UNIVERSAL
LIBRARY

OU_154599

UNIVERSAL
LIBRARY

ATOMIC WEIGHTS*

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.94
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.92
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.01
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.46
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
		41	92.91
		29	63.54
		66	162.46
		68	167.20
		63	152.00
		9	19.00
		64	156.90
		31	69.72
		32	72.60
		79	197.20
		72	178.60
		2	4.003
		67	164.94
		1	1.008
		49	114.76
		53	126.92
		77	193.10
		26	55.85
		36	83.70
		57	138.92
		82	207.21
		3	6.94
		71	174.99
		12	24.32
		25	54.93
Mercury	Hg	80	200.61

OUP—1700—8-11-77—7,000.

OSMANIA UNIVERSITY LIBRARY

540

Call No. B85C Accession No. G 25596

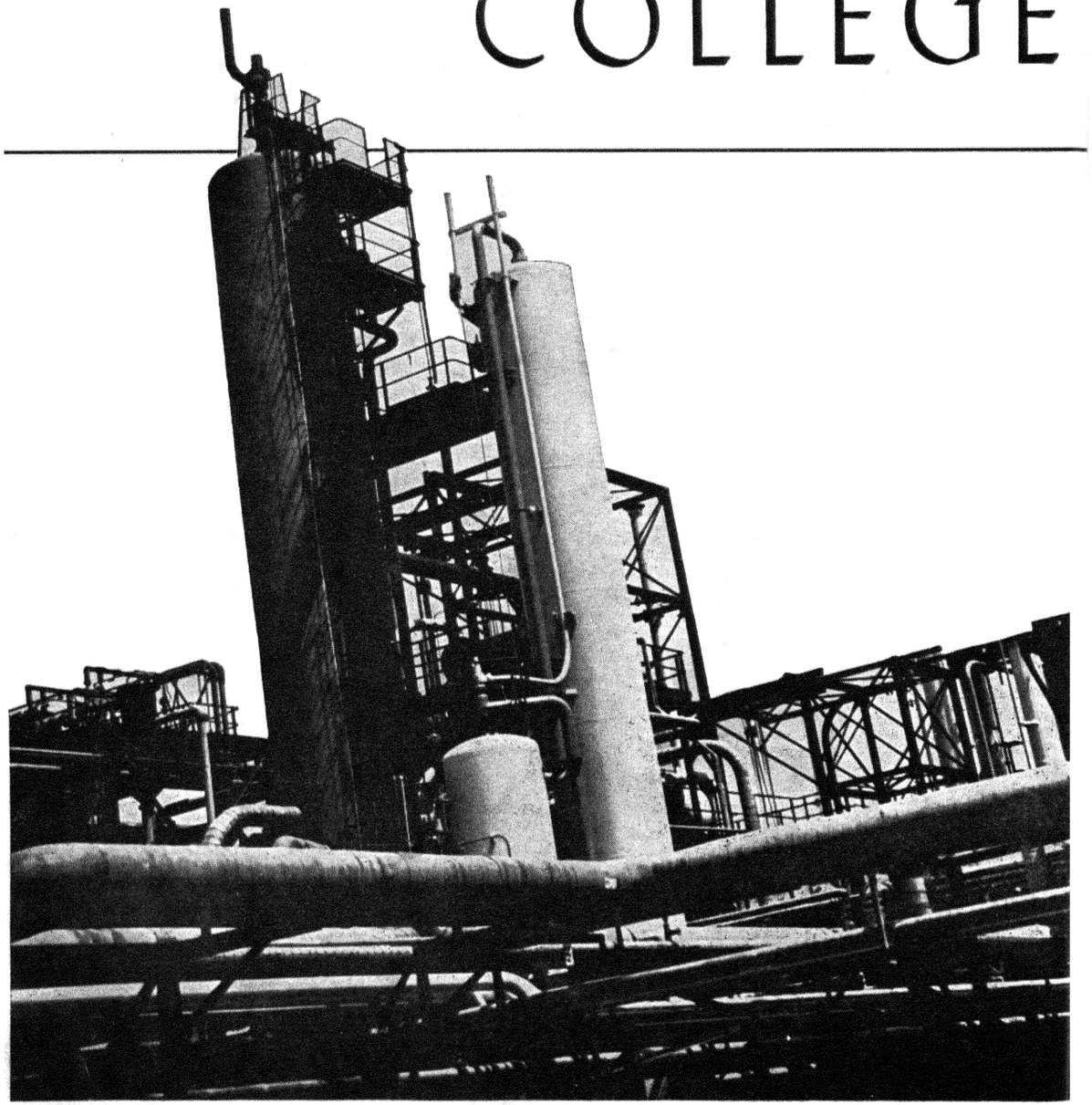
Author Briscoe, Herman T.

Title College chemistry. 1951.

This book should be returned on or before the date last marked below.

FOURTH EDITION

COLLEGE CHEMISTRY



HERMAN T. BRISCOE

PROFESSOR OF CHEMISTRY, INDIANA UNIVERSITY

HOUGHTON MIFFLIN COMPANY

BOSTON · The Riverside Press Cambridge

COPYRIGHT, 1951
by Herman T. Briscoe

Copyright, 1937, 1940, 1945, by Herman T Briscoe

All rights reserved including the right to reproduce
this book or parts thereof in any form

The Riverside Press
Cambridge · Massachusetts
Printed in the U.S.A.

PREFACE

THE GENERAL PLAN of this edition of *College Chemistry* is the same as that of previous editions. Its objective is to aid the student as fully as possible, within its scope, in understanding 1) the important steps in the development of the science of chemistry; 2) how data have been obtained and used in the formulation of basic principles and theories; 3) how chemical knowledge has been applied in industry and in other useful pursuits and activities of man; and 4) how recent information and theories of the structure of matter have contributed to the present status of the science.

