ultraviolet light is absorbed by oxygen, which is thus converted into ozone.

$$\text{Ultraviolet light} + 3O_2 \rightarrow 2O_3$$

This produces a blanket of ozone in the upper atmosphere and reduces the amount of short ultraviolet light. Only the less deadly rays reach the earth's surface, and these can cause a severe sunburn and even death if care is not exercised. The skin reacts to ultraviolet light, generating pigments to absorb it, and a coat of tan results. One beneficial effect is the production of vitamin D in the body.

New Terms

photochemistry
primuline
radiant energy

ultraviolet
photographic negative

print
fixing

We see easily how intimately our health depends on the chemical action of light. If light of shorter wave lengths penetrated the atmosphere, we should perish; if some ultraviolet light did not get through, again life would be impossible. The presence of vitamin D in fish oils goes back to its origin in the foods of fish, where it is produced also by the action of sunlight.

Photosynthesis. The most important chemical action of light is the conversion of carbon dioxide and water into cellulose and similar products, together with gaseous oxygen. For this process chlorophyll must be present. No one has yet been able to carry out this process artificially, but the action is being studied in laboratories all over the world.

The total reaction is known to be

$$\text{Red light} + 6CO_2 + 5H_2O \xrightarrow{\text{chlorophyll}} (C_6H_{10}O_5)x + 6O_2$$

The accumulation of stored sun's energy on the earth has resulted in enormous beds of coal (see page 546), vast deposits of petroleum (see page 533), and tremendously large volumes of natural gas (see page 529).

How the Firefly Lights Its Lantern. Most chemical reactions occur with the evolution of heat; some, called combustions, occur with the evolution of both light and heat; a few are known in which little heat and much light are emitted. The firefly and many other light-emitting organisms have developed chemical reactions of this sort. Boyle showed in 1667 that air was necessary for the glowing of luminous wood. One of the most spectacular experiments is the oxidation of luminol by means of hydrogen peroxide and potassium ferricyanide. The light evolved is so bright that it is possible to take photographs with it.

In the body of the firefly a similar oxidation of luciferin occurs in the presence of an enzyme catalyst, luciferase.

$$\underset{\text{luciferin}}{2LH_2} + O_2 \rightleftarrows \underset{\text{oxyluciferin}}{2L} + 2H_2O + \text{light}$$

In this equation L represents a compound, oxyluciferin, not an element.

Use of Light in Studying Chemical Reactions. If a mixture of chlorine and hydrogen is exposed to light, it explodes violently. It has been shown conclusively that the explosion is the result of a chain reaction, the product of one step of the reaction being the reactant for the next. The effect of light is to decompose the chlorine.

$$\text{Light} + Cl_2 \rightarrow 2Cl^* \quad \text{(Cl atoms with excess energy)}$$

The next step is the combination of the single chlorine atom with a hydrogen molecule to produce a molecule of hydrogen chloride and a free hydrogen atom containing excess energy.

$$Cl^* + H_2 \rightarrow HCl + H^* \quad \text{(H atom with excess energy)}$$

The hydrogen atom, in turn, can react with chlorine molecules.

$$H^* + Cl_2 \rightarrow HCl + Cl^*$$

Now we have an atom of chlorine to begin the chain all over again. The reaction goes with increasing rapidity, and an explosion results. By studies of this type, much has been learned about explosive mixtures—air and gasoline vapor, and the like. This is the branch of science called ***photochemistry.***

QUESTIONS

1. What is the source of the earth's energy?

2. What might happen to us if the short ultraviolet rays from the sun should reach the surface of the earth?

3. What photochemical reaction of oxygen makes life possible?

4. What is the origin of vitamin D in cod-liver oil?

5. How can workers on a night shift make up for their lack of vitamin D?

6. Does ordinary window glass transmit all wave lengths of light?

7. Do plants grow better in red or in ultraviolet light?

8. By what process does the chemist hope someday to trap part of the wasted energy of the sun?

9. What is the probable source of most of the oxygen in the atmosphere of the earth?

10. How does the firefly produce light?

11. Compile a list of plant and animal organisms that emit light. (Look in an encyclopedia under *luminescence.*)

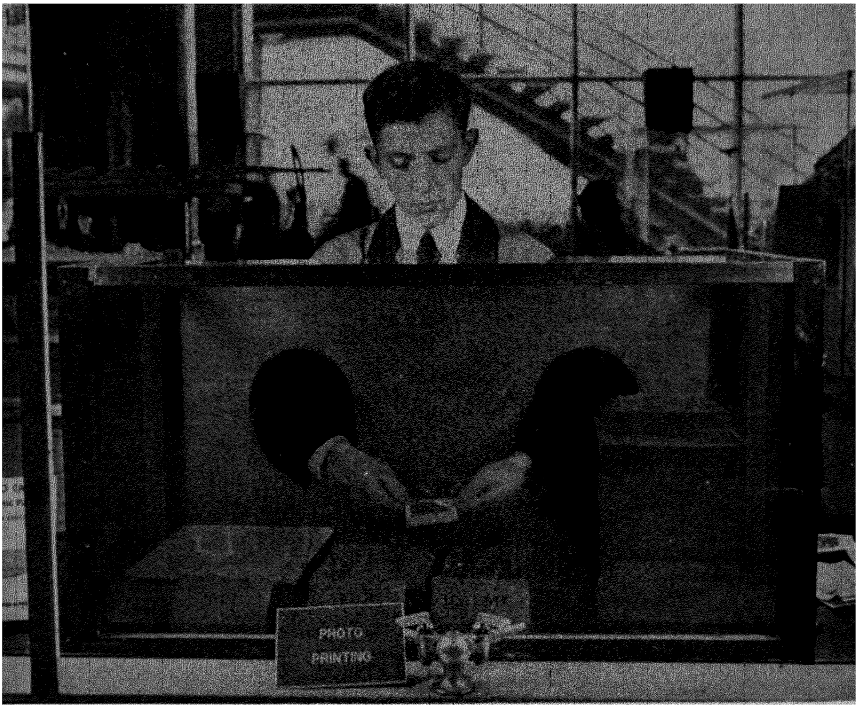
12. Is "cold light" ever emitted in chemical reactions?

13. Compile a list of chemical reactions that emit light. (Look in an encyclopedia under *chemi-luminescence.*)

14. What has the photochemist decided about the way an explosion of a mixture of hydrogen and chlorine in sunlight proceeds?

Photography. The candid-camera enthusiast can take pictures of the acts in the circus, of dimly lighted, rapidly moving objects; by studying a photographic plate the astronomer "discovers" new stars, the light from which has been traveling toward the earth for millions of years; the physicist detects the presence of traces of an impurity in steel by photographing its spectrum and reports his results back to the foundry within a few minutes after molten metal was poured into a mold; an X-ray motion picture shows a skeleton foot kicking a football; a camera 20 miles above New York takes a picture of Philadelphia, using infrared light, and incidentally revealing the curvature of the earth on the horizon; motion pictures have extensive uses. Photography is one of the most important tools of the laboratory worker and the source of continual pleasure to hundreds of milllions of people through all the reaches of the earth.

The basic chemical reaction of photography is quite simple. Let us precipitate silver chloride by adding hydrochloric acid to silver nitrate and allow the precipitate to settle. In the dark the silver chloride retains its pure white color, but in the light of the room it begins to turn purple. If a piece of magnesium is burned near it, the highly active blue-white light produced causes the silver chloride to darken instantly. The silver chloride decomposes into its elements. This decomposition was discovered by Scheele in 1777.



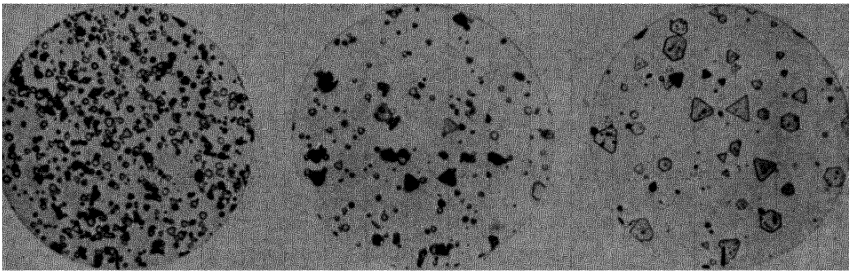
Courtesy of The American Institute

FIG. 38-1.—This amateur photographer is at work in his darkroom printing pictures. The box has gelatin-coated, transparent, red glass.

$$\text{Light} + 2AgCl \rightarrow 2Ag + Cl_2\uparrow$$

The early photographs were produced in just this way. The victim was clamped rigidly in a chair on the roof of a building and the camera aimed at him for a half hour or longer, while he remained motionless. In 1837 Louis Jacques Maudé Daguerre (1789–1851) discovered that even with a short exposure, during which only a little of the silver chloride decomposes, a permanent effect, or "latent image," is produced which can be intensified by various means. Daguerre used mercury to bring the picture to visibility, in what is called a daguerreotype. William Henry Fox Talbot (1800–1877) in 1839 found it was possible to "develop" the latent image by chemical reagents, by completing the reduction of the silver chloride, which has been exposed to light, to metallic silver.

One difficulty with early photographs was that they were not permanent. The remaining silver halide (chloride, bromide, or iodide) continued to decompose on further exposure to light. This problem was soon solved by removing the silver halide left undecomposed. The reagent universally used is sodium thiosulfate ($Na_2S_2O_3 \cdot H_2O$), erroneously called "hypo." This dissolves the unreacted silver halides by converting them into soluble, complex compounds. (See Fig. 38-1.)



Courtesy of Journal of Chemical Education

FIG. 38-2.—Types of photographic emulsions showing different grain sizes. Left: fine grain, low speed; center: coarse grain, high speed; right: silver bromide grains.

The steps in producing a picture are as follows:

1. Preparation of the film (done by the manufacturer)
2. Exposure in the camera ("taking the picture")

Operations that must be carried on in the dark or dim nonactive light:

3. Development by an alkaline mixture of reducing agents (always derivatives of benzene, an aromatic hydrocarbon) (see Fig. 38-2)
4. Washing to remove excess developer
5. Removal of excess silver halides by sodium thiosulfate ("fixing")

Operations that should be carried out in a lighted room:

1. Washing thoroughly to remove the last traces of thiosulfate
2. Drying carefully to prevent distortion

This produces a "negative" in which the scene or object photographed is in reverse; the light parts are opaque, and the dark parts are transparent. (See Fig. 38-3.)

The "positive" is produced by "printing" on film or paper in exactly the same way used in making the negative. A camera (for enlarging) may be used, or a contact print may be made by clamping the negative to the sensitized surface of the printing paper and exposing it to light through the negative. The paper is then developed, washed, fixed, washed, and dried.

Recently, tremendous advances have been made in extending the light range that can be photographed and in reducing the time required to produce a latent image that can be developed. But the essential chemistry is still the simple fact discovered over 150 years ago by Scheele, that silver halides are decomposed by exposure to light.

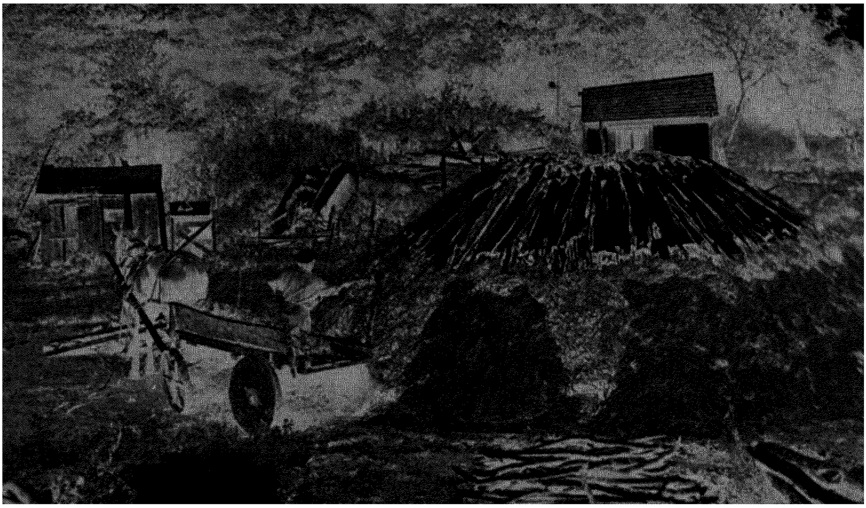


FIG. 38-3.—This is the negative of Fig. 30-17, page 549.

Modern Photography. Modern photography is a comparatively new industry. From America's research laboratories has come much of its advance.

When George Eastman started laboratory experiments that made possible the present ramifications of photography, an industry was born. Eastman made his first practical nitrocellulose film in 1889. Since that time rapid strides have been made in the development of delicate and complicated film emulsions. Cameras and camera equipment likewise have been designed to gain greater efficiency. The advance on the two fronts has widened the field of photography in many directions.

The development of motion pictures, safety film, high-speed film, and color film—these are but four of the many factors that have been responsible for the gigantic strides of this nearly 2-billion-dollar industry.

No longer is photography considered as a development for the amateur market. Even with 24 million amateurs using 26 million cameras and taking approximately 600 million snapshots yearly, the amateur market represents only about one-tenth of the bill for photography and its allied fields.

The professional motion-picture industry alone represents one-half of the volume—a cold billion. Lithography, photo-engraving, home "movies," newspapers (especially tabloids), magazines (especially those reporting the news in pictures), medicinal and industrial X rays, studio, industrial, and office photography make up the balance.

The growth of the photographic industry has been spectacular since 1935. Between 1935 and 1937 the sales of cameras tripled. Film sales grew by leaps and bounds. The manufacture and improvement of photographic emulsions or films became a challenge to the chemical industry, for the making of films is a chemical process from beginning to end. The purity of the chemicals and the quality of dyestuffs used in the manufacturing of film emulsions have a direct relationship to quality and speed. Moreover, any foreign matter in such a chemical as potassium bromide, ammonium bromide, potassium iodide, or silver nitrate will immediately be magnified when the film is projected. Manufacturers of gelatin faced similar problems of exacting purity.

The chemical industry has played no little part in giving the pleasure and thrill of making fine pictures. It has contributed widely and has kept pace with the needs of better photography. The chemical industry is still looking ahead—for photography is in its infancy. New discoveries and applications in all phases of film speed and photography are constantly broadening the scope of the industry, and research will have its rich reward.[1]

Photography without Silver. In the preparation of certain dyes (diazo compounds) there is an intermediate stage in which the material is easily affected both by light and by heat. At this stage the dye intermediate must be kept cool and in a subdued light. Such dyes are often called "ice dyes," for ice is used to keep them cool. Advantage may be taken of this light sensitivity to produce photographs without the use of silver. As early as 1887, the dyestuff ***primuline*** was used. The cloth is dyed with primuline and, while ice-cold, is immersed in an acidified solution of sodium nitrite ($NaNO_2$). This produces the light-sensitive diazonium intermediate. If the cloth is now surmounted by a stencil and exposed to bright light, the diazonium compound is decomposed where the light strikes it, but not the unexposed portions. The print is "developed" by immersing the cloth in an alkaline solution of beta-naphthol or some similar aromatic alcohol, whereupon the unexposed parts turn to a brilliant color (red) and the exposed parts remain yellow.

Recently the process has been improved greatly and made commercially feasible. A new film, designed particularly for sound tracks, is made by incorporating a mixture of diazo compounds into a strip of Cellophane (see page 568). The product is only faint yellow in color. Wherever light strikes, the diazo compounds are bleached. Developing and fixing are done by passing ammonia gas (NH_3) over the film in subdued daylight. The ammonia causes the "coupling" to occur to produce a dye. The result is a positive print. For sound-track recordings,

---

[1] WALDRICK, S. B. (editor), editorial comment in *Chemist-Analyst* of J. T. Baker Chemical Company, vol. 29, No. 4, p. 75, November, 1940. Used by permission.

the contrasts are very accurate and the film can be exposed, developed, and finished in a continuous operation at 80 ft per min.[1]

Because of the sharpness, the film can carry three times as much sound track per inch at one-tenth the cost of the usual film, in which silver salts are used.

Blueprints. Commercial processes of duplicating drawings may use silver salts—photostats—but, more commonly, "blueprints" are made. For these, paper is impregnated with a mixture of iron salts in the ferric condition. The action of light is to change part of the iron to the ferrous condition, which results in the formation of insoluble ***Turnbull's blue.*** In the unexposed portions the iron salts remain in the ferric condition and soluble and are removed by washing with water. In producing blueprints, a latent image is not developed, but the light must remain turned on until the reaction is complete. Hence brilliant arclights are used to speed up the production. The "fixing" operation is merely one of washing in clean water. The print is then dried.

The Mechanism of the Human Eye. One of the effects of light with which we are greatly concerned is the chemical action that occurs in the retina of the eye. A substance called "visual purple," present in the retina cells, is altered by the light reaching it. An impulse is sent along a nerve to the brain by this action. To regenerate the visual purple, vitamin A is required. Lack of this vitamin A slows up the recovery of the sensitivity of the eye, and night blindness results.

SUMMARY

Transmutation of elements in the sun produces an enormous amount of energy. Light from the sun covers a wide range of wave lengths, from the far ultraviolet to the far infrared. Harmful ultraviolet light is absorbed in the upper atmosphere. The remaining ultraviolet light is essential for life processes; that is, it produces vitamin D.

Photosynthesis is the conversion of carbon dioxide and water into plant cellulose and oxygen. The reaction occurs in sunlight in the presence of chlorophyll. In an early era of the earth's history, the atmosphere contained little oxygen; the 21 per cent now found in the air is the result of photosynthesis.

Light from a firefly is the result of oxidation of luciferin in the presence of the enzyme catalyst, luciferase. Photochemistry deals with the chemical reactions caused by light action.

Photography is an art based on photochemical reactions, especially the decomposition of silver halides. A latent image is produced, which can be developed by several reducing agents, in the presence of alkali. Residual silver salts are removed by sodium thiosulfate (hypo) and thorough washing in water. In the above operations a negative is produced; a positive print is made in a nearly identical manner (chemically speaking).

---

[1] Time Magazine, Aug. 24, 1942, p. 44.

In making blueprints, paper is treated with two ferric salts. One is reduced to a ferrous salt by the action of light. In the presence of water Turnbull's blue precipitates in the paper. Color photography without silver may be accomplished by means of photochemical reactions and dye formation.

In the eye, light causes a chemical reaction in the retina cells, and a nerve impulse is sent to the brain.

QUESTIONS

15. Write a series of three equations to show what happens when a photographic film is exposed and processed.

16. Consult a book on photography to find out about the process of "toning" a photographic print. Write an equation illustrating the process.

17. How does eating a carrot aid in preventing night blindness? What are the symptoms of night blindness?

18. Is sunlight necessary for the development of chlorophyll in a plant? (Allow a potato to sprout in the dark.)

19. Do you think that photography without silver will supplant the methods commonly used today? Why?

20. How does the Kodachrome film produce pictures? (Look up Kodachrome film in a book on color photography.)

21. How could one recover silver from used "fixing bath"?

22. Do all plants need chlorophyll? (What about a mushroom?)

23. What causes the color of blue overalls to fade?

24. Give an example of a photochemical reaction not cited in this chapter.

25. The glass in the windows of houses on Beacon Hill, Boston, Massachusetts is famous for its purple color. Explain its origin.

26. What are some of the newer methods of copying drawings, letters, and manuscripts? (Look up this topic in reference books.)

27. Explain the change from black to brown that may be noticed on photographic prints stored near rubber.

UNIT NINE .... CHAPTER XXXIX

THE NOBLE METALS AND SOME LESS FAMILIAR ELEMENTS

The noble metals were believed by the ancients to be more pure and precious than the ordinary metals that were readily corroded. It was the purpose of many alchemists to transmute "base" or more "corruptible" metals into gold.

The elements that are usually classified as ***noble*** are silver, mercury, gold, and platinum; but the list may also include the much less familiar elements ruthenium, rhodium, palladium, osmium, and iridium. These elements are all low in the replacement series (see page 89) and do not react with atmospheric oxygen—hence their seeming permanence and value compared with iron and copper. Their high price reflects in part their scarcity and lack of major industrial applications. Many of them have use as catalysts, but their compounds are not discussed extensively in elementary books.

Mercury

Mercury has been known since very early times. It is also called ***quicksilver***. It was named ***hydr argyrum*** ("water of silver") by the Romans. Some is found free in nature, but it is obtained mostly from a bright-red rock, cinnabar (HgS). The total amount mined is not large—8000 tons in 1937—mostly from Italy, Spain, and the United States. For a number of years Spain and Italy had control of the market, but now the United States has nearly enough for its own uses.