To attain the objective described above, the author is of the opinion that a textbook for beginners must begin with a discussion of general principles and basic concepts. The author believes that this story must be unfolded gradually and without the lengthy interruption that would result from the full presentation of atomic and molecular structure in the early pages of the book. The whole story of atoms and the compounds they form cannot be told in a few pages or even in a few chapters. To include this material in the chapter dealing with the atomic theory, or to place it in chapters immediately following that discussion, would, in the author's opinion, delay too long the student's introduction to what still must be regarded as the real substance of chemistry — the different forms of matter and their transformations. Therefore, the first eleven chapters have been devoted to the discussion of the concepts of matter and energy; elements and compounds; the fundamental laws of chemical change; the different kinds of chemical change, including oxidation and reduction; the atomic theory and arguments upon which it rests; the behavior of gases; atomic and molecular weights; valency; formulas and equations; a general classification of compounds; and Mendeleef's classification of the elements. One of the chapters in this group deals with concepts of the atom's structure, ionic and covalent compounds, atomic numbers, isotopes, and related topics. The full discussion of these topics, and especially the experimental evidence upon which these concepts depend, is not presented, however, until Chapter 12 is reached. Oxygen and hydrogen are introduced early in order that the student may become acquainted as soon as possible with simple kinds of chemical changes and some of the processes used in preparing elements and compounds. The outline just discussed for the first eleven chapters has also appeared, to the author, to be consistent with the thought that the student is to study chemistry as a laboratory science and, hence, that much of the early material of the book should be related to possible laboratory assignments.

The author has attempted to integrate the development of chemistry during the eighteenth and nineteenth centuries with the knowledge and concepts of atoms and molecules which the first half of the twentieth century has contributed to an understanding of the forms of matter and their chemical behavior. The old and the new are both necessary, because the story of chemistry is not merely a story of what chemistry *is*; it must also include the rich history of the beginning and the development of the science. Chemists of tomorrow will probably be much richer than those of today in their knowledge of atomic and molecular structure, the behavior of solutions of electrolytes, and many other subjects, but they will also be acquainted with the work of Lavoisier, Dalton, Avogadro, Cannizzaro, Mendeleef, Arrhenius, Kekule and the many others who did so much in laying the foundation and building the framework to which more recent accomplishments are but additions and modifications. The author has emphasized, therefore, current concepts of the structure of atoms and molecules, of the electron theory of valence, of the properties of solutions of electrolytes, of acid and bases, and of other subjects concerning which views have changed during recent years, but he has tried to present the newer views, not alone and apart as the whole story, but in relation to the views that preceded them, wherever the older views are still important.

To those teachers who are acquainted with *Introduction to College Chemistry* and the first edition of *College Chemistry* many changes will be evident. Considerable new material has been added, some material of the previous edition has been redistributed, some portions have been condensed, a few sections dealing with obsolete processes have been deleted, and many sections, or parts of sections, have been rewritten. The following are a few examples of changes that have been made in the preparation of the revision: a chapter on synthetic organic products has been added; new material on atomic energy, nuclear reactions, elements 93 to 98, tracer elements, and related topics have been added to the discussion of the structure of matter; organic nitrogen compounds, hydrous oxides, antibiotics, silicones, and several other topics not previously included have been introduced in appropriate places throughout the book; the discussion of Mendeleef's periodic classification of the elements has been combined with the chapter dealing with the general classification of compounds; spectra and the spectroscope are discussed immediately preceding Bohr's theory; the section on the Law of Combining Proportions has been rewritten as have all or parts of sections dealing with osmotic pressure, deviations in the behavior of gases from the gas laws, the kinetic energy of gas molecules, electrolysis, the silicic acids, hydrolysis of salts, and many other topics; oxidation numbers replace positive and negative valence numbers; new sketches have been added, and some have been revised; many new photographs picturing processes and products have been substituted for those in the previous edition; some of the exercises have been omitted, others have been revised, and several new ones have been added; the references for further reading have also been revised.

This book has been designed and written to provide material for a course covering an academic year, but there is probably more material than can be used in most courses of this length.

Most teachers of general chemistry can agree upon a core of essential information that must be taught in the course. The order in which the different portions of this core should be considered is not so easily agreed upon. Furthermore, each course, and therefore the textbook for the course, must offer more than this fundamental core of chemistry, and it is in this phase of our teaching that wide variations of practice and opinion become apparent. In what directions and to what extent shall we expand the subject when once we have allocated the proper amount of space and time to fundamental facts, principles, and concepts? Some may choose emphasis upon the descriptive aspects of elements and their compounds; others may think it wise to spend considerable time upon organic compounds, while still others may think the study of the metals is more important; some may decide that more time should be spent upon the elaboration of the properties of solutions of electrolytes, the activity concept, the structure of complex inorganic compounds, or other topics selected from theoretical and physical chemistry. Each teacher must determine the contents of his students' course in accordance with the time available, the students' needs, and his own ideas of what is most significant. The author of the textbook must attempt to make his treatment of the subject flexible enough to meet, not all, but at least several different requirements for the course. Even then, he cannot cover all subjects, or any subject, as fully as some teachers would like, and he is certain to include topics some teachers would omit and to exclude some that others would include. To provide for flexibility the text must include more material than can be covered in any single course. Furthermore, the sequence of topics must be flexible so that whole chapters may be moved forward or postponed, or parts of chapters may be shifted to other positions without confusion. To this end, it is necessary that some repetition be used in treating at least fundamental concepts. At the risk of being accused of repetition, the author has also followed the practice of introducing certain topics early in the book, but leaving until later their full discussion or at least certain related subject matter. For example, ions and ionic compounds are discussed in Chapter 3, but the properties of solutions of electrolytes are discussed in a much later chapter. Symbols, formulas, and equations are introduced briefly at the close of Chapter 3 because of the need for some knowledge of them in the chapters on oxygen and hydrogen, but they are not developed in full until they are taken up in Chapter 9. Chapter 3 discusses the structure of the atom only to the extent necessary for an understanding of such subjects as the difference between ionic and covalent compounds, atomic numbers, isotopes, valence numbers, oxidation and reduction. Some instructors may prefer to assign Chapter 11 immediately after Chapter 3 has been completed. Further examples of changes in the sequence of chapters may be given. Hydrogen may be placed after the study of the Kinetic Molecular Theory, Molecular Weights, and Atomic Weights. The chapter on

Colloids may be postponed to a position in the latter part of the course. Chapter 21, Oxidation and Reduction, deals primarily with equations for such reactions and is placed in the book just before the Compounds of the Halogens because it is here that the student finds it necessary for the first time to write many equations involving changes in oxidation numbers. This chapter, however, may be studied earlier in the course; for example, it might be assigned before Chapter 20, or at almost any time after the study of Chapter 10.