Metallurgy. Where mercury occurs in the free state, it is removed from the rock by distillation. It boils at 357°C. To obtain it from cinnabar, the ore is roasted, since mercury oxide is unstable (see page 41), and mercury distilled out.

$$HgS + O_2 \rightarrow Hg + SO_2$$

Properties and Uses. Mercury is the only common metal that is a liquid at room temperature. It is 13.6 times as dense as water. Above the

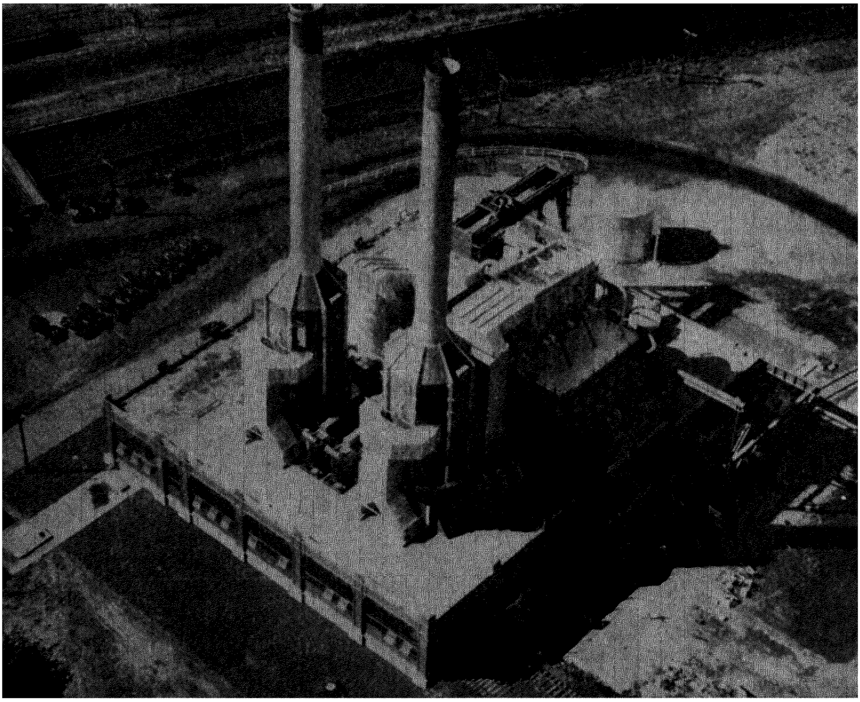
---

New Terms

quicksilver
amalgams
smelting
placer mining
Parkes process

boiling point, it exists as a colorless, nonmetallic, poisonous vapor with only one atom in the molecule.

Mercury-vapor turbine engines have been developed, but from some standpoints they are not as satisfactory as steam turbines. Their efficiency is high, however. (See Figs. 39-1, 39-2.) Mercury-vapor pumps are used in laboratories to produce a high vacuum. Liquid mercury is used extensively in thermometers and barometers. A relatively new use for mercury vapor is in fluorescent lights. The arc is struck by the argon present, but most of the ultraviolet light emitted comes from the glowing mercury vapor. This, in turn, is converted to visible light by the "phosphor powders" on the walls of the glass.

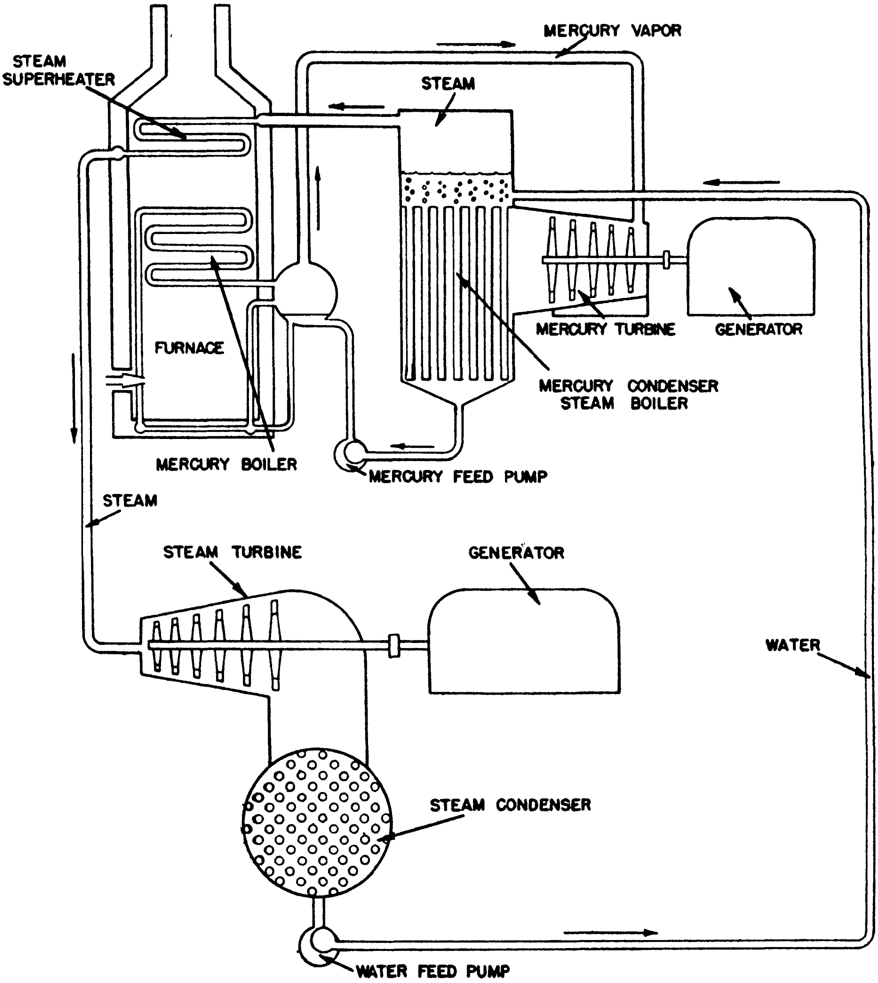


Courtesy of General Electric Company

FIG. 39-1.—This is a general view of a central power plant that uses mercury vapor.

Amalgams. Amalgams are alloys that contain mercury; they may be solid or liquid. If a small drop of mercury is added to silver nitrate solution, needles of silver amalgam slowly form. The mercury displaces the silver and forms a solid amalgam in the shape of fantastic needles of brilliant luster. For filling back teeth, dentists mix complicated mixtures of metals with a carefully determined amount of mercury. When the amalgam filling solidifies, it expands slightly and fills the cavity completely. Because of the dark color of amalgams, other filling materials are used to repair cavities in the front teeth.

Chemical Properties. Chemically, mercury is not an active metal, but when warmed[1] to 300°C it reacts slowly with oxygen in the air to produce the red oxide (HgO). When the temperature is raised still higher, well above 300°C, this compound decomposes into the elements. Mercury



Courtesy of General Electric Company

FIG. 39-2.—The diagrammatic plan of a mercury-vapor–steam-electric generating system shows two turbines: one run by mercury vapor, the other by steam produced by condensing mercury.

---

[1] Mercury vapor is very poisonous. This experiment must be carried out in a well-ventilated hood.

reacts with sulfur when two elements are ground together in a mortar.

$$Hg + S \rightarrow HgS$$

Metallic mercury reacts with warm dilute nitric acid and hot concentrated sulfuric acid.

Mercury Compounds in Two States of Oxidation. Mercury forms compounds in two states of oxidation.

$$\underset{\text{mercuric (II)}}{Hg(NO_3)_2} \qquad \underset{\text{mercurous (I)}}{Hg_2(NO_3)_2}$$

Mercury(I) chloride, ***calomel,*** exhibits the peculiar formula, Hg_2Cl_2, representing mercury as a radical $(Hg_2)^{++}$, which has valence 2. The two atoms are held together by a covalent bond $(Hg{:}Hg)^{++}$. Mercury(I) chloride is formed as a white precipitate when mercury(II) chloride is reduced with tin(II) chloride.

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2\downarrow + SnCl_4$$

Calomel is used in diseases of the secretory organs and is nowhere near as poisonous as mercury(II) chloride, which is known as corrosive sublimate, a powerful antiseptic.

Mercury fulminate $[Hg(ONC)_2]$ is the most important detonator for high explosives. It is made by treating mercury with strong nitric acid and alcohol.

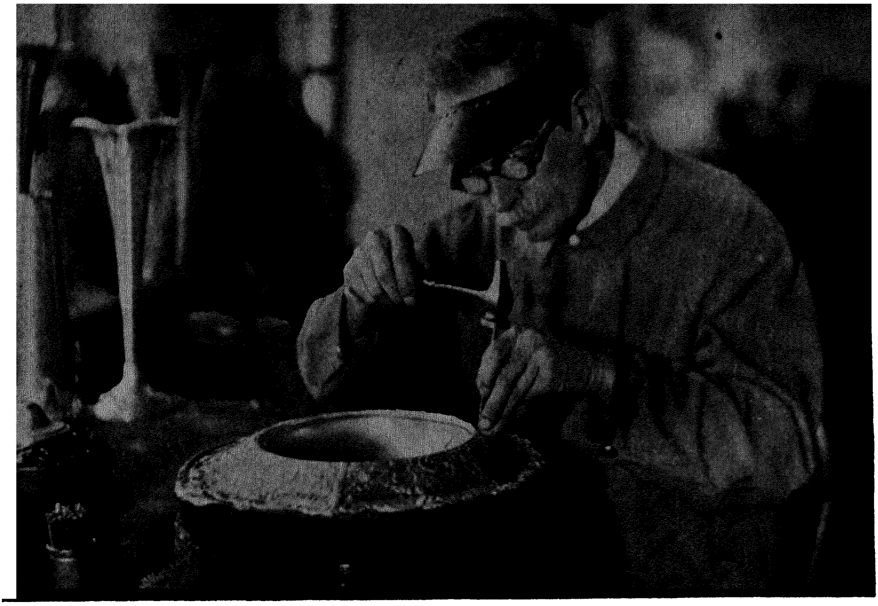
Silver

Silver occurs as the free element, but the sulfide ore, argentite (Ag_2S), found with copper and lead sulfides, is the most important source. Much of the silver produced is recovered from very low grade ores, often mined for these other metals (see page 468).

Metallurgy. Argentite ore is smelted by roasting and reduction with coke, after being mixed with lead ore. The alloy produced is then treated by Parkes process, which involves melting it and adding 1 per cent zinc. The zinc dissolves the silver, gold, and copper, but not the lead, and floats upon the lead. The solidified zinc crust is skimmed off. The silver is then recovered by distillation of the zinc and purifying the residue electrochemically. Silver is also obtained by a cyanide method similar to that for gold.

Properties. Silver is most familiar in alloys, sterling silver (92.5 per cent Ag, 7.5 per cent Cu) and coin silver (90 per cent Ag, 10 per cent Cu). It has a warm, slightly yellowish, metallic luster and is most popular for tableware. It is the best conductor of heat and electricity. It is deposited on glass for mirrors because of its high luster. Silver does not combine directly with oxygen but does form an oxide (Ag_2O) at room temperature, with ozone. The oxide decomposes on gentle warming, at 260°C. The metal dissolves readily in dilute nitric acid, forming silver nitrate ($AgNO_3$), a fairly stable compound. Upon being heated to 444°C silver nitrate yields silver, oxides of nitrogen, and oxygen; and on exposure to blue light it turns dark, owing to a similar decomposition. It must be stored in brown bottles.

Compounds. Silver usually has a valence of 1. The halides, AgCl, AgBr, AgI, are all very insoluble, but AgF is a very soluble salt. This is because AgF is ionic in structure but the other salts are increasingly covalent. This change in structure is accompanied by a deepening of the color. Silver chloride is white, the bromide is cream-colored, and the iodide pale yellow. These compounds are unstable in light and are the basis of the photographic industry (see page 655).



Courtesy of The Gorham Company

FIG. 39-3.—This expert craftsman in silver is chasing a sterling centerpiece.

When ammonia solution is added to silver nitrate solution, white silver hydroxide is precipitated. This soon turns dark as it is converted to black silver oxide.

$$Ag^+ + OH^- \rightarrow AgOH \downarrow$$
$$2AgOH \rightarrow Ag_2O + H_2O$$

If excess ammonia solution is added, the precipitate redissolves owing to the formation of a soluble complex silver salt.

$$AgOH + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + OH^-$$

This mixture is called "Tollen's reagent." It is used to test for aldehydes and ketones.

Silver Mirrors. Tollen's solution is readily reduced with formaldehyde to produce a beautiful mirror, but the article to be coated must be chemically clean. Glucose is also frequently used as the reducing agent. Care must be taken to discard the solution immediately after use, since silver fulminate (AgONC) or silver azide (AgN_3) may form and explode violently. As soon as the solution has been used, it is treated with hydrochloric acid to precipitate the silver as silver chloride (AgCl).

For astronomical mirrors, aluminum is evaporated on the glass surface. While a silver mirror is easier to produce, it does not reflect blue or ultraviolet light and rapidly tarnishes. The aluminum mirror is relatively permanent and much whiter. The reaction by which silver tarnishes is

$$2Ag + S \rightarrow Ag_2S$$

Tarnishing can be prevented by coating the metal with a colorless lacquer or by wrapping the article in Cellophane. Boxes designed to store table silver and to prevent tarnishing are lined with cloth that has been impregnated with silver or lead salts, which react with the hydrogen sulfide and thus keep it from the metal.

Gold

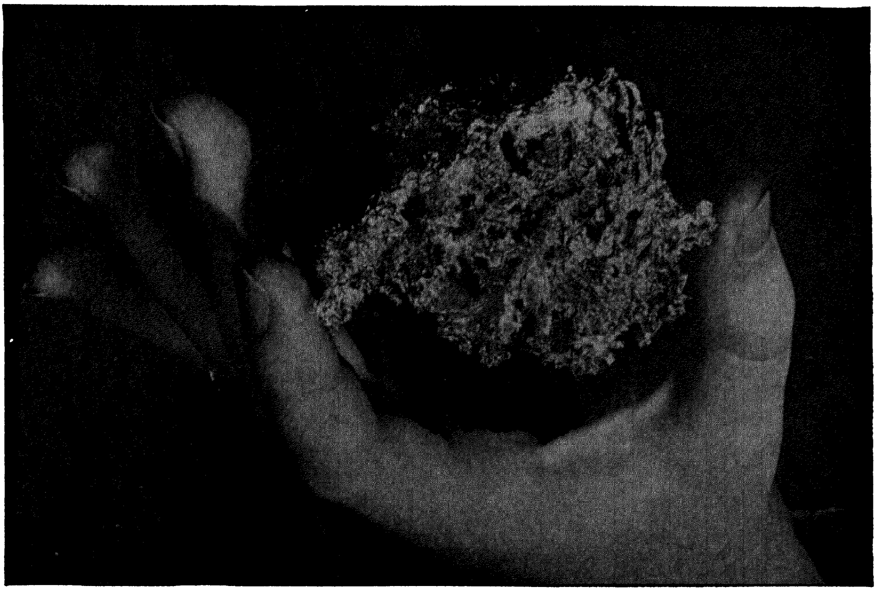
Gold is one of the rarer elements, but because it is not readily corroded it is found free in nature and was therefore one of the first metals used by prehistoric man. It has a beautiful yellow color, being the only metal besides copper that is not gray in tone. It is readily worked and was first used in jewelry and for ornamentation.

Metallurgy. About a quarter of the gold is recovered as by-products of the ***smelting*** industries, by the same processes used to recover zinc, lead, and copper. ***Placer*** mining accounts for another quarter; in this process the gold metal sinks in a flow of water that carries away the sand and other less dense gangue. Another quarter is recovered by the ***amalgamation*** process in which the gold is alloyed with mercury, on copper plates or cleats. The mercury is removed by distillation. The last quarter of the yearly production is based on the ***cyanide*** process. Metallic gold is oxidized by the atmospheric oxygen in the presence of sodium cyanide and dissolves as a complex compound [$NaAu(CN)_2$].

$$4Au + O_2 + 8NaCN + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH$$

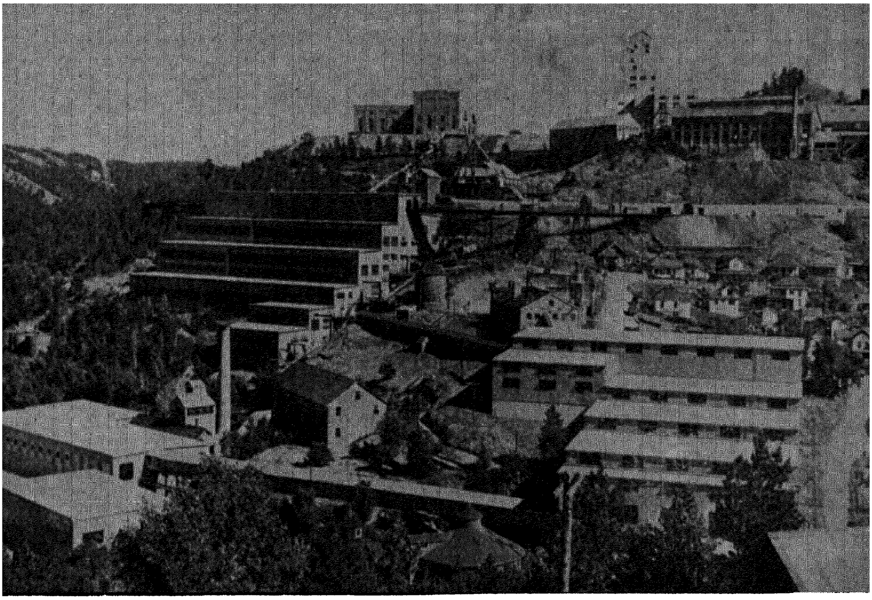
The gold is recovered electrochemically or by replacement by means of zinc or aluminum. Very low grade ore can be worked over by this process.

Properties. Gold is the most malleable and ductile of metals. It is beaten between "goldbeater's skins" to extremely thin sheets, known as



Courtesy of American Museum of Natural History

Fig. 39-4.—"Gold is where you find it." This chunk was located in Nevada County, California.

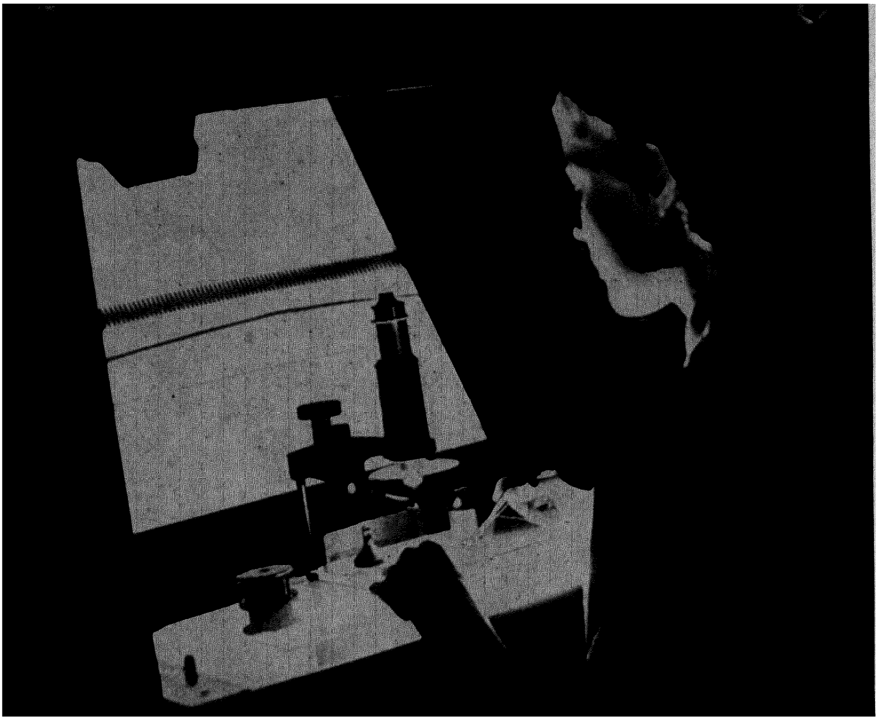


Courtesy of South Dakota Highway Commission

Fig. 39-5.—This view shows the Homestake mine at Lead, South Dakota, where gold is mined by the cyanide leaching process.

"gold leaf." This is used in making signs on plate-glass windows. It is usually alloyed with copper (yellow gold), nickel (white gold), or silver (green gold) to harden it. Fourteen-carat gold contains $^{14}/_{24}$ parts of gold and $^{10}/_{24}$ parts of copper.

Chemically, gold forms compounds with two states of oxidation, I and III, the latter being met with most frequently. If gold is dissolved in aqua regia (3 parts concentrated HCl and 1 part concentrated HNO_3), the yellow soluble compound formed is a complex chloroauric acid ($HAuCl_4$) in which gold(III) is present. All gold compounds are unstable.



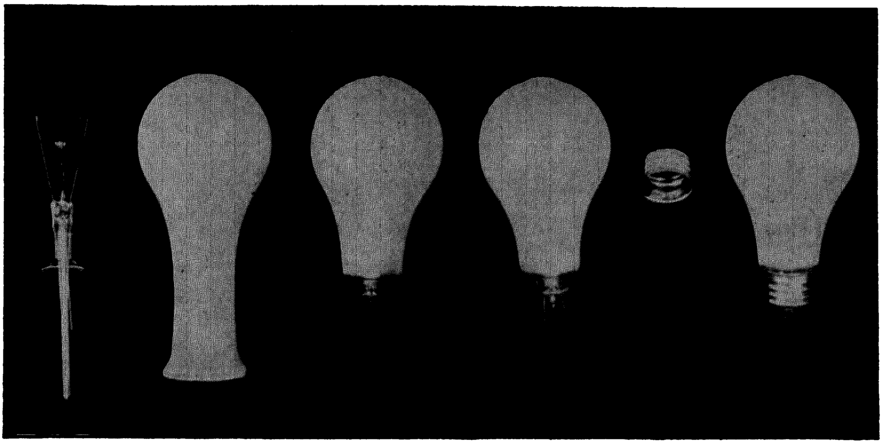
Courtesy of General Electric Lamp Department

FIG. 39-6.—The inspection of a tungsten filament wire used in an electric light is accomplished by magnifying and projecting the image on the screen before the inspector.

Uses. Gold has few uses other than for coins and jewelry. If it were less expensive, it would be used more widely for chemical apparatus and to coat other metals to prevent corrosion, but gold-plated milk pails are for the future. Gold-plated jewelry, available at very low prices, has a very thin coat and, because of the softness of gold, very poor wearing qualities.

Tungsten

Tungsten was discovered by Scheele in 1781. The symbol W comes from its German name ***wolfram.*** The most common ores are ***scheelite,*** composed of calcium tungstate ($CaWO_4$), and ***wolframite,*** iron and manganese tungstate [$(Fe,Mn)WO_4$]. These ores fluoresce in ultraviolet light. Tungsten is a dark-gray, hard metal with the highest boiling point of all the elements, 4727°C. It cannot be machined well and therefore is formed as a powder into blocks and compressed to a bar. The bars can be heated in an electric arc, hammered, and drawn into fine wires for lamp filaments. (See Figs. 39-6, 39-7.) High-speed tool steels contain 18 per cent tungsten, 4 per cent chromium, 1 per cent vanadium, and iron and carbon. Tungsten carbide (WC) and tungsten titanium carbide ($WTiC_2$) are embedded in metallic cobalt and used for the cutting edge of high-speed tools. These can be used at red heat without losing their keen edges.



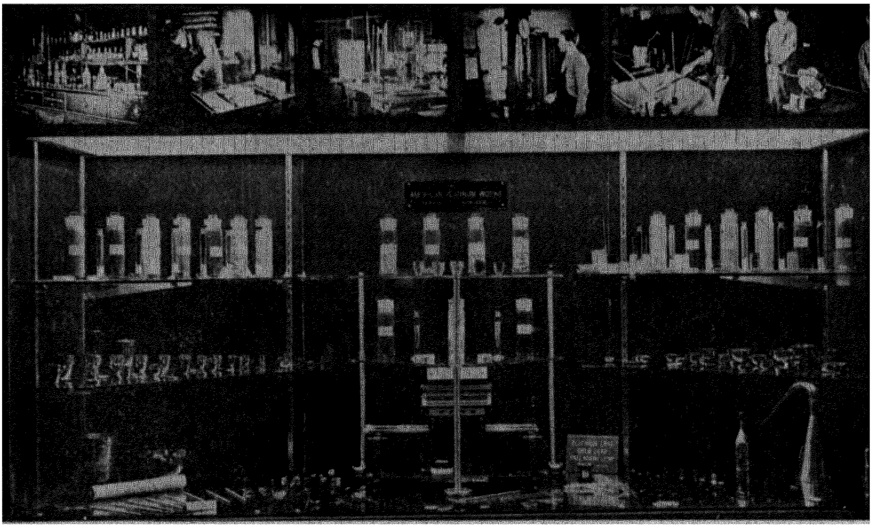
Courtesy of General Electric Lamp Department

FIG. 39-7.—The steps in the manufacture of an electric light bulb.

Platinum

Platinum occurs in nuggets containing the other metals of the platinum group—iridium, osmium, ruthenium, rhodium, and palladium. Russia has been the best source, but now the largest amount of platinum is obtained in the Canadian nickel ores, where it is an important impurity. Here it exists as ***sperrylite*** ($PtAs_2$). Platinum is used for jewelry, dental bridges, and laboratory apparatus. The chief industrial use is as a catalyst in producing sulfuric acid by the contact process. Platinum compounds, for the most part, are laboratory curiosities, but platinum oxide (PtO) has possibilities as a catalyst. It is fairly stable, not being decomposed until 550°C. When dissolved in ***aqua regia,*** platinum forms chloroplatinic acid (H_2PtCl_6). This is readily decomposed on asbestos fiber to produce a finely divided metal that can serve to demonstrate the catalytic properties of platinum.

$$H_2PtCl_6 \rightarrow Pt + 2HCl\uparrow + 2Cl_2\uparrow$$



Courtesy of American Platinum Works

FIG. 39-8.—This display of platinum and other precious metals emphasizes the usefulness of inactive metals for laboratory vessels.

SUMMARY

The noble metals are relatively inert elements. They do not react with atmospheric oxygen and do not corrode readily. They are generally found free in nature, though some are found in combination.

Mercury is found in ores free or in the compound cinnabar (HgS). It is a dense liquid with a metallic luster. It is a good conductor of electricity. It is readily vaporized. At 300°C mercury forms mercuric oxide in the air, but this decomposes at higher temperatures. Mercury reacts with warm dilute nitric acid. Compounds of mercury in two states of oxidation are common. For example, $Hg(NO_3)_2$ (mercuric nitrate), $Hg_2(NO_3)_2$ (mercurous nitrate). Mercury fulminate $Hg(ONC)_2$ is useful as a detonator for high explosives.

Much silver is recovered in the purification of copper and also of lead, since the ores occur together. Silver has a beautiful, soft, yellowish-white luster, making it valuable for tableware, jewelry, and mirrors. It does not oxidize readily but dissolves in hot dilute nitric acid. It reacts with sulfur and sulfide compounds to form the familiar black tarnish.

Silver salts of the halogens (except AgF) are insoluble and used as tests for halides. Halides are unstable in light and are used in photography. Silver compounds form complex compounds with ammonia. They tarnish with sulfides to form silver sulfide.

Silver mirrors are produced by chemical reduction of silver salts.

Much gold is recovered from smelting industries. Free gold is mined by three methods: (1) placer (hydraulic); (2) amalgamation; (3) cyanide. Gold has a pleasant, yellow, metallic luster. It is a good conductor of electricity. Gold is also extremely malleable; it can be made into very thin sheets, called gold leaf. Gold is used primarily for jewelry and for coins.

Tungsten is important for tool steels, superhard carbides (WC and $WTiC_2$). It is used for electric light filaments in the form of fine wire produced by powder metallurgy.

Platinum is found free, principally in Russia. In Canada it is recovered as a by-product of nickel smelting. Platinum is a very inactive element. It dissolves in aqua regia. Its chief industrial use is as a catalyst. It is also used in jewelry and dental alloys and for laboratory apparatus.

QUESTIONS

1. In what part of the replacement series of metals are the noble metals?

2. What can be said about the stability of the oxides of the noble metals?

3. Which of the metallic elements do not possess a silvery color?

4. What states of oxidation (valence) are exhibited by compounds of mercury, gold, silver, copper, platinum, tungsten, sodium, aluminum, iron, and zinc?

5. What properties of platinum or platinum alloys make this metal useful in the form of ribbons or wires for heating units in electric-resistance furnaces? Comment on the cost of building such a furnace.

6. In what reactions does platinum serve as a catalyst?

7. What function does mercury vapor serve in fluorescent lamps?

8. What happens to mercury oxide when it is heated in a test tube?

9. What happens to silver oxide when it is heated in a test tube?

10. Write equations for the chemical changes suggested by questions 8 and 9.

11. How can mercury be removed from a gold ring that has become amalgamated?

12. Tell how a dentist prepares an amalgam for filling tooth cavities.

13. Which is the more toxic, calomel or corrosive sublimate? Write the formula of each, and give its chemical name; state a use for each.

14. What is the chief use of mercury fulminate?

15. Mercury di-iodide exists in two forms, one yellow and the other red. What term is applied to such forms?

16. Write the formula equation for the reaction of mercury with dilute nitric acid.

17. Write ionic equations for the reaction of hydrogen sulfide on solutions of (*a*) silver acetate; (*b*) mercuric dichloride; (*c*) mercurous nitrate.

18. Write ionic equations for the reaction between (*a*) hydrochloric acid and silver nitrate solution; (*b*) hydrochloric acid and mercurous nitrate solution.

19. Outline the procedure for obtaining silver from silver sulfide ore.

20. How may one make a mirror of metallic silver on glass?

21. For astronomical purposes, what advantages has an aluminum mirror over a silver mirror?

22. Write a formula equation for the decomposition of silver nitrate when it is heated.

23. How can one prevent silver from tarnishing? How is this done in jewelry stores?

24. Describe three methods by which gold is obtained from low-grade ores.

25. Can gold be deposited electrochemically? Why does it drop as a sludge below the copper anode when impure copper is refined electrochemically?

26. Explain what is meant by 10-*carat gold;* 14-*carat gold;* 1-*carat diamond; solid silver; sterling silver; coin silver;* 1 *pennyweight of gold.* (Refer to a dictionary.)

27. How is gold applied to the edges of inexpensive drinking glasses?

28. Which countries have the greatest supply of tungsten?

29. Explain how the invention of the tungsten carbide cutting tool gave Germany temporary advantage in the machine-tool industry.

30. What novel means is used in prospecting for tungsten ores?

31. Make a labeled diagram of an apparatus for electroplating gold onto a vanity case.

32. Review the contact process for making sulfuric acid. Find out the approximate cost of the catalyst for a typical plant.

33. Which of the following materials could be chosen for the production of elementary fluorine (F_2): copper; glass; gold; platinum; Monel metal; stainless steel; aluminum?

34. Write an equation for the effect produced when a photographic plate containing silver is dipped into a gold cyanide solution [$Au(CN)_3$].

UNIT TEN .... CHAPTER XL

WHAT LIES AHEAD

Preparation for Further Training in Chemistry

If a pupil has decided to take additional chemistry courses when he reaches college, and particularly if he intends to enter a branch of the chemical profession, he is fortunate if he makes this decision while still in high school. He has then the opportunity to seek advice in regard to the best courses to select as a preparation for college work.

High-school Training. In addition to the course in chemistry a high-school pupil should elect as much mathematics as possible, take a thorough course in physics, and start his work in modern languages while still in the secondary school. If he cannot do this, it is not too late to start them in college.

Professional chemists emphasize the tremendous importance of training in English. The value of the ability to express oneself in clear, concise language, both written and oral, cannot be overemphasized. The results of chemical research must be conveyed to employers or to the public, and those who have been well trained in the use of the English language have an advantage over those of equal chemical ability who lack this power of expression.

Many colleges include in their requirements for the bachelor's degree in chemistry a reading knowledge in *two* foreign languages. For an American, German is still the most important second modern language and French is usually rated next. Russian is gaining in prominence, however; we may predict that in the future many chemists will wish to possess at least a reading knowledge of this language.

Students who plan to enter the medical and similar professions will be required to study chemistry intensively in the early part of their college training, and the same preparation for college is advised. Medical schools are glad to accept well-trained and able undergraduate chemists in their first-year classes. These students usually substitute biology courses for the more specialized advanced chemistry courses, but through the first two or three years of college the training of doctors and of chemists may be identical.

The high-school course in chemistry is the best starting point for those who wish to receive such professional training, and those who have done well in it may be encouraged to continue their work in this science in college. Many colleges give placement tests to entering freshmen and assign those who show ability to more advanced sections, where there is little repetition of the work covered in this book. By selecting the foundation courses in secondary school and working diligently, a student may even receive advanced standing in many colleges. This gives such a student a great advantage in that he may complete his elementary training at an earlier date; in the time gained he may elect cultural courses that otherwise would be denied him or take advanced work in the field of his profession.

College Training. The training of a professional chemist in college will include much of the following:

General

1. Language:
    - *a.* English—clear logical style in ***writing*** and ***speaking***
    - *b.* German—a reading knowledge of ***scientific German***
    - *c.* Other foreign languages—one of the following: French, Russian (Latin or Greek)
2. Cultural subjects:
    - *a.* History, psychology, sociology, philosophy, economics, and fine arts
3. Mathematics—all that the student can absorb:
    - *a.* High-school mathematics, including plane geometry, trigonometry, and solid geometry
    - *b.* College mathematics, including differential and integral calculus
    - *c.* Advanced courses in mathematics for those who plan to go to graduate schools

Special courses

1. Chemistry—general, analytical, organic, physical, and industrial; advanced courses in special fields of chemistry
2. Physics—general physics, mechanics, electricity and magnetism, electronics, and other specialized courses
3. Other sciences—at least one of the following: biology, bacteriology, geology, mineralogy, crystallography, metallurgy
4. Special fields of training—law (contracts, patent law, government regulations), finance, management, or engineering
5. Special skills—glassworking, machine-shop practice, drafting, photography

Graduate Training. After high school and college, many an ambitious young chemist will wish to complete the training for the degree of doctor of philosophy and enter the research work for which this advanced degree is frequently required. Usually he is able to receive some financial support during this period of training, and frequently he is asked to assist in the teaching of the undergraduate students at the institution in which he is enrolled.

College Chemistry Courses

General Chemistry. In colleges where there is a sufficient number of students to warrant it, the entering students are distributed, on the basis of ability and previous training, between two courses—***elementary chemistry*** and ***general chemistry*** (the specific designation of these courses varies). Those who have had good high-school courses are usually placed in the more advanced general chemistry course. The classwork is more theoretical here, and it emphasizes numerical calculations more than the descriptive elementary course. Frequently the time required for this course is only one term, and those who do well in it proceed with qualitative analysis during the second term.

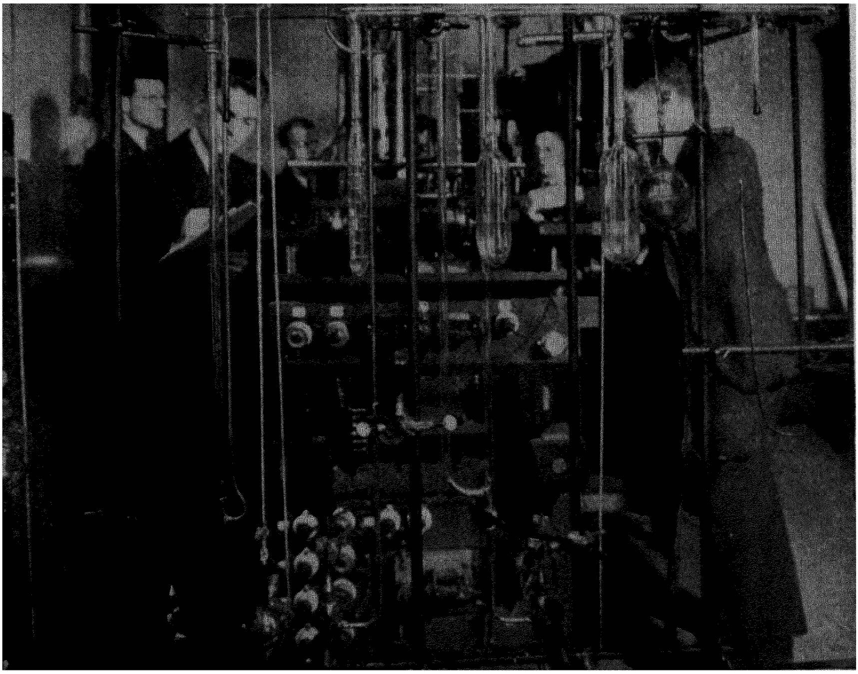
Qualitative Analysis. Much of the knowledge of inorganic chemistry expected of the undergraduate chemist is taught in the course in qualitative analysis. The emphasis here is on laboratory work and on the application of chemical principles learned in the first year of study. The analysis of solutions and solids, alloys and ores for about 26 of the common metallic elements is mastered. Frequently, analysis for a number of negative ions is also included. In recent years the laboratory work has been conducted with small amounts of material, on what is known as the ***semi-micro scale.*** The amount of each ion present in a mixture may be estimated but is not determined accurately.

Quantitative Analysis. In a course with this designation, the laboratory skill of the young chemist as an analyst is improved by emphasizing precise technique and accuracy. Various methods of carrying out the determination of the exact quantity of a substance present (in a mixture or solution) are studied. After a student has completed this course, he begins to feel that he is a chemist; no one can consider himself a chemist unless he has developed the skills and techniques of quantitative analysis.

Organic Chemistry. In college, the course in organic chemistry is a systematic examination of the various classes of organic compounds and their interrelations. The various types of reactions are studied, and in the laboratory the preparation of many typical carbon compounds is undertaken. In advanced courses the student also encounters qualitative and quantitative analysis of organic compounds and mixtures.

Physical or Theoretical Chemistry. The laws of physics and chemistry and their application to problems in chemistry are topics that are discussed in physical chemistry. The theoretical interpretation of the behavior of chemical substances is closely examined. The laboratory work emphasizes the methods by which various properties of substances are measured and by which information concerning the mechanism of chemical reactions is derived.

Industrial Chemistry. The methods of carrying out chemical reactions on a large scale are taken up in industrial chemistry. The work is usually divided into what are called ***unit processes,*** by which the commercial manufacture and processing of materials are undertaken. In this course the chemist gets away from the test tube and funnel and uses a barrel and a filter press. He needs more skill in pipe fitting and plumbing than in glassworking, and a floor mop is inadequate to clean up his floods. This is his introduction to the workaday world of chemistry, in which he applies all that he has learned in his long course of training.



From the News Service, Massachusetts Institute of Technology

FIG. 40-1.—These advanced college students are using their knowledge of chemistry in research work in a biology laboratory at the Massachusetts Institute of Technology, Cambridge, Massachusetts, which had one of the first departments of biology in this country.

Chemical Engineering. The work of the chemical engineer is the building of chemical plants and the supervision of their operation. His training includes much more engineering than that of the industrial chemist. His training is quite rigidly specified as he has to meet professional requirements.

Employment in the Chemical Industry

Following the college courses in chemistry and allied subjects, a small percentage of the students, particularly those who stand near the top of the class, may wish to continue their training in a graduate school. Those who complete their training with the bachelor's degree receive ready employment in various capacities in industry—in research laboratories, production departments, and sales departments. Many work in control laboratories where routine and special check analyses are carried out to ensure that the company's product will be up to the standards set.

Details of the jobs that chemists, both men and women, carry on in public and private laboratories are described in the following books: *The Chemist at Work*, Roy I. Grady and John W. Chittum, editors, published by the *Journal of Chemical Education*, Easton, Pennsylvania, 1940; a collection of papers describing the type of work done by professional chemists, written by chemists (men and women) actually engaged in specialized fields of chemistry. *Your Career in Chemistry*, Norman V. Carlisle, E. P. Dutton & Company, Inc., New York, 1943; Mr. Carlisle was formerly the vocational-guidance editor of *Scholastic*, the national high-school weekly. *So You Want to Be a Chemist?*—Herbert Coith, McGraw-Hill Book Company, Inc., New York, 1943; this little book describes the activities of chemists and chemical engineers, is packed with incidents from practical experience, and is written in an entertaining manner.

Happiness

And Science dawns though late upon the earth,
Peace cheers the mind, health renovates the frame;
Disease and pleasure cease to mingle here,
Reason and passion cease to combat there,
Whilst mind unfettered o'er the earth extends
Its all-subduing energies, and wields
The sceptre of a vast dominion there.
—SHELLEY

REVIEW EQUATIONS

(*Do not write in this book.*)

1. Sodium carbonate + hydrochloric acid →
2. Potassium carbonate + sulfuric acid →
3. Sodium hydroxide solution + carbonic acid →
4. Barium hydroxide solution + carbon dioxide →
5. Burning carbon monoxide →
6. Common salt + sulfuric acid →

7. Common salt + sulfuric acid + manganese dioxide →

8. Common salt solution + silver nitrate solution →

9. Calcium chloride solution + silver nitrate solution →

10. Copper + chlorine →

11. Arsenic + chlorine →

12. Hydrogen burned in chlorine →

13. Zinc + hydrochloric acid →

14. Hydrochloric acid + sodium hydroxide solution →

15. Hydrochloric acid + calcium hydroxide solution →

16. Manganese dioxide + hydrochloric acid →

17. Zinc chloride solution + silver nitrate solution →

18. Zinc hydroxide + hydrochloric acid →

19. Sodium + water →

20. Hydrogen chloride + sodium →

21. Aluminum hydroxide + nitric acid →

22. Ammonium nitrate heated →

23. Aluminum sulfide + water →

24. Lead acetate solution + zinc →

25. Copper + dilute nitric acid →

REVIEW QUESTIONS

1. Copy the following words in a vertical column: Haber, Dewar, Ostwald, Moseley, Solvay. Opposite each write the word or phrase from the following group that is most closely related: air conditioning; periodic law; nitric acid; liquid air; spectrum analysis; baking soda; fixation of nitrogen.

2. Use the words *acid, basic,* or *neutral* to predict how water solutions of the following salts would react toward litmus: copper chloride; sodium sulfate; lead acetate; potassium carbonate. Name the process that causes a salt solution to act as either an acid or a base.

3. Write the common name and one use of N_2O; $Na_2CO_3 \cdot 10H_2O$; CaO; Na_3PO_4; $NaHCO_3$.

4. Write three equations to show respectively, (*a*) the fixation of nitrogen; (*b*) replacement of one halogen by another; (*c*) a reversible reaction.