The author wishes to express his appreciation to many instructors who have made suggestions for the improvement of the book and to the companies that have furnished photographs.

H. T. BRISCOE

CONTENTS

INTRODUCTION 1

1. Matter and Energy 9

2. Particles of Matter 19

3. The Structure of the Atom 33

4. Oxygen 47

5. Combustion, Oxidation, and Reduction 59

6. Hydrogen 67

7. The Behavior of Gases and the Kinetic Molecular Theory 78

8. Molecular and Atomic Weights 92

9. Symbols, Formulas, and Equations 102

10. The General Classification of Elements and Compounds 114

11. Investigations of the Structure of Matter 130

12. Atomic Structure and the Properties of the Elements 150

13. The Liquid and Solid States of Matter 168

14. Water 183

15. Solutions 194

16. Solutions of Electrolytes 213

17. The Colloidal State 224

18. The Atmosphere 233

19. The Alkali Metals 240

20. The Halogens 254

21. Oxidation and Reduction 269

22. The Compounds of the Halogens 277

23. Carbon 290

24. The Oxides and Other Simple Compounds of Carbon 300

25. Chemical Equilibrium 310

26. Equilibria in Reactions of Ions 321

27. Nitrogen and Ammonia 337

28. Other Compounds of Nitrogen — Oxides, Oxygen Acids, Cyanides 348

29. The Sulfur Family 358

30. Other Elements of the Nitrogen Family 375

31. Silicon and Related Elements 388

32. Organic Chemistry: The Hydrocarbons 399

33. Derivatives of the Hydrocarbons 416

34. Carbohydrates and Proteins 429

35. Other Natural and Synthetic Organic Products 439

36. Electrochemistry 447

37. Metals 457

38. The Alkaline Earth Family 467

39. The Metals of the B Divisions of Groups One and Two 484

40. Aluminum 503

41. Tin and Lead 511

42. Chromium and Manganese 521

43. Metals of Group Eight 527

44. Other Elements 544

APPENDIX 549

INDEX 551

INTRODUCTION

THE SCIENCE OF CHEMISTRY: ITS AIMS AND METHODS

Before beginning the study of chemistry, it will be well to consider briefly the place that this subject occupies among the different fields of man's knowledge. What is chemistry? With what part of our world is it concerned? With what materials do the chemist and the chemical engineer work? What do they do with them? How is their work related to the work of other men and of what value is it to others? How has their work helped to shape our civilization and how has it influenced our lives? These are some of the questions that will be discussed in this Introduction in order that the student may have a proper setting for the study of the subjects that follow.

1. Science

Science is knowledge — not scattered, isolated bits of information — but knowledge that is classified and organized, or arranged in a systematic manner, in accordance with the subjects with which it deals. Thus, all of our knowledge about the earth — its history, its structure, the formations of land and water on its surface, and the changes that alter them — is classified as geology.

2. Chemistry is One of the Fields of Science

The different classifications of knowledge are the different kinds of science. Astronomy deals with the stars, galaxies, solar systems, planets, and the satellites of planets. Geology deals with the earth, earth-formations, their history, and their changes. Biology deals with the structure, growth, and reproduction of living materials. Psychology, sociology, and physiology deal with organic phenomena or the behavior of living forms of matter.

Chemistry deals with the *materials* of which our world and all that it contains are composed, with the *properties*, or characteristics, of these materials, with their *structures* and with the *changes* that these materials undergo as they are converted from one form of matter into another, as, for example, the change of iron ore into iron, or of iron into rust.

3. The Utility of Chemistry

The materials of the world are of deep concern to man because he uses them for food, clothing, fuel, and shelter; he produces them, transports them, and sells them; his money has value because with it he can buy them; they are the basis of his life and of all his agricultural, industrial, and economic activities.

The changes that convert one form of matter into another also interest and concern man, because they affect the conditions under which he lives. They include changes that affect the fertility of the soil, the

weathering of rocks, the decay of plants and animals, combustion, the digestion of food, and many other natural processes of importance to all of us. The chemist's studies, however, have not stopped with the materials to be found in nature. In many instances he has improved upon nature and in others he has been able to supply our needs and desires when nature failed. Paper and cloth have been produced from wood, glass from sand, sugar from corn starch, resin-like substances from carbolic acid, dyes of all colors from coal tar products, cement from shale, lime from limestone, steel of a hundred varieties from iron, explosives from cotton, and nitric acid from the nitrogen of the air. Gasoline, kerosene, vaseline, paraffin, and many other products are obtained from petroleum. When the farmer finds that his soil has become deficient in the nutrients required to support crops, studies made by chemists come to his rescue by supplying information concerning the plant foods and nutrients that are needed, where and how they can most cheaply be obtained, and how to prepare them for the plants' use. The fight against disease has called for the production of thousands of medicinal substances and for the extraction and purification of many others of natural origin. With scarcely an exception, the objects and materials that we use in our daily lives — food, clothing, paper, glass, steel, cement, ink, drugs, dyes, soap, coal, wood, gas, gasoline, paint — all are related in some way to chemistry. Chemical principles are employed in their production, and their chemical properties determine their uses.