5. Name three substances that are put into a blast furnace and three that come out.

(*Continued on next page.*)

Bars of cast iron, wrought iron, and steel are supported at both ends and struck sharply in the middle with a sledge hammer. What happens to each?

6. Name a steel alloy, and give its special use.

In the equation $2FeCl_3 + Fe \rightarrow 3FeCl_2$, point out (*a*) oxidation; (*b*) reduction.

Make a labeled diagram of a furnace for the production of aluminum.

7. Write equations for all chemical actions which occur in the following group, and indicate those in which no action takes place by the letters N R: (*a*) zinc and dilute hydrochloric acid; (*b*) copper and dilute hydrochloric acid; (*c*) aluminum and concentrated nitric acid; (*d*) lead and copper sulfate solution; (*e*) iron and silver nitrate solution.

8. What weight of magnesium can be made by the electrolysis of $\begin{cases}450\\200\end{cases}$ pounds of magnesium chloride that is 95 per cent pure? $MgCl_2 \rightarrow Mg + Cl_2$

9. Answer briefly:

Name two ways in which the casein in milk can be coagulated.

When a sample of an anhydrous substance takes up a definite amount of water and becomes crystallized, the product is then classed as what sort of substance?

What is the common name of a material produced by passing chlorine over moist calcium hydroxide suspension?

Tell how the famous Carlsbad (limestone) Caverns were formed.

What is Carborundum?

10. What two gases are present in the composition of water gas? Give one use for water gas.

Write a formula for (*a*) cane sugar; (*b*) corn sugar (glucose).

How would you identify each of the following: silk, wool; cotton?

Explain the cleansing action of soap.

11. Le Chatelier's principle may be stated thus: when an equilibrium mixture is put under stress of any sort (addition of any one of the reacting substances or products, changes in temperature or pressure, or alteration of other conditions), the amounts of all the different substances present will always change in such a way as to reduce the strain produced.

In an equilibrium mixture in general, what is the effect of (*a*) adding more of a reacting substance; (*b*) removing a product; (*c*) permitting a gaseous product to escape; (*d*) forming an un-ionized product from ions; (*d*) increasing the pressure, assuming at least one of the reacting substances is a gas; (*f*) increasing the temperature if an endothermic reaction; (*g*) increasing the temperature if an exothermic reaction; (*h*) adding a catalyst upon (1) the composition of equilibrium mixture and (2) the time required to attain equilibrium?

12. Does an equilibrium mixture ever go entirely to completion in either direction?

13. Predict which way each of these reactions will proceed and tell why the reaction goes in that direction:

(*a*) $CaCO_3 + 2HCl \rightleftarrows CaCl_2 + H_2O + CO_2$
(*b*) $2NaCl + CO_2 + H_2O \rightleftarrows Na_2CO_3 + 2HCl$
(*c*) $Fe_3O_4 + 4H_2 \rightleftarrows 4H_2O + 3Fe$
(*d*) $BaSO_4 + 2HCl \rightleftarrows BaCl_2 + H_2SO_4$
(*e*) $CaSO_4 + 2HF \rightleftarrows CaF_2 + H_2SO_4$
(*f*) $FeS + 2HCl \rightleftarrows H_2S + FeCl_2$
(*g*) $CuS + 2HCl$ (dilute) $\rightleftarrows CuCl_2 + H_2S$
(*h*) $NaCl + H_2O \rightleftarrows HCl + NaOH$

14. What is the percentage of nitrogen in ammonium carbonate?

15. State three physical properties of chlorine.

Give three uses for sodium hydroxide.

Sodium hydroxide should be kept in tightly sealed containers. Why?

16. What weight of lime can be made from 10 tons of limestone, assumed to be pure calcium carbonate?

17. Distinguish between liquid chlorine and chlorine water.

Explain why chlorine bleaches colored cloth better when the cloth is moist than when it is dry.

State three uses for chlorine.

18. Complete and balance formula equations for the following reactions: (*a*) electrolysis of salt and water; (*b*) action of sodium hydroxide on an acid; (*c*) action of phosphorus on copper; (*d*) decomposition of hypochlorous acid; (*e*) action of chlorine on cadmium.

19. Write four informative sentences, using in each, respectively, the following words or expressions: (*a*) impurities in common salt; (*b*) passive condition; (*c*) corrosion; (*d*) alkali.

20. Assuming that cottonseed oil is pure olein [$C_3H_5(C_{18}H_{33}O_2)_3$], determine the weight of soap made in a laboratory experiment from $\begin{cases}5\\8\end{cases}$ grams of cottonseed oil.

21. A compound contains 92.31 per cent carbon and 7.69 per cent hydrogen. One liter of its vapor at STP weighs 3.48 grams. Find its molecular formula.

22. What should the weight of 1 ton of blue vitriol become after it is completely dehydrated?

23. What mathematical ratio should be used to show the percentage of phosphorus in calcium phosphate?

24. Compute the cost per day of lighting a house with acetylene if $\begin{cases}160\\140\end{cases}$ liters (STP) of gas is used per day and calcium carbide costs $\begin{cases}10\\8\end{cases}$ cents per kilogram.

25. A wax candle is 85 per cent by weight carbon and the rest hydrogen. Find the weight of oxygen needed when $\begin{cases}60\\40\end{cases}$ grams of the candle burns.

26. How many pounds of iron could be obtained from 1 ton of ore consisting of 70 per cent magnetite?

27. A certain specimen of water contains 1.2 grams of calcium bicarbonate per gallon. What weight of calcium hydroxide should be added to soften 1000 gallons of this water?

28. Classify as physical or chemical changes: (*a*) heated iron expands; (*b*) iron dissolves in dilute sulfuric acid; (*c*) a ray of light changes silver chloride to metallic silver and chlorine; (*d*) water is heated from 14.5 to 15.5°C; (*e*) heated iodine forms a purple vapor; (*f*) iodine rubbed with mercury forms a red powder.

29. Why can you not light a lump of coal with a match?

30. In tabular form give (1) name, (2) formula, and (3) one use of (*a*) a fat; (*b*) a soap; (*c*) an acid found in vinegar; (*d*) an alcohol; (*e*) a sugar.

31. When $\left\{\begin{matrix}120\\100\end{matrix}\right.$ grams of wine was treated with iodine and lye solution, 78.8 grams of iodoform was precipitated. What percentage of alcohol was present in the wine?

32. How many liters of air are necessary for the complete combustion of $\left\{\begin{matrix}200\\500\end{matrix}\right.$ milliliters of acetylene gas?

33. Which is the richer source of carbon dioxide, sodium bicarbonate 90 per cent pure or dolomite 95 per cent pure?

34. In tabular form give (1) common name, (2) formula, and (3) one use of (*a*) calcium oxide; (*b*) calcium hydroxide; (*c*) zinc oxide; (*d*) aluminum oxide; (*e*) copper sulfate crystals.

35. Write equations for the following reactions, using formulas throughout: (*a*) burning methane; (*b*) action of soap on water containing calcium chloride; (*c*) heating copper nitrate; (*d*) the chief reduction in a blast furnace; (*e*) formation of slag from silica and limestone.

36. A compound colors a Bunsen flame green. When sodium sulfate solution is added, its solution forms a white precipitate, insoluble in hydrochloric acid. Also, when fresh ferrous sulfate solution and concentrated sulfuric acid are added carefully, a brown ring forms above the acid. Give the name and formula of this compound.

37. Answer briefly: (*a*) What is the most important source of iron? (*b*) What is the most important source of aluminum? (*c*) By what method is aluminum prepared commercially? (*d*) Name a zinc alloy, tell the metals present, and give a use for the alloy. (*e*) What is oxidation in terms of valence change?

38. (*a*) What property of aluminum is exhibited in the Thermit reaction? (*b*) In the following list write the name(s) and formula(s) of substances that do ***not*** have the formula $CaCO_3$: marble; gypsum; limestone; chalk; calcite. (*c*) $MgSO_4 \cdot 7H_2O$ is sold under what name? (*d*) Name a copper alloy, tell the metals present, and give a use for the alloy. (*e*) Name three substances that are used to make glass. Name another substance that may be added to color glass, and state the color produced.

39. (*a*) After metallic potassium acts with water, what is the effect on litmus of the resulting solution? (*b*) Write the equation for the action in (*a*). (*c*) What ions are dissociated when caustic soda is melted? (*d*) Select the correct conclusions: The formula of the most common natural compound of phosphorus is P_2O_5; H_3PO_4; Na_3PO_4; $Ca_3(PO_4)_2$; P_4S_3. (*e*) Give the name of a commercial abrasive made in an electric-resistance furnace.

40. Tell what conditions produce a dust explosion.

41. Examination of the stomach of a poison victim showed the presence of $\left\{\begin{matrix}1.5\\2.25\end{matrix}\right.$ grams of arsenic. How much white arsenic (As_2O_3) had been swallowed by the victim?

42. A compound analyzes as follows: magnesium 9.8 per cent; sulfur 13 per cent; oxygen 71.5 per cent; hydrogen 5.7 per cent. Find the simplest formula of this compound.

43. How many liters of air are needed to burn completely $\left\{\begin{matrix}20\\30\end{matrix}\right.$ liters of arsine (AsH_3)?

44. Describe a method for the complete purification of water, using a labeled sketch. Tell what impurities are removed.

45. Give the reason for the following: (*a*) filtered salt water tastes salty; (*b*) chemists use distilled water for making solutions; (*c*) soap is not made in aluminum vessels; (*d*) nylon is not a suitable material for making lampshades; (*e*) nitrates are scarce in wartime.

46. Name and state three important laws of chemistry.

47. Define and illustrate by an example: *catalyst; oxidation; reduction; replacement; electrolysis.*

48. Write equations for making each of the following compounds in four different ways: (*a*) sodium chloride; (*b*) potassium nitrate; (*c*) zinc sulfate; (*d*) magnesium chloride.

49. Show by equations the ions dissociated from each of the following compounds: (*a*) sodium chloride; (*b*) zinc nitrate; (*c*) calcium hydroxide; (*d*) sulfuric acid: (*e*) aluminum chloride.

50. Write formula equations for the following reactions, and below each write the equation in ionic form: (*a*) zinc + hydrochloric acid →; (*b*) iron + copper sulfate solution →; (*c*) ammonium hydroxide + phosphoric acid →; (*d*) sodium sulfate and barium chloride solutions →; (*e*) sodium carbonate solution + calcium hydroxide solution →.

51. Explain why a piece of wood burns with a flame at first and later without a flame.

GLOSSARY

abrasive. A hard substance used for grinding or polishing another substance. Sand and emery are much-used abrasives.

absolute temperature scale. A scale of temperatures, sometimes called the Kelvin scale. On the absolute scale the complete absence of heat is considered as 0°A, a point that corresponds to −273°C. The freezing point of pure water (0°C) is 273°A or 273°K.

absorption. The act of (1) swallowing up one substance by another; (2) taking in radiant energy and changing it to other forms. Sponges absorb water. Green leaves absorb sunlight, using the energy to carry on chemical changes.

acid. A compound that will neutralize an alkali. Water solutions of acids dissociate hydrogen ions. The most extensively used acid is sulfuric acid (H_2SO_4).

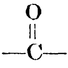
acid anhydride. An oxide that, when combined with water, forms an acid. Sulfur trioxide (SO_3) is the anhydride of sulfuric acid (H_2SO_4).

activity. The relative degree of ease or difficulty with which an element reacts in a chemical change. Potassium has the greatest activity of all common metals.

adsorption. The clinging of a gas, liquid, or solid to the surface of a solid. Activated charcoal is used in gas-mask canisters because of its adsorption of poisonous gases.

alchemy. An art, chiefly of the Middle Ages, in which those who practised it tried mainly to make gold from base metals. Alchemists are incorrectly called the predecessors of chemists.

alcohol. An organic compound containing the hydroxyl radical (OH). The most common alcohol is ethanol (C_2H_5OH).

aldehyde. An organic compound containing the  $-\overset{\displaystyle O}{\overset{\|}{C}}-H$ group of atoms. Formaldehyde (HCHO), the most common aldehyde, is used to make plastics.

alkali. A very active base. Sodium hydroxide (NaOH) is a widely used alkali.

allotropic. Referring to the different forms of an element, due to differences in the number and arrangement of atoms in a molecule. Sulfur has three common allotropic forms.

alloy. A mixture made by cooling two or more metals that have been melted together. Brass is a common alloy, containing zinc and copper.

alpha particle. The nucleus of a helium atom bearing a positive electric charge. Some radioactive materials, such as radium, emit alpha particles.

alum. A complex compound formed by crystallizing together the sulfates of a valence-1 (univalent) and a valence-3 (trivalent) metal. Common alum is hydrated potassium aluminum sulfate ($KAlSO_4 \cdot 12H_2O$).

amalgam. An alloy in which one of the metals is mercury. Dentists use amalgams for filling cavities in teeth.

amorphous. Lacking definite shape. In chemistry, crystalline and amorphous are opposite terms.

analysis. A process of decomposition. Also, the assay, or examination, of a substance. Chemists carry out an analysis of a substance in order to find out its composition.

anesthetic. A substance used to deaden pain. General anesthetics produce unconsciousness, while local anesthetics affect an area.

anhydrous. Without water. When gypsum ($CaSO_4 \cdot 2H_2O$) is very strongly heated, all the water combined in the crystalline material is removed; anhydrous calcium sulfate ($CaSO_4$) remains.

anode. A positively charged electrical terminal or plate. Electrons are lacking at the anode.

antiseptic. A substance used for killing bacteria or for slowing the rate of their growth. The word antiseptic literally means "against poisoning." It refers to substances that destroy micro-organisms.

aqua regia. A mixture containing three parts concentrated hydrochloric acid and one part concentrated nitric acid by volume. Aqua regia will dissolve gold.

atmosphere. The gaseous layer surrounding the earth's crust. The atmosphere at sea level normally exerts a pressure that balances a column of mercury 760 mm high in a closed tube.

atom. The smallest unit particle of an element. Atoms of the same element, due to isotopes, may differ in respect to nuclei, but their outer electron arrangements are the same.

atomic number. A number, assigned to an atom of an element, that designates the number of positive charges, or protons, in excess of the neutrons in the nucleus. The atomic number is a fundamental difference among atoms of different elements.

atomic weight. A number that compares the weight of a given atom with the weight of an oxygen atom considered as 16. The atomic weight of magnesium is 24; thus an atom of that metal weighs 1.5 times the weight of an oxygen atom.

barometer. An instrument for measuring pressure. Mercurial barometers are commonly used in laboratories.

base. Any compound that neutralizes an acid. Magnesium oxide and potassium hydroxide are bases; the latter is both a base and an alkali.

beta rays. Streams of electrons emitted by radioactive materials. Radium B (lead) emits beta rays in the course of its decomposition to form radium C (bismuth).

binary. Referring to compounds that contain two elements. Sodium chloride is a binary compound.

boiling point. The temperature at which the vapor pressure of a liquid just exceeds the pressure of the atmosphere above it. The boiling point of water is 100°C at 760 mm pressure.

British thermal unit (Btu). The amount of heat needed to change 1 lb of water 1°F. One Btu is equivalent to 252 cal.

burning (see combustion). The combining of elements accompanied by light and heat. In ordinary burning, oxygen combines with a material. Chlorine and sulfur, however, may combine with the same elements as oxygen and have burning take place.

calorie. The amount of heat needed to change the temperature of 1 g of water 1°C. A large Calorie (capitalized) is 1000 times the (small) calorie.

calorimeter. An apparatus for measuring the quantity of heat. In a calorimeter a weighed amount of water is allowed to undergo an observed temperature change.

carbohydrate. A compound consisting of carbon, hydrogen, and oxygen, the latter two elements usually in the proportion of 2 to 1. Common table sugar, sucrose ($C_{12}H_{22}O_{11}$), is a carbohydrate.

catalyst. A substance that changes the speed of a chemical action but is not itself permanently altered. Positive catalysts are sometimes called accelerators or promoters; negative catalysts are called retarders or inhibitors.

cathode. An electric terminal with an excess of electrons, hence negatively charged. In most electroplating the metal is plated out on the cathode.

ceramics. The art of producing useful articles from clay or similar materials. Ceramics is an interesting hobby with many people. The ceramics industry is extensive.

chemical. A term loosely applied to a substance used in a chemical laboratory or to a substance used to bring about a chemical change. Salt, soap, soda, and acids might be called "chemicals."

chemi-luminescence. The production of light energy directly as a result of a chemical change. Chemi-luminescence shows well in a darkened room.

chemistry. The science that deals with the composition of matter and the changes it undergoes. Chemistry and physics are two useful sciences.

coagulation. Clotting or forming lumps. The coagulation of egg white is brought about by heat.

colloidal condition (or **colloid**). A state of extremely small subdivision of particles. Particles in the colloidal condition do not settle out when suspended in a liquid.

combining number. The number of atoms that combine with or replace an atom of hydrogen. The combining number of oxygen is 2.

combining volume. The volume (liters, for example) of a gas that enters into a chemical change. The combining volumes of hydrogen and nitrogen have a ratio of 3 to 1 in forming ammonia.

combining weight. The weight of an element that combines with or displaces 1 g of hydrogen. The atomic weight of an element divided by its combining number is its combining weight.

combustion (see burning). The process of burning by which light and heat energy are emitted. The combustion of coal is a great source of industrial power.

component (see constituent). One of the substances in a mixture. Quartz is a component of granite. Zinc is a component of brass.

compound. A substance composed of two or more elements combined in definite proportions by weight. Water is a compound.

concentrated. The opposite of dilute. Molasses is a highly concentrated (and impure) sugar solution.

concentration. The amount of a substance in a given volume. The concentration of potassium nitrate in a certain solution might be 25 g per 100 ml of solution; it could also be expressed as the number of grams of the substance in 100 g of water.

condensation. The act of changing a gas or vapor to a liquid. The condensation of water vapor produces rain.

constituent (see component). A part of a whole; in chemistry usually one of the elements that make up a substance. Zinc is a constituent of zinc oxide (ZnO).

corrosion. The rusting or disintegrating of a material, sometimes caused by the weather. Chemists study the cause and prevention of corrosion.

covalent linkage. One type of binding force between atoms. It consists of one or more shared pairs of electrons. Hydrogen compounds are bonded by covalent linkages.

cracking. The process of decomposing a hydrocarbon by heating. Much gasoline is made by cracking heavier petroleum oils.

crucible. A thimble-shaped vessel made of clay, sand, graphite, alumina, or other material. A crucible is used for holding a substance that is being intensely heated.

crystals. A solid of regular geometrical form, flat surfaces, and sharp edges, so formed by nature. Common salt forms cubic-shaped crystals.

crystallization. The act of forming crystals. Crystallization takes place in freezing liquids or in saturated solutions.

decomposition. The process of breaking down a substance into simpler parts. The decomposition of mercury oxide takes place when the compound is heated.

dehydrated. That from which the water is removed. Dehydrated foods are usually shipped when much food must be packed into a limited space.

deliquescence. The property of a compound by which it takes moisture from the air and dissolves in the water so gained. Stick sodium hydroxide shows marked deliquescence.

denatured. Deprived of its natural properties or qualities. Denatured alcohol is violently poisonous for internal use.

density. A measure of the compactness of matter, expressed as weight per unit volume. The density of a gas is commonly expressed in terms of grams per liter.

destructive distillation. The process of heating a substance out of contact with air and condensing the volatile products different from the original material. Wood alcohol may be produced by the destructive distillation of wood.

detergent. An agent used for cleansing. Soapy water is a good detergent.

detonator. A violently explosive substance that decomposes almost instantly. In. mining, a detonator in a small copper cap is used to explode dynamite.

deuterium. Heavy hydrogen. Deuterium, atomic weight 2, is an isotope of hydrogen

developer. A chemical agent that makes a latent image visible. Developers are used in photography.

dibasic. An acid that contains 2 g of replaceable hydrogen ions per formula weight. Dilute sulfuric acid is dibasic.

diffusion. The act of intermingling. The diffusion of gases into the air takes place readily.

dilute. The opposite of concentrated. A dilute solution contains a relatively large amount of solvent and a little solute.

disinfectant. An agent that kills germs. Some coal-tar products, such as phenol, are good disinfectants.

displacement (often **replacement**). A chemical change in which an element takes the place of another element in a compound, setting the other element free. Setting hydrogen free from an acid by replacing it by zinc is an example of this type of reaction.

dissociation. Separation; the opposite of association. Ionic compounds dissolved in water dissociate into ions readily.

distillate. The material, usually liquid, that is vaporized and condensed in the process of distillation. The gasoline distillate is the most valuable petroleum product.

distillation. The process of heating a material and condensing the volatile products. Water is purified by distillation.

double replacement. A chemical change between two compounds in which two new compounds are formed. The action between solutions of sodium chloride and silver nitrate by which sodium nitrate and silver chloride are formed is called double replacement.

effervescence. The escape of a gas from a liquid, provided that the liquid and gas are different substances. When zinc and an acid react, effervescence of hydrogen takes place.

efflorescence. The process of losing water from a hydrated crystal. Sal soda crystals undergo rapid efflorescence forming a dry powder.

electrode. A plate or rod from which electrons leave or enter a liquid or a gas. Electric cells have two electrodes.

electrolysis. The process of bringing about chemical changes by passing an electric current through a liquid. Chlorine is produced by the electrolysis of common salt solution.

electrolyte. A liquid that conducts electricity. In electrolysis the electrolyte is decomposed.

electron. A unit of negative electricity. An electron is much lighter and smaller than a hydrogen atom.

element. A simple substance of uniform chemical composition that cannot be decomposed by chemical means. Sulfur is an element.

emulsion. A suspension of droplets of a liquid in another. Immiscible (not capable of being mixed or mingled) liquids, such as oil and water, form a temporary emulsion when shaken together.

endothermic. A chemical change in which heat must be continually supplied; the opposite of *exothermic.* The action of steam on hot coke is endothermic; the burning of coke, exothermic.

energy. Ability to do work. Heat, light, electricity, and chemical energy are some forms of energy.

enzyme. An organic catalyst produced by living organisms. Yeast contains a number of enzymes.

equation. A representation of a chemical change in symbol form. $C + O_2 \rightarrow CO_2$ is an equation that represents the burning of carbon.

equilibrium. A condition of balance between forces. In a chemical equilibrium two opposite chemical actions are proceeding at the same rate so that the relative proportion of the substances remains unchanged.

ester. An organic compound that may be formed by the action of an alcohol on an acid. Ethyl acetate ($CH_3COOC_2H_5$) is a common ester.

ether. An organic oxide. Common ether is diethyl oxide [$(C_2H_5)_2O$].

eudiometer. A stout graduated glass tube closed at one end and equipped with a pair of platinum wires that project through the glass, forming a spark gap. When chemical changes are carried out in a eudiometer, the volumes of gases used and produced can be measured.

explosion. A violent chemical or physical action in which the greatly increased pressure of an expanding gas (or liquid) causes it to erupt forcibly. The explosion of dynamite loosens ore in a mine.