4. The Methods of the Chemist

In addition to the *usefulness* of the information that it can give, the study of chemistry has other values. Just as there are values to be derived from an understanding of how art, music, religion, and the social and political institutions of mankind have developed, so, too, is there value in understanding how science started, how it has developed, and how it has played its part in fashioning the character and extending the boundaries of modern civilization.

With this purpose in view, therefore, our study will show how data have been collected and will describe the observations made by many investigators. It will show how these observations have been interpreted; how, from scattered facts, *general laws and principles* that give the science its foundation and framework have been formulated; how single bits of information have been pieced together and made to tell a story. Like the pieces of a giant "jigsaw" puzzle, these bits of information had to be found; then each had to be placed in its proper place. As each was added the design of the picture became a little clearer, and finally, perhaps, all the details were completed, and the whole story that the picture had to tell was revealed. Many of the pictures of chemistry are, however, not completed, and there are others not yet started.

As the scientist works toward the completion of his picture, he must have some plan — some reasonable and possible conception of the unfinished portion of the picture. He calls this plan a *theory*; to formulate it he draws, perhaps, upon his imagination to some extent, but he is guided largely by the finished portions of the picture and by the unassembled pieces that are available. Using his theory as a guide, he attempts to fit these pieces, and others that may be found, into the picture in accordance with the plan that he has accepted as the most reasonable and most probable. The theory must be in accord with all known, pertinent facts, and, by applying it, the scientist must be able to predict facts that can be sought by experiment. A hypothesis is an assumption or a set of assumptions that offer a possible explanation of a problem. When by experimental test the hypothesis is found to be supported by the

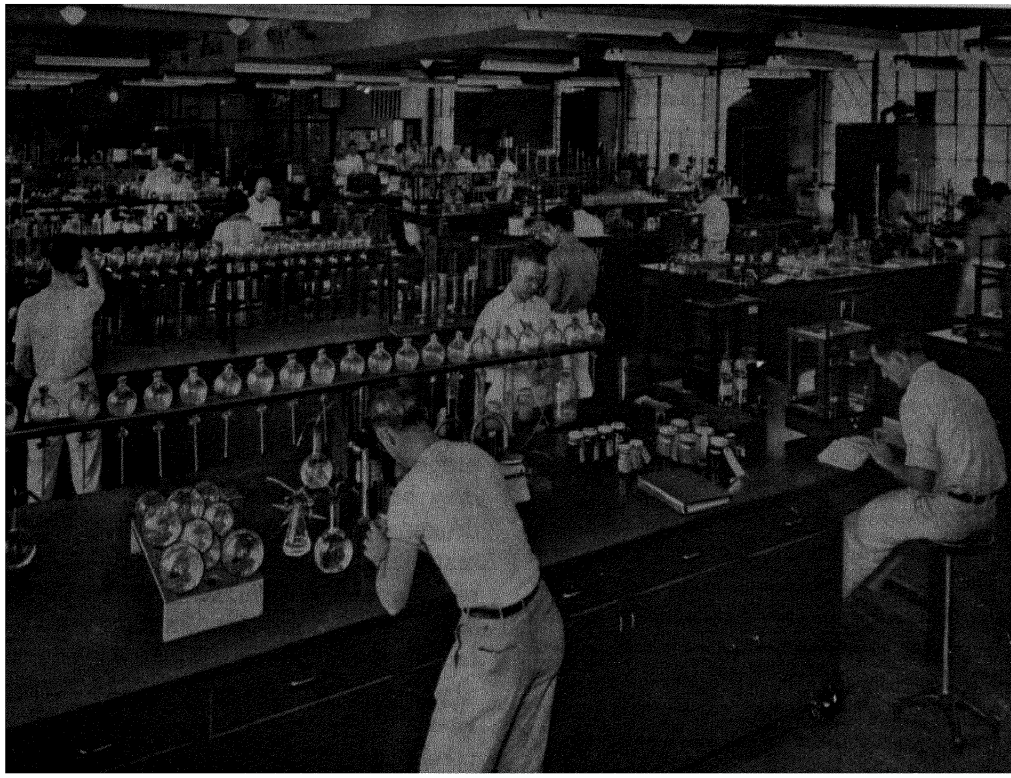


Figure 1. Industrial Chemical Laboratory

The chemical laboratory in industry is used for research, for testing, and for control of the quality of products
(Courtesy of Proctor and Gamble Company)

results of all possible methods of testing it, it can be called a theory.

5. One Example of the Chemist's Methods

Let us consider the application of the chemist's methods to the attack upon a single problem. Let us take as the problem. What happens when a metal rusts? First, we must observe the rusting process for different metals under different conditions as to temperature, moisture, and the nature of the atmosphere that surrounds them. We must study the properties of the metals before and after rusting occurs. We must determine whether they gain or lose weight when they rust. We must determine whether or not they rust in a vacuum. Perhaps, we may even attempt to determine whether or not it is possible to convert the rust back again into the metal. By such studies many facts bearing upon the problem will be collected. We find that not all metals rust under ordinary conditions, and that some do not rust under any conditions. The rate at which rusting occurs increases as the temperature rises. Moist metals rust more rapidly than dry ones. Air appears to be necessary, because we find that metals do not rust in its absence. When small pieces of iron are placed in different samples of air (in closed vessels) rusting ceases when one fifth of the air has been consumed, and *it must be consumed* in the process, because the decrease in volume can easily be measured. There is always a gain in weight of the metal during rusting, and this gain is exactly equal to the loss in weight suffered by the air. Other similar data can be secured.

From these data certain conclusions can be drawn about rusting in general. For example: Rusting is a change in which a metal combines with some part of air. From the facts revealed by this study and the general conclusions resulting from it, the chemist may see justification and

reason for the following theory concerning the nature and composition of the air: Air is a mixture of gases containing at least two substances, one of which is inactive and the other is active in promoting the rusting of metals and probably, also, the burning of combustible materials and the process of respiration in the body. This theory is supported by all of a considerable number of facts, and it offers a reasonable basis upon which we can proceed with further studies of the air and of other subjects, such as combustion.

6. The Work of the Chemist and the Chemical Engineer

In the chemical industries chemists and chemical engineers perform many kinds of work. Some analyze or test the raw materials that are used in the industry, and others test the purity or quality of the finished products. The chemical engineer designs and supervises the construction of the equipment in which the manufacturing processes are carried out. He also may act as the plant supervisor who controls the operation of the equipment. Other chemists are engaged in studying the possible uses that determine the market for the products of the plant. Others may devote their time to such problems as methods of decreasing the time required for different parts of the processes employed in the plant; methods of increasing the yields and the general efficiency of the operations; and methods of improving the quality of the products. The work of these chemists involves *research*. Other research workers may be employed in the development of new products and, therefore, of added business for their plant.

Other chemists are employed in the laboratories of hospitals and clinics, in public health laboratories, in government laboratories, in research institutes, in arsenals, and as teachers and research workers in the laboratories of educational institutions.

7. Research in Chemistry

Occasionally, a great discovery in science is made accidentally. An investigator may, quite by chance, produce a new substance, for example, during the course of investigations that he has undertaken for an entirely different purpose. Perkin discovered the first synthetic dye while he was seeking a method of making quinine. Most of the discoveries in science, however, are the results of carefully planned and outlined programs of research, aimed at definite goals, and requiring hard work and patience.

Through his research the chemist or chemical engineer opens up new sources of information concerning materials, their properties, and their uses. His research may be in the direction of producing new drugs, dyes, textiles, perfumes, or other materials; of improving the methods of manufacturing them; or of finding new uses for them. On the other hand, research may be aimed at obtaining information that has no direct, practical value. The investigation may be concerned, for example, with conditions that affect the velocity with which a change of one material into another occurs, or it may deal with theoretical subjects, such as the effect of the structure and composition of a substance upon its properties or behavior. Such studies as these advance and expand the science by including within its boundaries more and more explanations of the behavior of the materials with which the chemist works and of the changes in which they participate.

In planning the investigation of a problem, in collecting data, and in studying the data to find the final solution of the problem, the chemist uses the methods that we have already described. Taken all together, these are sometimes referred to as the *scientific method*. Much of what has been written about this method leads one to think of it as something novel and peculiar to the problems of science, but there is nothing novel, or peculiar, or strange about it. The method of the scientist is the simple, logical, and direct method of

finding the answer to any question that can be subjected to inquiry and investigation.

8. The Subdivisions of Chemistry

Just as science grew to such proportions that division into several branches became necessary, the science of chemistry has grown until it, too, must be divided into different fields. The five principal divisions are *organic*, *analytical*, *physical*, *inorganic*, and *biological*. Organic chemistry deals with the substances that are composed in part of carbon, and many of which are associated in some way with living organisms. Analytical chemistry is concerned with the identification and separation of different substances and with quantitative studies and measurements of their composition. Physical chemistry includes the laws, principles, and theories of the subject. Inorganic chemistry deals with substances obtained directly or indirectly from minerals, ores, and similar sources. Biological chemistry is the chemistry of the materials of living organisms and of the changes that they undergo.

UNITS OF MEASUREMENT USED IN CHEMISTRY

The chemist in his industrial or research laboratory, and the student in his laboratory at school, must compare, frequently, one material with another or one action involving these materials with another action. For these comparisons we must have *units of measurement.*

9. Measurement of Temperature

A *thermometer* is an instrument used to measure temperature. The most common type of thermometer consists of a glass bulb filled with mercury and attached to a long capillary tube or stem. Changes in the temperature of the mercury cause it to expand or to contract and. therefore. to rise

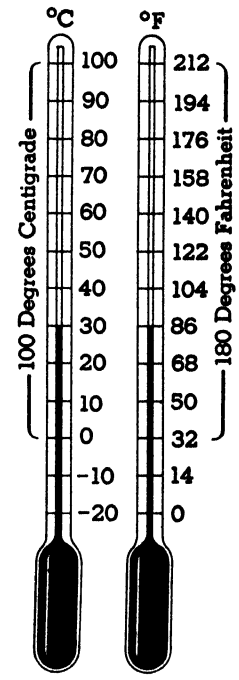


Figure 2. Comparison of the Two Temperature Scales

or fall in the capillary. In the chemical laboratory, temperature is usually measured on the *Centigrade*, instead of the *Fahrenheit*, scale. Zero on the Centigrade scale is the temperature at which pure water freezes; the zero point on the thermometer is the point at which the level of mercury rests in the capillary when the thermometer is placed in a bath of melting ice. The boiling point of water, at what is called the average pressure of the atmosphere at sea level, is called 100°. This gives 100 equal divisions between the boiling and freezing points of water. On the Fahrenheit scale this same range of temperature is divided into 180 divisions, since on this scale water freezes at 32° and boils at 212°. The divisions are extended on either side of the temperatures representing the freezing and boiling points of water to complete the two scales. Each division of the Fahrenheit scale is five-ninths of a division on the Centigrade scale. Centigrade temperature readings can be converted into the corre-

sponding Fahrenheit readings, and *vice versa*, by means of the following formula:

$$C.^\circ = (F.^\circ - 32) \times \tfrac{5}{9}.$$

10. Linear Measurements

The unit employed in measuring lengths or distances is the *meter*. This unit is the distance between two lines, at 0° C., on a bar made of platinum and iridium and deposited in the vaults of the International Bureau of Weights and Measures near Paris. The meter is subdivided into *centimeters* (1 meter = 100 centimeters) and *millimeters* (1 centimeter = 10 millimeters). The abbreviations for these units are *m.*, *cm.*, and *mm.*, respectively.