Fahrenheit. A thermometer scale in which the boiling point and the freezing point of water at standard pressure are 212° and 32°, respectively. The Fahrenheit scale is used extensively in the United States.

fermentation. Chemical changes of organic matter brought about by living organisms. Changing cider (alcohol) into vinegar (acetic acid) is an example of fermentation.

fertilizer. Material added to the soil to promote growth of plants. Lack of fertilizer will produce meager crops if the soil does not possess the needed food material for the particular plants being grown.

filtration. The act of separating a solid from a liquid by passing the liquid through cloth, paper, porcelain, or similar porous material. Filtration removes suspended particles.

flame. Glowing burning gas. Wood burns at first with a flame.

flux. (1) A substance that aids the melting of other materials. (2) A cleaning agent used in soldering. Silica is used as a flux in metallurgy; zinc chloride is used as a flux in soldering.

formula. A group of symbols and figures representing an element or a compound and showing its composition. The formula for water is H_2O.

fractional distillation. A variation in the process of distillation in which portions of the distillate are collected between different boiling-point ranges. Water and alcohol cannot be completely separated by fractional distillation.

free. Native, uncombined, or alone. Gold is found free in nature.

freezing point. The temperature at which the solid and the liquid states of the same substance can exist in equilibrium when mixed without an apparent change in either. A cooling liquid remains at its freezing point until it has entirely solidified.

fusion. Melting. Brass is made by the fusion of copper and zinc together.

galvanize. To coat iron or steel with zinc. A steel nail can be galvanized by dipping it into molten zinc.

gamma rays. Short X rays emitted from some radioactive substances. Radioactive elements that emit beta rays also emit gamma rays.

gas. A state of matter having neither shape nor volume and consisting of independent molecules. When coal is heated, a gas escapes.

glass. A fused hard mixture, usually of silicates, and often transparent. Glassmaking is an ancient art.

gram. A unit of weight in the metric system. One gram is equal to $\frac{1}{1000}$ kg, or the weight of 1 ml of pure water at 4°C, or 0.0022 lb, avoirdupois.

gram-atomic weight. Atomic weight of an element expressed in terms of grams. The gram-atomic weight of oxygen is 16 g.

gram-molecular volume. The volume that holds one gram-molecular weight of a gas at STP. The gram-molecular volume of any gas is 22.4 liters.

gram-molecular weight (or **mole**). The molecular weight of a compound or element expressed in grams. The gram-molecular weight of water is 18 g.

gravimetric. Measured by weight. The result of the gravimetric analysis of sulfur dioxide indicates 50 per cent of each element.

Haber process. A method of making ammonia by direct union of nitrogen and hydrogen under proper conditions. The Haber process is of great economic importance.

halide. A fluoride, chloride, bromide, or iodide. The halides of a given element have similar properties.

halogen. A family of elements containing fluorine, chlorine, bromine, and iodine. The halogens are active nonmetals; they combine with metals to form salts.

heat. A form of energy that may cause a rise in temperature of substances. Heat is evolved by chemical action and by friction.

heavy water. Water in which the atoms of hydrogen are replaced by atoms of deuterium. The density of heavy water is slightly above that for normal water.

homogeneous. Alike in all its parts. Elements and compounds are homogeneous. Solutions are also homogeneous.

hormone. A chemical regulator of a function of the body. Hormones are put into the blood stream by secretions from glands. Adrenalin is a hormone that prepares the body for action in sudden emergencies.

hydrate. A crystal in which is incorporated a definite proportion of water. Blue vitriol ($CuSO_4 \cdot 5H_2O$) is a well-known hydrate.

hydrocarbon. A compound containing only hydrogen and carbon. Petroleum is a mixture of hydrocarbons.

hydrogenation. The process of adding hydrogen to a compound, usually with the aid of a catalyst. The hydrogenation of vegetable oils produces fats.

hydrolysis. The process by which the ions of a dissolved salt act on water. The hydrolysis of sodium phosphate in water produces a strongly alkaline solution.

hydroxide. A compound containing the radical OH. Soluble metallic hydroxides are bases.

hydroxyl. The hydroxide group of elements. The hydroxyl radical, represented by the symbol OH, is found in alcohols and in some alkalies.

identification. Definite recognition. Certain chemical tests are used in the identification of a substance.

indicator. A substance that shows the nature of a solution. Some indicators, such as litmus, show by their color change whether a solution is acid or alkaline.

inert. Inactive or slow in combining with another element. Helium is an inert gas, as it forms no chemical compounds.

ingredient. A constituent of a substance or material. Carbonated water is an ingredient of soda pop.

inorganic. Not organic. Refers to compounds that do not contain carbon, except carbonates and cyanides. Common salt is an inorganic compound.

insecticide. An agent for killing insects. Many insecticides contain arsenic.

ion. An atom or a radical carrying an electric charge as a result of the gain or loss of one or more electrons. The sulfate ion (SO_4^{--}) is derived from the sulfate radical (SO_4) by the gain of two electrons.

ionization. The process of transferring electrons to an element or radical so that it becomes an ion. Common salt is formed from its elements by the process of ionization.

isomers. Compounds with the same composition, but differing in arrangement of atoms within the molecule. Dimethyl ether and ethyl alcohol are isomers.

isotopes. Forms of the same element having identical outer-electron arrangement but different weight nuclei. Isotopes differ in respect to atomic weight.

Kelvin scale. See absolute temperature scale.

ketone. An organic compound containing the characteristic group $=C=O$. Acetone $[(CH_3)_2CO]$ is the best-known ketone.

kilogram. One thousand grams. A kilogram weighs 2.2 lb avoirdupois.

kindling temperature. The lowest temperature at which a material catches fire and burns. The kindling temperature is not a definite temperature but depends upon the rate of heat conduction of a material and other factors.

kinetic molecular theory. The present accepted theory that gases are composed of tiny moving particles. The truth of the kinetic molecular theory is well established.

lake. An insoluble coloring agent or pigment formed by a precipitated metallic hydroxide adsorbing a dye. Some lakes are used as pigments by artists.

law. The statement of an observed generalization in the behavior of nature, based upon many related experiments. Scientific laws seldom change.

liquid. A state of matter in which a substance flows freely; a state that is intermediate between the solid and gaseous states. Liquids are formless and fluid, taking the shape of the container. Liquid air is made by cooling and compressing gaseous air.

liter. The space occupied by 1000 g of water at 4°C. A liter is 1000.027 cc or 1000 ml.

litmus. A dye extracted from certain plants called lichens. Litmus is used as an indicator.

lye. Sodium (or potassium) hydroxide. Lye is a strong alkali.

malleability. Ability to be rolled or hammered into a thin sheet. Gold has high malleability.

matter. Anything that has weight and occupies space. Matter is a fundamental idea (concept) in chemistry.

melting point. Same as freezing point. The melting point is reached when the temperature of a substance is increasing and a solid is changing into a liquid.

metal. Any one of a group of elements that is characterized by the formation of positive ions and other general properties. Metals are good conductors of heat and electricity. Most of them have a silvery luster.

metallurgy. The process of extracting metals from ores; the detailed study of the properties of metals. Metallurgy is an important branch of applied chemistry.

mineral. An inorganic substance of definite composition found in the earth's crust. Sulfur is a mineral obtained in the United States, Sicily, and elsewhere.

mixture. A material consisting of two or more intermingled substances without regular composition. Brass is a mixture.

molal solution. A solution that contains a gram-molecular weight (mole) of a compound in 1000 grams of water. Molal solutions are used in molecular-weight calculations.

molar solution. A solution that contains a gram-molecular weight (mole) of a compound with enough water to make a liter of solution. A one-tenth molar solution of common table sugar contains 34.2 g of sugar in 1 liter of solution.

mole. See gram-molecular weight.

molecular weight. A number that represents the relative weight of a molecule of a substance compared with the weight of an oxygen molecule. The latter is taken as 32.

molecule. The smallest unit quantity of matter that can exist by itself in the gaseous state. The hydrogen molecule is composed of two atoms.

monobasic. An acid that contains 1 g of replaceable hydrogen per formula weight. Hydrochloric acid is a monobasic acid.

mordant. A sticky metallic hydroxide used for bonding dyes to cloth fibers. Aluminum hydroxide is widely used as a mordant.

multiple proportions. A law in chemistry. The law of multiple proportions was first stated by John Dalton.

nascent. Freshly formed. Nascent hydrogen seems more active than hydrogen formed some time before.

natural. Pertaining to nature. Natural chlorine is a mixture of several isotopes.

natural gas. A gas that comes out of a cave, volcano, or hole drilled into the earth. Some natural gases are good fuels.

neutralization. A complete action between an acid and a base so that the products have the characteristics of neither. Neutralization reactions are examples of proton transfer reactions.

neutron. A unit of matter consisting of a closely connected electron-proton pair. A neutron has no electric charge.

nonmetal. Opposite of a metal. Sulfur is a nonmetal.

normal solution. (1) Of an acid—contains 1 g of replaceable hydrogen per liter. (2) Of a soluble metallic hydroxide—contains 17 g of hydroxide radical per liter. Equal volumes of normal solutions of acids and soluble hydroxides entirely neutralize each other.

nucleus. Central portion of an atom. Practically the entire weight of an atom is concentrated in the nucleus.

octane. A hydrocarbon containing eight carbon atoms. The formula for octane is C_8H_{18}.

octane number. A number that gives the relative knocking rating of a motor fuel. Aviation gasoline may be 100 or more in its octane rating number.

ore. A mineral from which a metal may be extracted profitably. Bauxite is an ore of aluminum.

organic. An adjective that means pertaining to organisms or life. Organic chemistry is a study of the compounds of carbon except carbonates or cyanides.

organism. A living creature, plant, or animal. Yeast is an organism.

oxidation. A chemical change involving (1) the combination of oxygen with a substance and (2) the loss of electron(s) by the substance oxidized. Simple burning is an example of oxidation. (Memory aid: LEO, *l*oss of *e*lectrons is *o*xidation.)

oxide. A compound containing oxygen and another element chemically combined. Copper has two common oxides, red cuprous (Cu_2O) and black cupric (CuO).

ozone. An allotropic form of oxygen that can be made by passing oxygen through a region of an electric discharge. Ozone (O_3) is more vigorous in its chemical actions than ordinary oxygen (O_2).

paraffin. (1) A compound with small attractive force between itself and elements or other compounds. (2) A waxlike fraction from the refining of petroleum. Methane is the simplest member of the paraffin series of hydrocarbons. Paraffin is used to cover the tops of jelly glasses.

pasteurization. A process of heating milk or other liquids to destroy bacteria. Pasteurization improves milk from a health standpoint.

percentage. A part based upon the whole taken as 100 parts. The percentage composition tells the per cent of each element present in the substance.

petroleum. Natural oil. Petroleum is a mixture of hydrocarbons.

photosynthesis. A process that takes place in the green cells of plants whereby water and carbon dioxide are changed into starch in the presence of sunlight by the aid of chlorophyll. Photosynthesis is the most important chemical reaction in that much of the food thus formed is consumed by humans and animals.

physics. The science that deals with energy and its changes. In physical changes no new products are formed.

pickling. The process of removing scale or rust from the surface of a metal. Sulfuric acid is used in the pickling of steel.

pigment. An insoluble, finely divided, colored substance used as a coloring agent in paints, cosmetics, or pottery. Chrome yellow ($PbCrO_4$) is a bright-yellow pigment.

plastics. Materials that take a useful shape under one set of conditions and harden or "set," under another. The plastics industry is advancing rapidly.

polymer. A group or cluster of molecules, often a multiple of a definite structural group. Many synthetic plastics are polymers; some are copolymers.

precipitate. An insoluble compound formed in a solution. A white precipitate forming in limewater is a positive test for the presence of carbon dioxide.

properties. Characteristics, qualities. Color, odor, solubility, and density are described in listing the physical properties of a substance.

protein. A complex nitrogen-containing organic compound. All proteins turn yellow when concentrated nitric acid is added to them.

proton. The nucleus of the light hydrogen atom. The number of excess protons in the nucleus of a neutral atom balances the number of electrons in its shells or orbits.

qualitative. Dealing with the kind of material. A qualitative analysis discovers what elements or compounds are present in a material or substance.

quantitative. Dealing with the amount of material. A quantitative analysis discovers how much of each element is present in a compound.

quicksilver. An old name for the element mercury. Quicksilver is used in thermometers.

radical. A group of elements that act as a unit through several chemical changes. A common radical is the sulfate group (SO_4).

radioactivity. The property of elements of decomposing spontaneously. During this process they emit particles and rays of great penetrating power. Radium shows the property of radioactivity.

rare. Uncommon. The rare earths are elements found in relatively small amounts.

rayon. A synthetic fiber made of reprecipitated cellulose. Rayon cloth has a pleasing luster.

reaction. A chemical change. Some reactions are promoted by catalysts.

reagent. A reacting substance in a chemical change. Iodine is used as a reagent in the chemical test for identifying starch.

reducing agent. An element or a compound that causes reduction, the opposite of oxidation. Coke is a commercial reducing agent.

reduction. The gaining of electrons. Metals are obtained from their oxides by the process of reduction.

replacement (sometimes **displacement**). A type of chemical change in which one element or radical takes the place of another. Chlorine will replace bromine from sodium bromide solution.

reversible. Interchangeable. A reversible reaction can take place in either direction, depending on conditions.

rust. Red-brown corrosion on iron. Iron changes to rust in the presence of moist air.

salt. A crystalline compound consisting of a positive ion (other than hydrogen) and a negative ion. Salts are conductors of electricity when fused. Common salt is sodium chloride (Na^+Cl^-).

saturated. Holding all that is possible under given conditions. A saturated solution holds all solute possible at a given temperature in equilibrium with excess solute.

science. A systematic study of nature. Chemistry is a physical science.

slag. A glassy material formed by the combination of flux and gangue in a furnace. Blast-furnace slag is an almost useless by-product of smelting iron.

smoke. Finely divided solid particles suspended in a gas. Smoke is a result of incomplete burning.

smelting. The process of treating an ore to obtain a metal. The smelting of tin ore is a relatively simple process.

solder. An alloy used to join metal surfaces. Soft solder, an alloy of tin and lead, melts at a low temperature.

solid. A state of matter that does not flow. Solids have definite crystalline forms. Dry Ice is solid carbon dioxide.

solubility. The amount of solute that will dissolve in a given amount of solvent at a given temperature usually expressed as the number of grams in 100 g of solvent. The solubility of common salt increases only slightly when the temperature is raised.

solute. A substance dissolved in a solvent. Sugar is the solute in "simple sirup."

solution. A homogeneous mixture of solvent and solute. Water and salt shaken together form a solution.

solvent. A liquid that dissolves a substance. Water is the most commonly used solvent.

spectroscope. An instrument used for analyzing light by means of a prism. The spectroscope is used in chemical analysis.

spontaneous. Of its own accord. In spontaneous ignition a substance catches fire by the heat from its own slow oxidation.

stable. Not easily decomposed by raising the temperature. Water is a stable compound.

standard. An accepted model. The standard conditions for measuring a gas (STP) are 0°C temperature and 760 mm of mercury pressure (1 atm).

strength. Of an acid or base—the ease of dissociating ions. A strong acid, such as hydrochloric acid (HCl), has completely dissociated into ions in dilute solution in water.

structure. Construction. A structural formula shows the probable arrangement of atoms within a molecule of an organic compound, sometimes for inorganic compounds also.

sublimation. The process of changing a solid to a gas, omitting (or almost entirely omitting) the liquid condition. Dry Ice (solid carbon dioxide) sublimes.

substance. A material of uniform composition. Limestone is a substance. Hay is called a material, not a substance.

supersaturated. Above saturation. Crystals form when seed crystals are dropped into a supersaturated solution.

suspension. A finely divided state of matter distributed through a less dense state of matter. Rivers hold clay particles in suspension.

symbol. The letter or letters that represent the atom of an element. Zn is the symbol for zinc.

synthesis. The process of joining simple substances to form more complex ones. The synthesis of water can be accomplished by burning hydrogen in air or in oxygen.

technique. The way of conducting a laboratory experiment. The technique of a beginner improves rapidly.

temper. The state of hardness and toughness of steel. The temper of steel is lost by heating strongly and cooling slowly.

temperature. Degree of heat. Temperature may be measured by means of a thermometer.

ternary. Referring to compounds that contain three elements. Nitric acid (HNO_3) is a ternary compound.

tincture. A solution in which alcohol is the solvent. Tincture of iodine is used as an antiseptic.

tribasic. An acid that contains 3 g of replaceable hydrogen ions per formula weight. Phosphoric acid (H_3PO_4) is a tribasic acid.

ultraviolet. Short light waves. Ultraviolet light is not visible to the unaided eye. It is active in causing certain chemical changes.

valence (or **combining number**). (1) Electrovalence—the charge on an ion. (2) Covalence—the number of shared pairs of electrons associated with an element. The valence of oxygen is 2 in water (H_2O).

vitamin. Organic compounds found in foods and needed in small amounts in the body to maintain health. Vitamin B_1 is often lacking in sufficient amounts.

volatile. Evaporating readily at low temperatures. Camphor is a volatile solid. Ether is a volatile liquid.

vulcanize. The curing of rubber by heating it with sulfur. A patch is vulcanized onto a rubber inner tube.

water glass. Soluble silicates. A solution of water glass is used in fireproofing fabrics.

water of hydration (see hydrate). Water combined in a crystal.

weak (see strength). Opposite of strong. Acetic acid is a weak acid because it is weakly dissociated into ions in dilute solution.

welding. The process of joining metals by melting them together. Good welding requires skillful use of fluxes and torches.

X rays. Short-wave-length energy radiations that penetrate matter. X rays penetrate flesh.

INDEX TO APPENDIX

APPENDIX

The Metric System

The Meter. At the close of the French Revolution, the government of France appointed a commission to establish a more satisfactory system of weights and measures. This group decided that one ten-millionth of a quadrant (quarter circumference) of the earth measured on the meridian of Paris would be the unit of length. This distance, 39.37 in., they called the ***meter.***

$$\text{Meter} = \frac{\text{quadrant}}{10{,}000{,}000} \qquad \text{or} \qquad \text{meter} = \frac{\text{circumference}}{4} \times 10^{-7}$$

The length of the meter was determined with extreme care; in fact, the distance was marked on a standard meter bar of noncorroding platinum-iridium alloy by two parallel scratches. This bar is preserved in France, and copies have been made for the use of all governments and laboratories requiring standards of extreme accuracy.

If all meter bars were destroyed, we should still be able to reproduce the distance accurately, for it is 1,553,164.13 times the wave length of the red line of the spectrum of cadmium in air at 760 mm pressure at 15°C.

Prefixes. The meter and all other units in the metric system are divided into 10 parts, something as the United States dollar is divided into dimes, cents, and mills. Here is one of the advantages of metric system, for units are interchangeable by merely changing the position of the decimal point.

1⁄10 or 0.1 meter = ***deci***meter or dm
1⁄100 or 0.01 meter = ***centi***meter or cm
1⁄1000 or 0.001 meter = ***milli***meter or mm
1000 × the meter = ***kilo***meter or km

The same prefixes are used throughout the system with the same meanings: ***deci-,*** one-tenth; ***centi-,*** one-hundredth; ***milli-,*** one-thousandth; ***kilo-,*** one thousand times.