11. Measurement of Weight and Volume

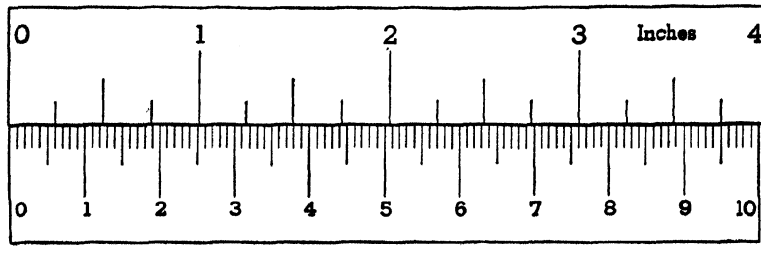
The unit employed in weighing objects is the *gram* (g.). This unit is one-thousandth part of the weight of a piece of metal containing platinum and iridium, which is deposited in the International Bureau of Weights and Measures. The weight of the entire piece of metal is, therefore, 1000 grams or one *kilogram* (kg.). The *liter* (l.) is the volume occupied by the quantity of distilled water which, at 4° C., will exactly balance the standard kilogram. The original idea was to select a weight of the platinum-iridium metal which would exactly balance 1000 *cubic centimeters* (cc.) of pure water at 4°. This would have made one cubic centimeter of water weigh one gram. As it turned out, however, the weight of metal actually selected is equal to the weight of 1000.027 cubic centimeters of water at 4°. The liter representing the volume of water required to balance the standard kilogram is, therefore, not equal exactly to 1000 cc. The difference is only slight and is often neglected. Instead of using the cubic centimeter as a unit in measuring small volumes, the *milliliter* (ml.) is often used. This, of course, is the one-thousandth part of a liter.

12. Density

The density of any body is defined as the mass per unit volume of the body. The volume usually selected is the cubic centimeter. Since this volume of water at 4° C. weighs almost exactly 1 gram, the density of water is 1. The density of gold is 19.3; therefore, 1 cubic centimeter of gold weighs 19.3 grams, or 19.3 times as much as the same volume of water. Both above and below 4° C., the density of water is slightly less than 1. The densities of gases, which are very light as compared with liquids and solids, are usually expressed as the weight per liter. The temperature and pressure must be specified, because the density, especially of a gas, varies considerably with changes in both of these conditions. The weight of a liter is called the *liter-density* of the gas. If expressed as the weight of one cubic centimeter, the term *absolute density* is used.

13. Measurement of Time

In the laboratory, time is usually measured and expressed in *seconds* as the unit.



100 Millimeters = 10 Centimeters

Figure 3. Lengths of Four Inches and Ten Centimeters

The mean solar day consists of twenty-four hours or 86,400 seconds. In describing experiments or natural events that occur during longer periods of time, minutes, hours, days or even years may be used.

14. Comparison of Metric and Common Units

The following table may be helpful in the comparison of the units with which you are familiar and the units of the *metric* system, which includes the units described above.

1 meter is equivalent to 39.37 inches
1 centimeter is equivalent to 0.3937 inch
0.9144 meter is equivalent to 1 yard
1 inch is equivalent to 2.5400 centimeters
1 liter is equivalent to 1.0567 quarts
1 kilogram is equivalent to 2.205 pounds
1 pound is equivalent to 453.6 grams
1 gram is equivalent to 15.4324 grains
1 cubic foot is equivalent to 28,317 cubic centimeters
1 quart is equivalent to 0.9464 liter
1 ounce (avoirdupois) is equivalent to 28.35 grams
1 gallon is equivalent to 3.785 liters
1 mile is equivalent to 1609.33 meters

REVIEW EXERCISES

1. How are the meter, centimeter, and millimeter related?
2. Convert 225 centimeters to feet; 100 yards to meters; 2 miles to centimeters.
3. What is the basis of the liter as the unit of volume?
4. Convert 10 gallons to liters; 10 quarts to milliliters; and 50 milliliters to pints.
5. Convert your own weight into kilograms.
6. State the units which the following abbreviations represent: cm., g., kg., C.°, l., ml., mm., m., cc.
7. The density of copper is 8.92. Calculate the weight in grams of a bar of copper 5 in. × 3 in. × 10 in. What is the weight of the same bar in pounds?
8. What is the volume (in cc.) of a bar of gold weighing 5 pounds?
9. If a liter of air weighs 1.293g., what does a cubic foot weigh (in grams) under the same conditions?
10. Convert the following temperatures on the Fahrenheit scale to the corresponding Centigrade readings: 42°, 98.6°, 210°, − 10°. Convert the following Centigrade readings to the corresponding Fahrenheit readings: 0°, − 20°, 100°, 58°.
11. If the freezing point of ethyl alcohol on the Centigrade Scale is − 117°, what is it on the Fahrenheit Scale?
12. How much longer or shorter is a meter stick (exactly one meter long) than a yard stick?
13. The speed of a train is 65 miles per hour. What is the speed expressed as kilometers (1000 meters) per hour? as meters per second?

REFERENCES FOR FURTHER READING

Part Played by Chemistry in the Modern World

Beery, P. G., *Stuff; the Story of Materials in the Service of Man.* New York: D. Appleton-Century Company, 1930.

Clarke, B. L., *The Marvels of Modern Chemistry.* New York: Harper and Brothers, 1935.

Findlay, A., *Chemistry in the Service of Man,* New York: Longmans Green Company, 1940.

Haynes, W., *Men, Money and Molecules.* New York: Doubleday, Doran and Company, 1936.

Morrison, A. C., *Man in a Chemical World.* New York: Charles Scribner's Sons, 1937.

Stokley, J., *Science Remakes Our World.* New York: Ives Washburn, Inc., 1942.

Tilden, Sir W. A., and S. Glasstone, *Chemical Discovery and Invention in the Twentieth Century.* 6th ed.; New York: E. P. Dutton and Company, 1936.

Chemists and Their Work

Carlisle, N. V., *Your Career in Chemistry.* New York: E. P. Dutton and Company, 1943.

Coith, H., *So You Want to Be a Chemist.* New York: McGraw Hill Book Company, 1943.

Foster, W., *The Romance of Chemistry.* 2d ed.; New York: D. Appleton-Century Company, 1936.

French, S. J., *The Drama of Chemistry.* New York: University Society, 1937.

Grady, R. I., J. W. Chittum, *et al.*, *The Chemist at Work.* Easton, Penna.: Journal of Chemical Education, 1940.

Harrow, B., *Eminent Chemists of Our Times.* New York: D. Van Nostrand Company, Inc., 1927.

Jaffe, B., *Crucibles; the Lives and Achievements of the Great Chemists.* New York: Simon and Schuster, 1939.

General References

Ind. and Eng. Chem., **14,** 887 (1922); **16,** 447 (1924); **16,** 1105 (1924); **20,** 884 (1928); **27,** 103 (1935); **31,** 520 (1939); *J. Chem. Ed.*, **12,** 3 (1935); **26,** 383 (1949); **27,** 121 (1950); *Science,* **88,** 133 (1938).

Shapley, H., Wright, H., and Rapport, S., *Readings in the Physical Sciences.* New York: Appleton, Century, Crofts, 1948.

1

MATTER AND ENERGY: THEIR FORMS AND CHANGES

MATTER, MASS, AND WEIGHT

1. Matter

Matter can be defined, as nearly as it can be defined at all, as that which is necessary for physical, or material, existence. Every object in the physical universe is composed of one or more forms of it, and because of the different kinds and quantities of matter that they contain one body can be distinguished from another. Because they contain matter, bodies occupy space, have weight, and possess inertia, i.e., they remain at rest or, if moving, continue to move in the same direction unless acted upon by forces outside themselves.

Matter exists in many different forms, most of which can be converted into certain other forms of different composition. Thus, iron, a simple or single form of matter, is changed into another form by combining with oxygen from the air when it rusts. The sugar of milk is converted into an acid when the milk sours. During digestion in our bodies, starch is changed into sugar. When it burns or decays, wood is changed for the most part into water and carbon dioxide, an invisible gas, which mixes with the air. During all these and similar changes that occur in nature or which we employ in the laboratory and in industry, the form of matter may change, but matter itself is not destroyed, and it is not created. We regard it, therefore, as an ultimate reality of nature, a fundamental something that survives changes and is as lasting as the universe that it composes.

Until a few years ago it was thought that under no circumstances could matter be made from or converted into anything else. The "atomic bomb," however, has taught us that under extraordinary conditions and by changes much different from those commonly occurring in nature or in the laboratory, matter is converted into energy. So far only very small portions of a few forms of matter have been converted into energy, but the energy thus liberated is tremendous, as the destructive effects of an atomic bomb show. In certain other changes, of a still more unusual character, energy has been converted into matter. So far as the accuracy of methods of measurement permit, we are still certain, however, that no such changes involving matter occur in ordinary processes, such as burning, or in the many transformations of forms of matter into others which we study in the science of chemistry.

The statements made in the paragraphs above describe a few properties or characteristics that are associated with matter, but they do not really define matter. We cannot formulate a definition that explains what matter really *is*. To define a thing we must state what it is in terms of something simpler and more familiar. There is in all nature nothing simpler or more funda-

mental than matter itself, and, therefore, no exact or satisfying definition is possible. Sometimes we define matter, or we try to define matter, by saying that it is anything that occupies space.[1] But what is space? Certainly it is not real; instead it is a mere convenience by means of which we locate one object with respect to another.

2. Mass and Weight

Every body contains a definite quantity of matter and this is called the *mass* of the body. This definition of mass is not much more satisfactory than our definition of matter itself, but at least we can compare the masses of two bodies because of the force of gravitation with which the earth attracts the two bodies; this attraction, or pull, depends upon the quantity of matter, or mass, that the bodies contain and upon the distances of the bodies from the center of the earth. The attraction of the earth for a body is called the *weight* of the body.

3. Measurement of Weight

The weight of a body is measured by *weighing*, a process by which the body is balanced against standard "weights" for which the gravitational attraction of the earth is expressed in arbitrary units. In scientific work the usual weight unit is the *gram* (page 6). The *chemical balance* is used for weighing objects. It consists of two pans attached to the ends of a beam that rests at its center upon a knife-edge. The gravitational attraction of the earth for a standard one-gram weight and for any other object containing the same quantity of matter as the weight is the same; when they are placed in the two pans of the balance, the earth pulls each downward with the same attraction, and the beam of the balance rests in a horizontal position. The weight of any body is calculated as the sum of all the standard one-gram, two-gram, five-gram, and other weights that must be placed on one pan to balance the weight of the body on the other.

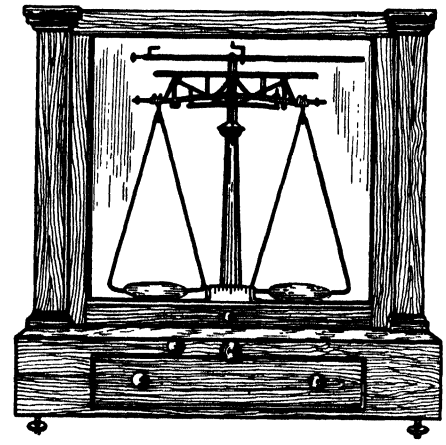


Figure 4. The Chemical Balance

The mass and weight of a body are not the same. For example, the mass of a body is the same regardless of its location on the surface of the earth. The body's weight, however, varies with the distance between the body and the center of the earth, and this distance is not the same at all points on the earth; it is greater near the equator, for example, than at one of the poles. The weights used in weighing the body, however, are subject to the same changes with distance from the center of the earth as the body itself. Hence, the weight of a body is the same when measured on the chemical balance and with the same standard weights, regardless of the locality in which it is weighed.