The Liter. A cube 1 decimeter (dm) on an edge contains a volume of 1 cubic decimeter (dm^3), or about 1.06 quarts. This cube, if hollow, holds about 1 liter. Accurately, the volume occupied by 1 kilogram (kg), or 2.2 pounds, of pure water at 4°C is called a ***liter.***

Since 1 decimeter equals 10 centimeters, it follows that 1 cubic decimeter equals 1000 cubic centimeters (cc or cm^3). One thousand cubic centimeters or, more accurately, 1000 milliliters (ml) is the same as 1 liter. A liter of water, however, is not exactly 1000 cc, but 1000.027 cc, a difference of 27 parts in 1 million. For most practical purposes, the cubic centimeter and the milliliter may be used interchangeably.

The Gram. The weight of a liter of water at 4°C is 1 kilogram (kg). By dividing each by 1000, we find that 1 milliliter of water at 4°C weighs 1 ***gram*** (g). The gram is the unit of weight in the metric system. A United States nickel weighs about 5 g. Another advantage of the metric system will now become evident. If we measure out some water in a graduated glass cylinder and find that we have, for example, 42 ml volume, then the water weighs just about 42 g. If the liquid were mercury with specific gravity 13.6, then the weight of the same volume would be 42 × 13.6 = 571 2 g, about 1¼ lb.

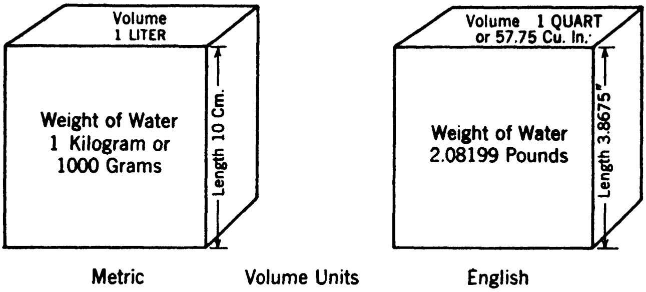


FIG. A-1.—The relative size of the liter and the quart.

	Unit	1000 fold	0.1	0.01	0.001
Length	Meter	km	dm	cm	mm
Volume	Liter	kl	dl	cl	ml or cc
Weight	Gram	kg	dg	cg	mg

Except for trading in the United States and England, the metric system is used extensively throughout the world. It is the official United States system and is coming more and more into use. It is used particularly in scientific work, although many engineers still use the English system.

Relationships between the English and the Metric Systems. Four simple relationships between the English and the metric systems are sufficient for most purposes.

1 meter (m) = 39.37 inches
1 inch = 2.54 centimeters (cm)
1 liter (l) = 1.06 quarts
1 kilogram (kg) = 2.2 pounds

The following relationships may be used for reference.

1 mile = 1.6 kilometers (km)
1 kilometer (km) = 0.62 mile
1 ounce (avoirdupois) = 28.3 grams (g)
1 pound = 453.6 grams (g)
1 gallon (U.S.) = 3.8 liters (l)
1 ounce (fluid, U.S.) = 29.57 milliliters (ml)

QUESTIONS

1. How many milligrams are in a gram? In a centigram? In a kilogram? In $\left\{\begin{matrix}63.4\\52.5\end{matrix}\right.$ grams? In $\left\{\begin{matrix}7.45\\4.32\end{matrix}\right.$ grams?

2. A Swedish girl writes to Helen that she is $\left\{\begin{matrix}1.42\\1.50\end{matrix}\right.$ meters tall. Helen is 5 feet 2 inches tall. Which of the girls is taller?

3. A swimming pool is $\left\{\begin{matrix}75\\60\end{matrix}\right.$ feet long. Find its length in yards and also in meters.

4. Harry weighs $\left\{\begin{matrix}140\\130\end{matrix}\right.$ pounds. What is his weight in kilograms?

5. Butter is sold for $\left\{\begin{matrix}51\\53\end{matrix}\right.$ cents per pound. What should be its price per kilogram?

6. A camera film measures $\left\{\begin{matrix}\text{6.5 by 11 centimeters}\\2\frac{3}{8}\text{ by }4\frac{1}{4}\text{ inches}\end{matrix}\right.$. What is the size (two dimensions) $\left\{\begin{matrix}\text{in inches?}\\\text{in centimeters?}\end{matrix}\right.$

7. If you were driving a car in South Africa and wished to buy $\left\{\begin{matrix}5\\8\end{matrix}\right.$ gallons of gasoline, how many liters would you buy?

8. $\left.\begin{matrix}\text{Light}\\\text{Sound}\end{matrix}\right\}$ travels at the speed of approximately $\left\{\begin{matrix}\text{300,000 kilometers}\\\text{1100 feet}\end{matrix}\right.$ per sec. What is the speed in miles per second? In meters per second?

9. An automobile tire is $\left\{\begin{matrix}40\\38\end{matrix}\right.$ inches in diameter, and it weighs $\left\{\begin{matrix}66\\55\end{matrix}\right.$ lbs. Change the diameter to centimeters and the weight to kilograms.

10. A tank is $\left\{\begin{matrix}12\\15\end{matrix}\right.$ centimeters long, $\left\{\begin{matrix}50\\40\end{matrix}\right.$ millimeters wide, and $\left\{\begin{matrix}2.0\\1.5\end{matrix}\right.$ inches deep. Find its volume in milliliters. How many kilograms of water will it hold? Of mercury?

Temperature Measurement

A common way to find the temperature of a liquid, solid, or gas is to bring a thermometer into intimate contact with the substance and, after waiting a sufficient time for both the thermometer and the substance to come to the same temperature, to "read the thermometer." The volume of the mercury in the thermometer changes with the temperature. The glass stem of the thermometer has scale markings, or graduations, etched on it, showing the volume of the mercury at those temperatures. Among these markings the boiling and freezing points of water are called the fixed points. They are 100° and 0° on the centigrade scale and 212° and 32° on the Fahrenheit scale, respectively, at 760 mm pressure. (See Fig. A-2.)

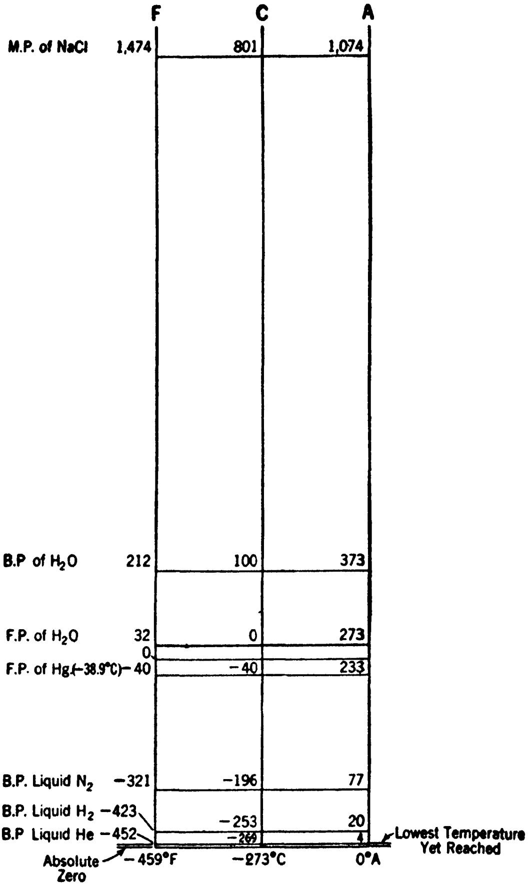


FIG. A-2.—Fahrenheit, centigrade, and Kelvin temperature scales.

Since the number of degrees between the fixed points centigrade is

100 and between them Fahrenheit is 180, on the same thermometer, the ratio of the number of degrees centigrade to the number of degrees Fahrenheit is 100 to 180 or 5 to 9.

$$\frac{°\mathrm{C}}{°\mathrm{F}} = \frac{100}{180} = \frac{5}{9}.$$

But since the Fahrenheit scale does not start at zero, we must subtract 32° in order to get an accurate relationship.

$$\frac{°\mathrm{C}}{°\mathrm{F} - 32°} = \frac{5}{9} \qquad \text{or} \qquad 1.8°\mathrm{C} = °\mathrm{F} - 32$$

A comfortable room is 70°F. What is the temperature on the centigrade scale? We use the value 70 for F, substitute it in the equation, and solve for C, as follows:

$$\frac{C}{70 - 32} = \frac{5}{9} \qquad \frac{C}{38} = \frac{5}{9} \qquad C = \frac{38 \times 5}{9} = 21.1°\mathrm{C} \quad \textit{Ans.}$$

When the thermometer reads −10°C, what is the corresponding Fahrenheit reading?

$$\frac{-10}{F - 32} = \frac{5}{9} \qquad 5F - 160 = 9 \times -10 \qquad 5F = [9 \times (-10)] + 160$$

$$F = 14°\mathrm{F} \quad \textit{Ans.}$$

Absolute temperatures, or temperatures on the Kelvin scale, are found by adding 273 to the centigrade reading. Absolute temperatures are always used in gas-volume change problems.

Gas-volume Corrections for Changes in Temperature and Pressure

The Effect of Pressure Changes. Experiments show that if the temperature of a given quantity of gas is kept constant (unchanged) and the pressure on it is doubled, its volume becomes one-half. If the pressure is halved, the volume becomes doubled. In general, when the temperature is constant, the volume of a given amount of gas is inversely proportional to the pressure (Boyle's law) (page 118).

Let us assume that we have collected 400 ml of oxygen. We observe that the temperature is 20°C by a thermometer reading and that the pressure is 750 mm by a barometer reading. What volume will the oxygen occupy if the pressure is changed to standard pressure, 760 mm, the temperature remaining unchanged?

We reason that since the pressure is changed from 750 to 760 mm, an increase, the volume is decreased. Hence we should multiply the original volume, 400 ml, by a fraction composed of 750 mm and 760 mm in such a manner that the answer will be less than 400. Such a fraction has a value less than 1; that is, it is a proper fraction composed of 750 over 760, namely, 750 mm/760 mm.

The new volume, therefore, is

$$\frac{750\,\cancel{\text{mm}}}{760\,\cancel{\text{mm}}} \times 400 \text{ ml} = 394.7 \text{ ml.} \quad \textit{Ans.}$$

Notice that the units are included in the problem and canceled where possible. This shows the unit(s) in the answer.

Again, let us assume that we have collected 600 cu in. of hydrogen at a pressure of 35 in. of mercury and at a temperature of 18°C. We wish to find out what volume the hydrogen will occupy when the pressure changes to standard, 30 in.[1] of mercury, and the temperature is unchanged.

We reason that the change in pressure from 35 to 30 in. is a decrease. Hence the volume of the gas should increase. We should, therefore, multiply 600 by a fraction made up of 35 in. and 30 in. in such a manner that the value of 600 is increased. Such a fraction is an improper fraction, or 35 in. over 30 in.

The new volume, thus, is

$$\frac{35\,\cancel{\text{in.}}}{30\,\cancel{\text{in.}}} \times 600 \text{ cu in.} = 700 \text{ cu in. of hydrogen.} \quad \textit{Ans.}$$

In case we wish to find the pressure change needed to expand 1.0 liter of carbon dioxide at 735 mm of mercury pressure and 0°C to 1.25 liters at the same temperature, we use similar reasoning. Since the volume is to increase, the pressure must decrease. Hence 735 mm must be multiplied by a fraction made up of 1.0 l and 1.25 l in such a fashion that the value of 735 mm will decrease. Such a fraction is the proper fraction, 1.0 l over 1.25 l.

The new pressure, therefore, is

$$\frac{1.0\,\cancel{\text{l}}}{1.25\,\cancel{\text{l}}} \times 735 \text{ mm} = 588 \text{ mm.} \quad \textit{Ans.}$$

QUESTIONS

1. When 200 milliliters of chlorine is collected at 30°C and 740 millimeters of mercury pressure, what does the volume become when the pressure is changed to $\left\{\begin{matrix}1080\\900\end{matrix}\right.$ millimeters while the temperature remains at 30°C?

2. Five liters of air is collected at $\left\{\begin{matrix}720\\740\end{matrix}\right.$ millimeters. What is the volume of this sample of air at standard pressure, 760 millimeters, if the temperature is unchanged?

---

[1] Standard pressure is more accurately 29.92 in. of mercury.

3. When the pressure on 44 liters of sulfur dioxide at 40°C is changed from 780 millimeters to $\left\{\begin{matrix}390\\585\end{matrix}\right.$ millimeters, what is the new volume if the temperature is unchanged?

4. If a liter of hydrogen at atmospheric pressure is subjected to a pressure $\left\{\begin{matrix}\text{six}\\\text{five}\end{matrix}\right.$ times that of the atmosphere, what is the new volume if the temperature is unchanged?

5. When the pressure on 7 liters of oxygen at 77.0 centimeters pressure is changed from 77 centimeters to $\left\{\begin{matrix}66\\55\end{matrix}\right.$ centimeters what is the new volume if the temperature is constant?

MORE CHALLENGING QUESTIONS

6. What is the volume of 14.3 cubic feet of oxygen at $\left\{\begin{matrix}12.6\\10.5\end{matrix}\right.$ pounds per square inch if the pressure becomes standard (14.7 pounds per square inch) and the temperature is unchanged?

7. What new pressure will change 1.25 liters of nitrogen collected at 760 millimeters into 1.75 liters without changing the temperature?

8. What volume of oxygen at $\left\{\begin{matrix}800\\780\end{matrix}\right.$ millimeters and 0°C will be generated by the decomposition of 490 grams of potassium chlorate?

9. What is the new volume occupied by 100 liters of air when the pressure changes from 14.7 pounds per square inch to 294 pounds per square inch?

10. A tank of air holds $\left\{\begin{matrix}75\\50\end{matrix}\right.$ cubic feet, and the gauge reads 75 pounds per square inch. Gauge pressure is the additional pressure above the atmospheric pressure of 14.7 pounds per square inch. What volume of air escapes when the valve is opened?

The Effect of Temperature Changes. Experiments show that, when the pressure is unchanged, the volume of a given quantity of any dry gas is directly proportional to its ***Kelvin,*** or ***absolute,*** temperature. The absolute temperature is the centigrade reading plus 273. Thus, when the temperature of a given volume of gas changes from 20°C to 313°C, the volume is doubled, provided that the pressure does not change. The absolute temperature in this case has doubled, 293 (20 + 273) to 586 (313 + 273). This behavior of gases is summarized in Gay-Lussac's (Charles's) law.

In applying the principle we understand that when a gas is heated it expands and, conversely, that when a gas is cooled it contracts. Let us find the new volume occupied by 60 liters of carbon dioxide when the temperature changes from 27 to 57°C and the pressure remains constant. We must remember to use ***absolute temperatures;*** 300° K and 330° K [or absolute] are the temperatures to be used. In this case the gas is being warmed from 27 to 57°C, and therefore the volume will increase. We must thus multiply 60 liters by a fraction made up of 300° K and 330° K in a manner to make the value greater than 60. Such a fraction is an improper fraction with its value more than 1, or 330° K over 300° K. Thus we multiply 60 liters by 330° K/300° K, obtaining 66 liters. *Ans.*

Again, what is the volume occupied by 586 ml of hydrogen collected at 20°C, at standard temperature (0°C), assuming no change in pressure? First we change the temperatures to absolute, or 293° K and 273° K, respectively. Here the gas has cooled, and therefore the volume has decreased. We thus multiply 586 ml by a fraction made up of 273° K and 293° K in a manner to decrease the value of 586 ml. The fraction to be used is a proper fraction in which the numerator is smaller than the denominator, or 273° K/293° K.

Hence,

$$586\text{ ml} \times \frac{273^\circ\,\cancel{K}}{293^\circ\,\cancel{K}} = 546\text{ ml.} \quad \textit{Ans.}$$

To what temperature must 1.2 liters of oxygen at 37°C be heated in order that it may become 1.5 liters? We reason that, if the volume is to increase, the absolute temperature must be increased in proportion. First we convert 37°C to 310° K and multiply it by 1.5 liters/1.2 liters.

$$310^\circ\text{ K} \times \frac{1.5\,\cancel{\text{liters}}}{1.2\,\cancel{\text{liters}}} = 387.5^\circ\text{ K}$$

$$387.5^\circ\text{ K} - 273^\circ = 114.5^\circ\text{C} \quad \textit{Ans.}$$

QUESTIONS

11. When the temperature of $\left\{\begin{matrix}60\\90\end{matrix}\right.$ liters of nitrogen collected at 17°C changes to standard, 0°C, assuming no change in pressure, what new volume does it occupy?

12. What is the effect of heating $\left\{\begin{matrix}44\\66\end{matrix}\right.$ milliliters of oxygen from 27 to 47°C without changing the pressure?

13. The volume of a captive balloon containing illuminating gas is 10,000 cubic feet when the sun is shining on it, and the average temperature of the gas is 52°C. When the balloon goes into a cloud and the average temperature becomes $\left\{\begin{matrix}20\\15\end{matrix}\right.$°C, what new volume does the gas in the balloon occupy? Assume that the pressure is unchanged. Does the balloon tend to rise or fall as it cools?

14. An inverted bottle holds 250 milliliters of hydrogen collected at $\left\{\begin{matrix}20\\18\end{matrix}\right.$°C. What is the volume of the gas at standard temperature, 0°C, assuming no change in pressure?

15. When the temperature changes from $\left\{\begin{matrix}-73\\-173\end{matrix}\right.$°C to 0°C, what does the volume of a liter of oxygen become if the pressure does not change?

MORE CHALLENGING QUESTIONS

16. What new temperature is required if 1.2 liters of air at 0°C is to occupy $\left\{\begin{matrix}1.4\\1.6\end{matrix}\right.$ liters without a change in pressure?

17. If the volume of a certain gas is represented by V, its centigrade temperature by T, and its absolute temperature by $T + 273$, what is the new centigrade temperature when the volume is $\left\{\begin{matrix}\text{doubled}\\\text{halved}\end{matrix}\right.$ or $\left\{\begin{matrix}2V\\V/2\end{matrix}\right.$?

18. What is the volume occupied at 323°C by the carbon dioxide formed by the burning of $\left\{\begin{matrix}2\\5\end{matrix}\right.$ liters of methane, measured at 23°C? Assume that the pressure is unchanged.

19. What volume of acetylene, at 0°C, should be burned in order to form $\left\{\begin{matrix}50\\75\end{matrix}\right.$ liters of carbon dioxide measured at $\left\{\begin{matrix}300^\circ\\250\end{matrix}\right.$ C?

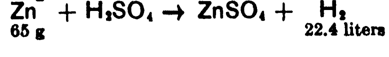
20. What volume does 15 liters of hydrogen, measured at $\left\{\begin{matrix}20\\30\end{matrix}\right.$°C, occupy when the centigrade temperature is doubled? When the absolute temperature is doubled?

The Combined Effect of Pressure and Temperature Changes. When both pressure and temperature change, corrections for both changes are applied together, one after the other, in the same manner as that for the changes separately.

For example, what is the volume at standard conditions (STP, 760 mm and 0°C) of 1172 ml of sulfur dioxide collected at 700 mm and 20°C? The change in pressure from 700 to 760 mm tends to decrease the volume; therefore we use 700 mm/760 mm. The change in temperature, 293 to 273°K, tends to decrease the volume; therefore we use 273° K/293° K. Hence,

$$1172 \text{ ml} \times \frac{700\,\cancel{\text{mm}}}{760\,\cancel{\text{mm}}} \times \frac{273^\circ\,\cancel{K}}{293^\circ\,\cancel{K}} = 1005.8 \text{ ml.} \quad \textit{Ans.}$$

Again, what volume of hydrogen, measured at 780 mm and 77°C, is released when 1300 g of zinc acts with an excess of dilute sulfuric acid?



$$\underset{65\text{ g}}{\overset{1300\text{ g}}{\mathrm{Zn}}} + H_2SO_4 \rightarrow ZnSO_4 + \underset{22.4\text{ liters}}{\overset{x\text{ liters}}{H_2}}$$

$$\text{Volume of hydrogen, } x = \frac{1300\,\cancel{g}}{65\,\cancel{g}} \times 22.4 \text{ liters} = 448 \text{ liters at STP}$$

$$448 \text{ liters} \times \frac{760\,\cancel{mm}}{780\,\cancel{mm}} \times \frac{350°\,\cancel{K}}{273°\,\cancel{K}} = 560 \text{ liters. } \textit{Ans.}$$

Gas-law-equation Method of Gas-volume Corrections. The foregoing relationships of temperature, pressure, and volume changes are summarized by the gas-law equation,

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

where P, V, and T are the original pressure, volume, and absolute temperature and P', V', and T' are the new pressure, volume, and absolute temperature. This equation is sometimes called the law of ideal gases.

What volume will 138 ml of hydrogen collected at 25°C and 790 mm occupy at standard conditions (0°C and 760 mm)?

Here

$P = 790$ mm $\quad$ $P' = 760$ mm
$V = 138$ ml $\quad$ $V' =$ unknown
$T = (25 + 273)\ 298°$ K $\quad$ $T' = 273°$ K

We substitute these values in the gas-law equation and solve for the one unknown value V'.

$$\frac{790 \text{ mm} \times 138 \text{ ml}}{298° \text{ K}} = \frac{760 \text{ mm} \times V'}{273° \text{ K}}$$

$$V' = \frac{790\,\cancel{mm} \times 273°\,\cancel{K} \times 138 \text{ ml}}{760\,\cancel{mm} \times 298°\,\cancel{K}} = 131.4 \text{ ml. } \textit{Ans.}$$

If the temperature is constant, the value of T equals that of T' in the formula and cancels. This leaves $PV = P'V'$, a formula for Boyle's law. The value for $V' = PV/P'$.

If the pressure does not change, the value of P equals that of P' in the formula and cancels, leaving $V/T = V'/T'$ or $VT' = V'T$, formulas for Charles's (Gay-Lussac's) law. The value for $V' = VT'/T$. Here, as before, T and T' refer to absolute, or Kelvin, temperature.

The use of the gas-law-equation method depends on remembering a formula; the use of the reasoning method involves less rote memory and depends on an understanding of the principles involved.

QUESTIONS

21. $\left\{\begin{matrix}\text{Sixty}\\ \text{Fifty}\end{matrix}\right.$ **liters of oxygen is collected at 27°C and 780 millimeters pressure. What is the volume at standard conditions?**

22. What is the volume of 75 milliliters of argon at 700 millimeters pressure and −53°C when put under a pressure of $\left\{\begin{matrix}2100\\2800\end{matrix}\right.$ millimeters and warmed to $\left\{\begin{matrix}127\\177\end{matrix}\right.$°C?

23. A neon tube holds 300 milliliters at $\left\{\begin{matrix}3\\5\end{matrix}\right.$ millimeters pressure and $\left\{\begin{matrix}27\\47\end{matrix}\right.$°C. A sealed flask of neon holds 1 liter at 780 millimeters and 17°C. How many tubes can be filled from the neon in the flask? HINT: Change the volume of one to the conditions of the other.

24. A balloon on the surface of the earth holds 3 million cubic feet of helium-hydrogen mixture at pressure 14.7 pounds per square inch and temperature 15°C. What does the volume become when the balloon rises to a place where the pressure is $\left\{\begin{matrix}2.1\\4.2\end{matrix}\right.$ pounds per square inch and the temperature is $\left\{\begin{matrix}-13\\-3\end{matrix}\right.$°C?

25. A student generates 90 milliliters of hydrogen at $\left\{\begin{matrix}20\\18\end{matrix}\right.$°C and $\left\{\begin{matrix}758\\762\end{matrix}\right.$ millimeters pressure. What volume does this hydrogen occupy at standard conditions?

MORE CHALLENGING QUESTIONS

26. What volume (liters) of hydrogen at 780 millimeters and 27°C is liberated when $\left\{\begin{matrix}2.4\\7.2\end{matrix}\right.$ grams of magnesium reacts with an excess of hydrochloric acid?

27. What volume of oxygen is liberated at 740 millimeters and 47°C when $\left\{\begin{matrix}426\\852\end{matrix}\right.$ grams of sodium chlorate is strongly heated?

28. Steam from a certain boiler is supplied at 150°C and 150 pounds per square inch pressure above that of the atmosphere. It is exhausted from a turbine at 100°C and 4.7 pounds per square inch pressure above that of the atmosphere. How many times its original volume has the steam expanded? HINT: Consider the original volume as 1 cubic foot. Atmosphere pressure is 14.7 pounds per square inch.

29. A bubble of carbon dioxide is generated in an oil well where the pressure is 10,000 pounds per square inch and the temperature is 97°C. How many times its original volume is the bubble when it has risen to the surface of the earth?

30. When $\left\{\begin{matrix}500\\300\end{matrix}\right.$ grams of pure calcium carbonate is dissolved in an excess of hydrochloric acid, how many liters of carbon dioxide are liberated, measured at 27°C and 765 millimeters pressure?

Collecting Gases over Water. When a gas is collected over mercury, the pressure of the gas is that exerted by the bombardment of the molecules of the gas against the surface of the mercury that encloses it. We assume that mercury has only a very slight tendency to evaporate and that very few mercury molecules are mixed with the gas molecules.

When a gas is collected over water, on the other hand, the water does evaporate, and the gas contains considerable quantities of water-vapor molecules. These water-vapor molecules exert a pressure, and thus the pressure exerted by the gas is composed of two parts, the force exerted by the molecules of the gas itself and that exerted by the water-vapor molecules mixed with the gas on each unit of area (Dalton's law of partial pressures).

The amount of pressure exerted by the water-vapor molecules depends on the temperature only and may be found by consulting the table on page 709.

For example, an experimenter collects 250 ml of oxygen by displacement of water and reads a barometer at the same level. It is 762.0 mm. The level of the water inside and outside the bottle are the same. The temperature of both the gas and the water is observed to be 22°C, both being at room temperature. From the table on page 709, the vapor pressure of water at 22°C is 19.8 mm. The pressure due to oxygen alone is 762.0 mm − 19.8 mm or 742.2 mm.

The corrections for the vapor pressure of water should be applied in making measurements in the laboratory, but the correction should be used in problems only when specific directions are given, as, for example, when a definite statement is made to the effect that the gas under consideration was collected by displacing water.

QUESTIONS

31. What is the partial pressure of a gas when the barometer reads 758.8 millimeters and the gas is collected over water at (*a*) $\left\{{5 \atop 10}\right.{}^\circ\mathrm{C}$; (*b*) $\left\{{12 \atop 14}\right.{}^\circ\mathrm{C}$; (*c*) $\left\{{20 \atop 22}\right.{}^\circ\mathrm{C}$; (*d*) $\left\{{30 \atop 40}\right.{}^\circ\mathrm{C}$; (*e*) $\left\{{21 \atop 25}\right.{}^\circ\mathrm{C}$?

32. Fifty liters of oxygen is collected over water at a temperature of $\left\{{17 \atop 27}\right.{}^\circ\mathrm{C}$ and a total pressure of $\left\{{877.5 \atop 777.5}\right.$ millimeters. What is the volume of the dry gas at STP?

33. What is the pressure due to hydrogen alone at 23°C if the gas is collected over water and the barometer reads 765.9 millimeters?

34. With the temperature at 50°C, a bottle contains $\left\{{420 \atop 360}\right.$ milliliters of nitrous oxide at $\left\{{792.5 \atop 892.5}\right.$ millimeters pressure. What is the volume of the gas at STP?

35. What volume of hydrogen will be collected from the action of 195 grams of zinc on dilute sulfuric acid if the gas is collected over water at $\left\{\begin{matrix}22\\30\end{matrix}\right.$°C and $\left\{\begin{matrix}750\\770\end{matrix}\right.$ millimeters pressure?

VAPOR PRESSURE OF WATER

(Aqueous vapor over water)

Temperature, °C	Pressure, mm of Hg	Temperature, °C	Pressure, mm of Hg
0	4.6	28	28.3
5	6.5	30	31.8
10	9.2	40	55.3
12	10.5	50	92.5
14	12.0	60	149.4
16	13.6	70	233.7
18	15.5	78.6	335.6
20	17.5	80	355.1
22	19.8	90	525.8
24	22.4	100	760.0
26	25.2		

Normal Solutions

Let us assume that we have a solution that contains just one formula weight of sodium hydroxide, 40 g, dissolved in enough water to make one liter of solution. One formula weight, or 36.5 g, of hydrogen chloride in solution is just enough to react with the sodium hydroxide solution to produce complete neutralization.

$$\underset{40}{\mathrm{NaOH}} + \underset{36.5}{\mathrm{HCl}} \rightarrow \underset{58.5}{\mathrm{NaCl}} + \underset{18}{\mathrm{H_2O}}$$

When sulfuric acid is used to neutralize a liter of the same sodium hydroxide solution, one-half a formula weight, or 49 g, of hydrogen sulfate is required.

$$\underset{80}{\mathrm{2NaOH}} + \underset{98}{\mathrm{H_2SO_4}} \rightarrow \underset{142}{\mathrm{Na_2SO_4}} + \underset{36}{\mathrm{2H_2O}}$$

A solution of sodium hydroxide that contains 40 grams dissolved in enough water to make a liter is called a ***normal*** solution of sodium hydroxide. Such a solution contains 17 g of replaceable OH^- ion.

A solution of hydrogen chloride that contains 36.5 g of hydrogen chloride in a liter of solution is called a normal solution of hydrochloric acid, and one that contains 49 g per liter, one-half the formula weight, is called a normal solution of sulfuric acid. Such normal acid solutions contain 1 g of replaceable hydrogen per liter. A normal solution of phosphoric acid contains 98 g (formula weight) ÷ 3, or 32.67 g of hydrogen phosphate (H_3PO_4) with enough water to make a liter.

Fundamentally, a normal solution thus contains enough solute, dissolved to make 1 liter of solution, to be connected directly or indirectly to 8 g of oxygen or 1 (accurately 1.008) g of hydrogen in a chemical reaction.

Normal solutions of acids contain 1 g of replaceable hydrogen ions per liter, and normal solutions of metallic hydroxides contain 17g of OH^- ions per liter in these basic solutions.

Solutions that are more or less concentrated than a normal solution are used frequently. Such concentrations are expressed as follows, for example: $6N$ HCl means a solution containing six times the formula weight of hydrogen chloride per liter. $0.1N$, $\frac{1}{10}N$, or $N/10$ NaOH means a solution having one-tenth the formula weight of sodium hydroxide, or 4 g, dissolved per liter of solution.

A $0.5N$ solution of calcium chloride contains one-fourth the formula weight (formula weight divided by combining number of calcium) of calcium chloride (27.8 g of $CaCl_2$) per liter.

One liter of N solution of Na_2CO_3 contains $106 \div 2 = 53$ g.

One liter of N solution of $AlCl_3$ contains $133.5 \div 3 = 44.5$ g.

QUESTIONS

1. How many grams of the following compounds are required to make a liter of a normal solution: (*a*) KOH; (*b*) $Ca(OH)_2$; (*c*) H_2SO_3; (*d*) HNO_3; (*e*) CH_3COOH?

2. How many grams of solid are present in a liter of $\left\{\begin{matrix}6\\5\end{matrix}\right.N$ NaOH solution?

3. A pupil needs $\left\{\begin{matrix}300\\200\end{matrix}\right.$ milliliters of $0.1N$ NaOH. What supplies are required?

4. How many grams of hydrogen sulfate are present in 700 milliliters of $\left\{\begin{matrix}8\\5\end{matrix}\right.N$ sulfuric acid?

5. What volume of water must be added to a liter of N NaOH solution so that the final solution will be $0.2N$?

Careful study of the previous discussion will show clearly that equal volumes of basic and acid solutions of the same normality neutralize each other.

If a one-tenth normal solution should be substituted for a normal solution, it is obvious that ten times the volume of the weaker solution is required for the same effect as the stronger. Likewise, one-fifth the volume of a $5N$ solution will be required for the same job that a certain volume of normal solution does. That is, the more concentrated the solution, the less volume is required for a given reaction. This may be expressed in general as

$$V_1 \times N_1 = V_2 \times N_2$$

where V_1 is the volume of the solution with normality N_1 and V_2 is the volume of the solution with normality N_2.

Examples: How many milliliters of 0.4N KOH solution will neutralize 100 ml of 0.05N phosphoric acid?

$$100\text{ ml} \times 0.05N = V_2 \times 0.4N$$

$$V_2 = \frac{100\text{ ml} \times 0.05\cancel{N}}{0.4\cancel{N}} = 12.5\text{ ml} \quad \textit{Ans.}$$

What weight of hydrogen nitrate is present in 3 liters of nitric acid that just neutralize 234 ml of 4N sodium hydroxide solution?

$$3\text{ liters} \times N_1 = 0.234\text{ liter} \times 4N$$

$$N_1 = \frac{0.234\,\cancel{\text{liters}} \times 4N}{3\,\cancel{\text{liters}}} = 0.312N \quad \textit{Ans.}$$

A normal solution of nitric acid contains (1 + 14 + 48) 63 g of hydrogen nitrate per liter. Three liters of 0.312N HNO_3 contains

$$63 \times 0.312 \times 3 = 58.97\text{ g.} \quad \textit{Ans.}$$

QUESTIONS

6. What volume of 0.1N hydrochloric acid will be needed to neutralize $\left\{\begin{matrix}500\\400\end{matrix}\right.$ milliliters of 0.01N calcium hydroxide solution?

7. What is the normality of a sulfuric acid solution if 42 milliliters of it neutralizes $\left\{\begin{matrix}77\\66\end{matrix}\right.$ milliliters of 6N sodium hydroxide solution?

8. How many grams of sodium sulfate are needed to make $\left\{\begin{matrix}4\\5\end{matrix}\right.$ liters of $\left\{\begin{matrix}4\\5\end{matrix}\right.N$ solution?

9. What is the normality of an acetic acid solution if $\left\{\begin{matrix}35\\25\end{matrix}\right.$ milliliters of it neutralizes $\left\{\begin{matrix}70\\50\end{matrix}\right.$ milliliters of 0.2N sodium carbonate solution?

10. How many grams of anhydrous sodium carbonate (Na_2CO_3) are needed to prepare the $\left\{\begin{matrix}70\\50\end{matrix}\right.$ milliliters of 0.2N solution mentioned in the previous question?

MORE CHALLENGING QUESTIONS

11. How many grams of hydrated sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) are needed to make $\left\{\begin{matrix}70\\50\end{matrix}\right.$ milliliters of 0.2N solution?

12. What volume of 6N HCl is needed to precipitate all the silver ions in $\left\{\begin{matrix}300\\450\end{matrix}\right.$ milliliters of 0.75N silver nitrate solution? What weight of silver chloride will form?

13. What volume of 6*N* HCl will be needed to react completely with $\left\{\begin{matrix}6.5\\19.5\end{matrix}\right.$ grams of zinc? What volume of hydrogen gas at STP is liberated? What volume of gas at $\left\{\begin{matrix}750\\770\end{matrix}\right.$ millimeters and $\left\{\begin{matrix}20\\13\end{matrix}\right.$°C is liberated?

14. At 18°C, 0.0023 grams of barium sulfate dissolves in a liter of water. Find the normality of this saturated solution.

15. When hydrogen sulfide gas is passed into $\left\{\begin{matrix}500\\400\end{matrix}\right.$ milliliters of $\left\{\begin{matrix}2\\3\end{matrix}\right.$*N* silver nitrate solution until no more precipitate forms, how many grams does the precipitate weigh?

pH VALUE FOR 0.1*N* SOLUTIONS*	pH
Hydrochloric acid (HCl)	1.0
Sulfuric acid (H_2SO_4)	1.2
Phosphoric acid (H_3PO_4)	1.8
Tartaric acid ($H_2{\cdot}C_2H_4O_6$)	2.2
Citric acid ($H_3{\cdot}C_6H_3O_7$)	2.3
Lactic acid ($H{\cdot}C_3H_5O_3$)	2.4
Boric acid (H_3BO_3)	5.1
Sodium bicarbonate ($NaHCO_3$)	8.4
Disodium hydrogen phosphate (Na_2HPO_4)	9.0
Borax ($Na_2B_4O_7$)	9.2
Ammonia water (NH_4OH)	11.1
Sodium carbonate (Na_2CO_3)	11.3
Trisodium phosphate (Na_3PO_4)	12.0
Sodium hydroxide ($NaOH$)	13.0

FLAME TESTS

Sodium compounds	Yellow
Lithium compounds	Crimson
Strontium compounds	Red-scarlet
Calcium compounds	Orange-yellow
Barium compounds	Yellow-green
Copper chloride	Blue-green
Potassium compounds	Violet

BORAX-BEAD COLORS (AFTER COOLING)

	Oxidizing flame	Reducing flame
Cobalt	Blue	Blue
Copper	Blue	Red
Iron	Yellow	Green
Manganese	Violet	Colorless
Uranium	Yellow	Green

---

* READ, ALLEN B., LaMotte Chemical Products Company, Towson, Baltimore, Maryland. Used by permission.

Recipe for Cold Cream or Cleansing Cream

Creams are essentially an emulsion of water and oil, the water evaporating when the cream is applied.

In pan No. 1 place 1 qt mineral oil, light grade, specific gravity 0.845 to 0.865; 2 oz absorption base (a concentrate of cholesterol): 1 oz lanolin, anhydrous; 7 oz beeswax, best grade, sun-bleached.

In pan No. 2 place 1 pt water; ½ oz borax.

Heat both mixtures gently up to 150°F. Pour slowly contents of pan No. 2 (water) into pan No. 1 (oils), stirring slowly until well mixed. When mixture is cooled to about 120°F, add 2 drams of a perfume oil. Stir, and then pour into jars.

FACTS ABOUT FUEL GASES
(Per cent by volume)

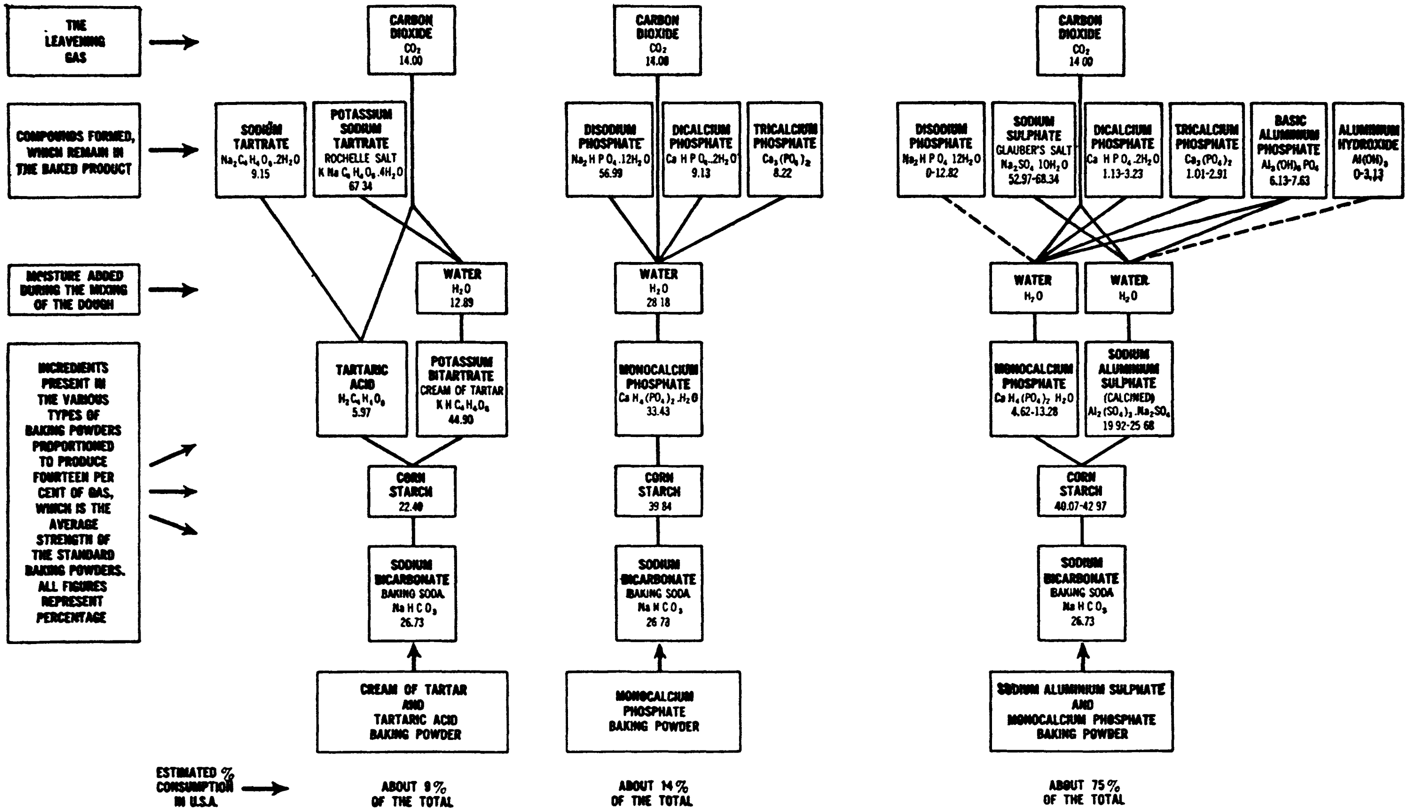
Type of gas	Methane (CH_4)	Hydrogen (H_2)	Carbon monoxide (CO)	Other combustible gases	Inert gases	Relative heat value, Btu/cu ft
Coke oven gas	30.3	49.2	5.5	3.2	11.8	555
Water gas	0.6	47.9	42.3	.....	9.2	299
Enriched water gas	12.4	35.4	31.6	10.3	10.3	574
Producer gas	1.8	14.4	26.3	1.0	56.5	155.6
Natural gas	90.0	....	....	8.8	1.2	1110
Blast-furnace gas	....	1.0	26.0	.....	73.0	87
Bottled fuel gas ("Pyrofax")	....	....	....	100	....	2509

PROPERTIES OF THE GASES IN THE AIR*

Name	% by volume	Boiling point, °C	Freezing point, °C	Atomic weight
Helium	0.0004	−268.9	−268.9 (140 atm)	4
Nitrogen	78.0	−195	−214	14
Oxygen	21.0	−182.5	−227	16
Neon	0.0012	−245.9	−248.7	20.2
Argon	0.94	−185.7	−189.2	39.91
Krypton	0.0005	−151.8	−169	82.9
Xenon	0.000006	−109.1	−140	130.2
Radon	....	− 61.8	− 71	222

---

* Iddles, H. A., J. A. Funkhouser, and A. H. Taylor, *Report, New England Association of Chemistry Teachers*, vol. 35, Part 1, p. 21.



Courtesy of Jaques Manufacturing Company

FIG. A-3.—Baking-powder chart.

THE COMMON GASES*

Name	Formula	Commercial, purity %	Melting point, °C	Boiling point, °C	Density, g/liter, STP	Solubility in cold water
1. Ammonia	NH_3	99	− 77.7	− 33.4	0.77	vs
2. Argon	A	99	−189.2	−185.7	1.78	ss
3. Butane (normal)	C_4H_{10}	99	−135	− 0.5	2.60	ss
4. Carbon dioxide	CO_2	99	− 56.5	− 78.2	1.97	ms
5. Carbon monoxide	CO		−207	−192	1.25	ss
6. Chlorine	Cl_2	99.5	−101.6	− 34.6	3.22	ms
7. Ethane	C_2H_6	95	−171.4	− 89.5	1.35	ss
8. Ethyl chloride	C_2H_5Cl	99.5	−141.6	14.0	Liquid 0.92 g/ml	ss
9. Ethylene	C_2H_4	98	−169	−102.7	1.26	ss
10. Freon	CCl_2F_2			− 29.2	1.49	ss
11. Helium	He	98	−272.2	−268.9	0.18	ss
12. Hydrogen	H_2	99.8	−258.9	−252.7	0.09	ss
13. Hydrogen chloride	HCl	97.5	−112	− 83.7	1.64	vs
14. Hydrogen sulfide	H_2S	99.9	− 83	− 60.2	1.54	ms
15. Isobutane	C_4H_{10}	98	−145	− 10.2	2.61	ss
16. Methane	CH_4	92 or 99	−184	−161.5	0.72	ss
17. Nitrogen	N_2	99.8	−209.9	−195.8	1.25	ss
18. Nitrous oxide	N_2O	98	−102.4	− 89.4	1.98	ms
19. Oxygen	O_2	99.5	−218.4	−183.0	1.43	ss
20. Phosgene	$COCl_2$	99.5	−104	8.3	Liquid 1.39 g/ml	Decomposes
21. Propane	C_3H_8	99.9	−189.9	− 44.5	2.01	ss
22. Sulfur dioxide	SO_2	99.5	− 72.7	− 10.1	2.93	vs

* Data supplied chiefly by The Matheson Company, East Rutherford, New Jersey. Used by permission.

vs = very soluble, ms = moderately soluble, ss = slightly soluble.

COMPOSITION OF FOODS*
(Edible portion)

Name	Percentage by weight							Vitamin content					Cal/ 100 g
	Pro-tein	Car-bohy-drate (not fiber)	Fat	Crude fiber	Ash	Ca	P	A	B_1	C	G (B_2)	Nico-tinic acid (B_5)	
Vegetables:													
Bamboo shoots	2.5	4.3	0.3	0.8	0.8	0.005	0.040	22	18	110	Fair	...	30
Beans, dried	22	58.2	1.5	3.9	3.9	0.160	0.471	110	130	0	95	0	334
Beans, green	2.4	6.3	0.2	1.4	0.8	0.046	0.052	1,100	31	430	60	<1	37
Beets	1.6	8.7	0.1	0.9	1.1	0.029	0.039	50	15	160	11	<1	42
Carrots	1.2	8.2	0.3	1.1	1.0	0.056	0.046	7,700	23	75	30	<1	40
Celery	1.3	3.0	0.2	0.7	1.1	0.078	0.037	35	10	170	14	...	19
Corn (green)	3.7	19.7	1.2	0.8	0.7	0.006	0.103	560	50	850	40	...	104
Cucumbers	0.7	2.2	0.1	0.5	0.4	0.016	0.033	35	30	200	18	...	13
Lettuce	1.2	2.3	0.2	0.6	0.9	0.043	0.042	2,200	29	250	30	<1	16
Mushrooms	....	....	0.3	0.9	1.1	0.017	0.108	0	50	35	23		
Onions	1.4	9.5	0.2	0.8	0.6	0.034	0.045	0	11	190	40	<1	45
Peas (green)	6.7	15.5	0.4	2.2	0.9	0.028	0.127	2,000	130	500	70	1	92
Peppers, green	1.2	4.3	0.2	1.4	0.5	0.006	0.026	5,000	6	3,600	55	1	24
Potatoes, sweet	1.8	26.9	0.7	1.0	1.1	0.019	0.045	4,200	35	650	28	0	121
Potatoes, white	2.0	18.7	0.1	0.4	1.0	0.014	0.058	56	40	560	20	1	84
Sauerkraut	1.3	3.5	0.2	1.4	2.4	0.040	0.025	20	8	0–190	Fair	...	21
Spinach	2.3	2.6	0.3	0.6	1.5	0.067	0.068	8,400	35	1,500	100	1	22
Tomatoes	1.0	3.4	0.3	0.6	0.6	0.011	0.026	2,000	26	540	36	<1	20
Turnips	1.1	6.0	0.2	1.1	0.7	0.064	0.046	15	20	600	17	<1	15
Turnip greens	2.9	4.2	0.4	1.2	1.8	0.216	0.075	11,000	45	2,600	150	Good	32

Fruits:													
Apples	0.3	13.9	0.4	1.0	0.3	0.007	0.012	110	15	120	29	<1	60
Bananas	1.2	22.4	0.2	0.6	0.8	0.009	0.031	320	20	560	38	...	96
Dates, dried	2.2	73.0	0.6	2.4	1.8	0.065	0.056	210	20	0	18	...	306
Figs, dried	4.0	62.6	1.2	5.8	2.4	0.162	0.116	45	24	0	40	...	277
Grapefruit	0.5	9.8	0.2	0.3	0.4	0.021	0.020	0	24	820	40	...	43
Oranges	0.9	10.6	0.2	0.6	0.5	0.045	0.021	90	26	960	25	...	48
Peaches	0.5	11.4	0.1	0.6	0.5	0.016	0.024	980	6	200	26	...	49
Pears	0.7	14.4	0.4	1.4	0.4	0.015	0.026	15	19	100	30	...	64
Pineapples	0.4	13.3	0.2	0.4	0.4	0.018	0.028	100	25	760	23	...	57
Prunes, dried	2.3	69.4	0.6	1.6	2.1	0.054	0.105	2,500	60	0	260	0	2,500
Raisins	2.3	69.5	0.5	1.7	2.0	0.064	0.132	84	24	0	50	...	292
Strawberries	0.8	6.9	0.6	1.2	0.5	0.041	0.028	120	11	1,200	120	...	36
Cereals:													
Bread, white	8.5	52.0	2.0	0.3	1.3	0.080	0.098	0	30	0	26	...	260
" , whole wheat	9.5	47.0	3.5	1.0	2.0	0.050	0.185	0	120	0	41	1	258
Corn meal, yellow	9.1	71.9	3.7	2.0	1.3	0.018	0.190	420	78	0	32	1	357
Flour, soybean	37.3	9.5	20.2	2.5	4.7	0.200	0.450	Fair	Fair	0	Fair	...	379
Flour, white, enriched max.	10.8	75.6	0.9	0.3	0.4	0.441	0.092	0	185	0	133	2	354
Flour, white (natural)	10.8	75.6	0.9	0.3	0.4	0.020	0.092	0	29	0	16	1	354
Macaroni or spaghetti	13.0	73.5	1.4	0.4	0.7	0.022	0.144	0	43	0	0	...	359
Oatmeal	14.2	67.0	7.4	1.2	1.9	0.069	0.392	0	270	0	88	1	391
Rice, unpolished	7.5	77.1	1.7	0.6	1.1	0.084	0.290	50	100	0	60	2	354
Rice, white	7.6	79.2	0.3	0.2	0.4	0.009	0.096	0	7	0	32	...	350
Wheat, whole	11.7	74.0	2.0	1.8	1.8	0.045	0.423	14	170	0	40	5	361
Nuts:													
Almonds	18.6	16.9	54.1	2.7	3.0	0.239	0.465	580	100	0	240	...	629
Brazil nuts	14.4	8.9	65.9	2.1	3.4	0.176	0.592	10	340	0	Good	...	686
Coconuts, dried	6.3	28.1	57.4	3.4	1.3	0.059	0.155	Fair	24	0	42	...	654

COMPOSITION OF FOODS.*—(*Continued*)

Name	Percentage by weight							Vitamin content					Cal/ 100 g
	Protein	Carbohydrate (not fiber)	Fat	Crude fiber	Ash	Ca	P	A	B_1	C	G (B_2)	Nicotinic acid (B_1)	
Peanuts	26.9	21.2	44.2	2.4	2.7	0.071	0.399	360	220	0	200	13	590
Pecans	9.4	10.8	73.0	2.2	1.6	0.089	0.335	400	350	0	100	...	738
Meat, fish, poultry:													
Bacon	12.2	1.4	53.0	...	4.7	0.006	0.108	0	90	0	61	...	531
Beefsteak	18.7	1.4	17.0	...	0.9	0.012	0.216	21	70	36	110	6	233
Chicken	21.1	0.0	4.5	...	1.1	0.012	0.232	Fair	40	80	68	12	125
Clams	12.8	3.4	1.4	...	2.1	0.109	0.099	28	7	600	5	...	77
Codfish	16.5	0.0	0.4	...	1.2	0.012	0.120	10	40	0	64	2	70
Eggs	12.8	0.7	11.5	...	1.0	0.067	0.180	1,000	50	0	120	7	158
Frankfurters	14.1	0.0	20.8	...	2.8	0.007	0.117	......	Fair	.....	Good	...	244
Ham (fat)	14.6	0.3	44.0	...	5.1	0.012	0.215	Fair	480	0	100	11	456
Lamb chops	21.7	0.7	29.9	...	1.3	0.021	0.180	0	100	0	110	...	359
Mackerel	18.7	0.0	12.0	...	1.2	0.011	0.273	150	40	0	240	6	183
Oysters	9.8	5.9	2.0	...	2.0	0.052	0.155	140	50	60	180	...	81
Pork chops	14.8	0.0	32.0	..	0.8	0.010	0.180	Fair	450	38	100	7	347
Veal chops	18.6	0.0	15.0	...	1.0	0.012	0.220	Fair	90	.....	96	13	209
Dairy products:													
Butter	0.6	0.4	81.0	...	2.5	0.015	0.017	2,400	0–39	0	0	Fair	733
Cheese, American	23.9	1.7	32.3	...	3.1	0.930	0.683	2,000	14	0	170	...	393
Ice cream	3.9	20.3	13.0	...	0.8	0.150	0.120	900	8	0	20	...	214
Milk, evaporated	7.0	9.9	7.9	...	1.5	0.250	0.200	590	19	30	130	Fair	139
Milk, whole, (pasteurized)	3.5	4.9	3.9	...	0.7	0.120	0.093	170	12	14	62	<1	69

---

* Data from ***Nutritional Charts*** of H. J. Heinz Company, Pittsburgh, Pennsylvania, 10th ed.; used by permission.

FACTS ABOUT COMMON SUBSTANCES

Formula	Common name	Melting point, °C	Boiling point, °C	Solubility in 100 g. water, 20°C g	Use
$AlCl_3$	...	190 at 37 lb/in.²	Sublimes at 177.8	46	Catalyst
$Al_2(SO_4)_3 \cdot 18H_2O$	...	Decomposes at 86.5	...	36	For clearing water
$(NH_4)_2CO_3 \cdot H_2O$	...	Decomposes at 58	...	100	In smelling salts
NH_4Cl	Sal ammoniac	Decomposes at 350	Sublimes at 520	37	In dry cells
NH_4OH	Ammonia water	−77	Unstable	...	Kitchen cleaner
NH_4NO_3	...	169.6	Decomposes at 210	192	In explosives
$(NH_4)_2SO_4$	...	Decomposes at 100	...	76	Fertilizer
$SbCl_3$	...	73.4	223	999	
As_2O_3	.	Sublimes at 193	...	Highly insoluble	Making insecticides
$BaCl_2 \cdot 2H_2O$	. .	−2H₂O at 113	...	36	Laboratory test for SO_4^{--}
$BaSO_4$	Barite	1580	...	Highly insoluble	In paints
BiONO	Bismuth oxynitrate or bismuth subnitrate	Decomposes at 260	...	Highly insoluble	In medicine
H_3BO_3	Boric acid	Decomposes at 185	...	6	Antiseptic
$CaCO_3$	Precipitated chalk	Decomposes at 825	...	Highly insoluble	Mild abrasive
$CaCl_2$	...	772	Above 1600	73	Dehydrating agent
$CuCl$ (Cu_2Cl_2)	...	422	1366	1	
$CuCl_2$	...	498	Decomposes to Cu_2Cl_2 at 993	75	
$CuSO_4$	...	200	Decomposes to CuO at 650	21	
$CuSO_4 \cdot 5H_2O$	Blue vitriol	−4H₂O at 110	−5H₂O at 150	21	Electrolyte for copperplating
I_2	...	114	183	Highly insoluble	Antiseptic
$FeCl_2$	...	670	...	66	
$FeCl_3$	...	282	315	92	Etching in metallurgy, water purification
$FeSO_4 \cdot 7H_2O$	Green vitriol or copperas	−6H₂O at 100	−7H₂O at 300	27	Kills weeds
$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	Sugar of lead	75	280	46	
$PbCl_2$	...	501	950	1	

$-H_2O$ = loses water.

FACTS ABOUT COMMON SUBSTANCES.—(*Continued*)

Formula	Common name	Melting point, °C	Boiling point, °C	Solubility in 100 g. water, 20°C g	Use
$PbCrO_4$	...	844	Decomposes	Highly insoluble	Chrome yellow pigment
PbO	Litharge	888	...	Highly insoluble	Pigment, yellow
Pb_3O_4	Minium	Decomposes at 500	...	Highly insoluble	Pigment, red
PbO_2	Lead dioxide	Decomposes at 290	...	Highly insoluble	Oxidizing agent; positive plate in battery
$LiCl$	...	613	1353	79	In air-conditioning equipment
$MgSO_4 \cdot 7H_2O$	Epsom salts	$-6H_2O$ at 150	$-7H_2O$ at 200	34	Purgative
Hg_2Cl_2	Calomel	302	383.7	Highly insoluble	Medicine
$HgCl_2$	Corrosive sublimate	276	302	7	Antiseptic
HgO	...	Decomposes at 100	...	Highly insoluble	Historic compound
HgS	Cinnabar, vermilion	Sublimes at 583.5	...	Highly insoluble	Ore of Hg; pigment
$NiSO_4 \cdot 7H_2O$	...	$-SO_3$ at 840	$-6H_2O$ at 103	38	For nickel-plating
P_2O_5	...	563	Sublimes at 347	Decomposes	Dehydrating agent
KBr	...	730	1380	65	In photography
K_2CO_3	Potash	891	Decomposes	111	Fertilizer
$KClO_3$	Chlorate of potash	368.4	Decomposes at 400	7	Preparation of oxygen
KCl	Sylvite	776	Sublimes at 1500	34	Fertilizer
K_2CrO_4	Chromate of potash	968.3	...	62	Anticorrosion agents in radiators of automobiles
$K_2Cr_2O_7$	Dichromate of potash	398	Decomposes at 500		
KCN	Cyanide of potash	634.5	...	...	For casehardening
KF	...	880	1500	92	
KOH	Caustic potash	360.4	1320	112	To make soft soap
KI	...	678	1420	144	In iodized salt
$KMnO_4$	...	Decomposes at 240	...	8	Strong oxidizing agent
KNO_3	Saltpeter	334	Decomposes 400	32	In corned-beef brine
K_2SO_4	...	1076	...	11	
$KHSO_4$	...	210	Decomposes	51	

$-H_2O$ = loses water.

FACTS ABOUT COMMON SUBSTANCES.—(*Continued*)

Formula	Common name	Melting point, °C	Boiling point, °C	Solubility in 100 g. water, 20°C g	Use
SiC	Carborundum, Crystalon	Above 2700	Sublimes 2000, decomposes at 2210	Highly insoluble	Abrasive
SiO_2	Quartz	1710	2230	Highly insoluble	Making glass
AgCl	....	455	1550	Highly insoluble	Test compound; in photography; photosensitive
$AgNO_3$	Lunar caustic	212	Decomposes at 444	222	Antiseptic
$Na_2B_4O_7 \cdot 10H_2O$	Borax	$-8H_2O$ at 60	$-10H_2O$ at 200	2.8	Water softener; making glass
NaBr	....	742	1390	90	Sedative in medicine
Na_2CO_3	Soda ash	851	Decomposes	22	In scouring powders; water softener
$Na_2CO_3 \cdot 10H_2O$	Washing soda	32.5	$-H_2O$ at 33.5	22	Water softener
$NaHCO_3$	Baking soda	$-CO_2$ at 270	....	10	Leavening agent in dough
NaCl	Common salt	801	1413	36	Preservative
NaF	.. ..	980	1700	4	Insecticide
NaOH	Caustic soda, lye	318.4	1390	109	Making soap
NaI	....	651	1300	179	
$Na_2SO_4 \cdot 10H_2O$	Glauber's salt	Decomposes at 32.4	....	19	Horse medicine
$SrCl_2$	....	873	....	53	Gives red flame
$SnCl_2$	Stannous chloride	Decomposes at 50	....	231	
$SnCl_4$	Stannic chloride	37.7	Decomposes	....	Mordant in dyeing
$ZnCl_2$	....	262	732	368	Wood preservative
$ZnSO_4 \cdot 7H_2O$	White vitriol	$-7H_2O$ at 280	....	54	

$-H_2O$ = loses water.

THE MORE COMMON ELEMENTS

Name	Symbol	Atomic number	Approximate atomic weight	Electron arrangement	Combining number(s) (valence)
Aluminum	Al	13	27	•2)8)3	3
Calcium	Ca	20	40	•2)8)8)2	2
Carbon	C	6	12	•2)4	4 (2)
Chlorine	Cl	17	35.5	•2)8)7	1 (3, 5, 7)
Copper	Cu	29	63.6	•2)8)18)1	1, 2
Hydrogen	H	1	1	•1	1
Iron	Fe	26	56	•2)8)14)2	2, 3
Magnesium	Mg	12	24	•2)8)2	2
Mercury	Hg	80	200	•2)8)18)32)18)2	1, 2
Nitrogen	N	7	14	•2)5	3, 5
Oxygen	O	8	16	•2)6	2
Phosphorus	P	15	31	•2)8)5	3, 5
Potassium	K	19	39	•2)8)8)1	1
Silver	Ag	47	108	•2)8)18)18)1	1
Sodium	Na	11	23	•2)8)1	1
Sulfur	S	16	32	•2)8)6	2, 4, 6
Zinc	Zn	30	65	•2)8)18)2	2

The following elements are not included in the table of international atomic weights, for if these exist in nature they have never been found in amounts sufficient for an experimental determination of their atomic weights: 43 (masurium); 61 (illinium); 84 (polonium); 85, 87, 89 (actinium), 93, 94, 95, 96.

INTERNATIONAL ATOMIC WEIGHTS—1943*

Name	Symbol	Atomic number	Atomic weight	Name	Symbol	Atomic number	Atomic weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35 457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92 91	Rubidium	Rb	37	85.48
Copper	Cu	29	63 57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32 06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180 88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164 94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114 76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200 61	Zirconium	Zr	40	91.22

* From the *Journal of the American Chemical Society.*

INDEX

THE MORE COMMON ELEMENTS

Name	Symbol	Atomic number	Approximate atomic weight	Electron arrangement	Combining number(s) (valence)
Aluminum...	Al	13	27	•2)8)3	3
Calcium.....	Ca	20	40	•2)8)8)2	2
Carbon......	C	6	12	•2)4	4 (2)
Chlorine.....	Cl	17	35.5	[illegible])8)7	1 (3, 5, 7)
Copper......	Cu	29	63.6	•2)8)18)1	1, 2
Hydrogen....	H	1	1	•1	1
Iron.........	Fe	26	56	•2)8)14)2	2, 3
Magnesium..	Mg	12	24	•2)8)2	2
Mercury.....	Hg	80	200	•2)8)18)32)18)2	1, 2
Nitrogen....	N	7	14	•2)5	3, 5
Oxygen......	O	8	16	•2)6	2
Phosphorus..	P	15	31	•2)8)5	3, 5
Potassium...	K	19	39	•2)8)8)1	1
Silver.......	Ag	47	108	•2)8)18)18)1	1
Sodium......	Na	11	23	•2)8)1	1
Sulfur.......	S	16	32	•2)8)6	2, 4, 6
Zinc.........	Zn	30	65	•2)8)18)2	2