ENERGY

Energy is necessary for the performance of work by or upon a body, and, therefore, it is sometimes defined as the capacity for doing work. Like matter, energy is one of the basic realities of nature, and so we find that a definition in terms of something simpler and more fundamental than itself is impossible. To the chemist, matter and energy are closely associated, because changes in the forms of matter are accompanied by changes in energy.

4. Forms of Energy

Heat, light, and electricity are familiar forms of energy. A body in motion possesses kinetic energy the quantity of which depends upon the mass m of the body and the square of its velocity v:

$$\text{Kinetic Energy} = \tfrac{1}{2} mv^2.$$

A body at rest may possess *potential energy;* if the position, temperature, electrical condition, or composition are changed in a certain way, the potential energy of the body is changed into some other form which can perform work. Thus, a book resting on a table has potential energy. If it is pushed off and falls toward the floor, its potential energy is converted into kinetic energy, which, if the book strikes some other object as it falls, may perform work by moving that object.

We sometimes use the term *chemical energy* to indicate the energy contained in a body of matter and which depends upon the characteristic composition of the body. We believe that the different forms of matter that compose all bodies are, themselves, composed of small structural units or particles. The patterns, or arrangements, of these particles are different for different kinds of matter. If these patterns, in the changes by which forms of matter are converted into others, are rearranged — i.e., torn down and built up again in a different manner — there is a change in chemical energy. Usually the change is one in which particles of two different forms of matter are reshuffled, so to speak, and form one, or perhaps two, new patterns. This change may result in the liberation *or* in the absorption of energy, depending upon whether the old forms *or* the new ones contain the greater amounts of chemical energy.

5. How Chemical Energy Changes are Expressed

The absolute quantity of chemical energy possessed by a body of matter cannot be measured. Thus, we cannot measure the total energy contained in a ton of coal or the energy remaining in the products of its combustion — the ash and the gases that escape into the air — but we can measure the quantity of energy released when the ton of coal burns.

Changes in energy that occur during changes in the forms of matter are most frequently expressed in terms of *calories.* The calorie is the unit of *heat.* It represents the quantity of heat required to raise the temperature of one gram of water one degree on the Centigrade scale, or more exactly from 14.5° to 15.5° C. The *kilogram-calorie* (Cal.) is 1000 times as great as the calorie (cal.).

6. Conservation of Energy

Within the limits of accuracy of the methods used to measure energy, it is quite certain that there is no change in the total energy involved in any ordinary process in which there is a transformation of one form of energy into another, e.g., a change of kinetic energy into heat. This fact is expressed by the Law of the Conservation of Energy: *The quantity of energy involved in a transformation is constant.* This law does not state that all the energy involved in any process can be used to do the work for which the process is operated. Not all of the energy of the steam in the cylinders of a locomotive can be used to move a train of loaded cars. Some of the energy may be wasted, but none of it is destroyed; it is all converted into different forms of energy, but only some of these are useful, or available for work.

THE DIFFERENT FORMS OF MATTER AND THEIR PROPERTIES

7. Substances and Their Properties

Bodies are composed of materials, such as wood, porcelain, cement, iron, and cloth. These materials may be either

homogeneous or non-homogeneous. If homogeneous and of definite composition, the material is a substance. Any sample of a material of this kind possesses the same properties and composition, regardless of its source.

Each substance is characterized by specific *physical properties*, such as color, odor, density, hardness, melting point, boiling point, and crystalline structure. Such properties as these are said to be specific, because they are always the same for one substance, and because by means of them a substance can be identified. Certain other qualities are not specific; they can be applied only to one sample of a substance. Thus, two bars of iron may have different weights and dimensions, but the substance of which each is composed is known to be the same because the material in each bar possesses the specific properties of iron. Still other qualities that are not specific can be called conditions of a substance or of a body composed of it. These include temperature, pressure, and electrical charge, all of which may vary for the same substance, or they may be the same for samples of many different substances.

It is not often that a substance can be identified by a single specific property; it must be found to possess a whole set of properties which we recognize as peculiar to that substance. Thus, we cannot be certain that a sample of a granular, white substance is salt until we can determine certain other properties, such as taste, which we know all samples of salt possess.

Each substance also possesses definite *chemical properties*, which concern its transformations into other substances and, particularly, the different kinds of substances into which it can be transformed. Thus, the rusting of iron, the burning of coal, and the decay of wood are all possible because of certain chemical properties possessed by the substances that compose them.

All samples of a substance possess the same physical and chemical properties under the same conditions of temperature and pressure. The conditions must be the same, because, for example, at a low temperature water may be a hard, brittle solid — ice — and at a high temperature, an invisible gas — water vapor. The importance of conditions must also be recognized in the description of the chemical properties of a substance. For example, a piece of paper does not burn in air at ordinary temperatures, but it does so when heated to a much higher temperature.

8. Mixtures

One sample of milk is not exactly like another sample from the same bottle. If the sample comes from the top of a bottle that has been standing for some time, it will contain more cream than a sample from the lower part of the same bottle. Milk is not a single substance, for, obviously, it is not homogeneous. Granite, cement, butter, flour, and coal are other examples of nonhomogeneous materials. These materials consist of *mixtures* of substances. Thus, granite is a mixture of silica, feldspar, and mica, each of which possesses its own set of properties. Coal is not a substance, because different samples contain different amounts of ash, water, carbon, and other constituents. Soils contain varying amounts of clay, sand, water, and organic substances resulting from the decay of vegetation; and hence, samples of different soils differ in composition and in properties.

A solution of sugar in water is a mixture. Although a single solution may be homogeneous — it has the same composition throughout — two solutions of sugar may have, and likely will have, different compositions. Furthermore, the properties of sugar solutions vary with the composition, and, therefore, different solutions of the same substances have different properties; for example, they boil at different temperatures. Solutions, therefore, cannot be

single substances; they are mixtures of substances.

9. Physical and Chemical Changes

We are constantly aware of the many changes which alter the different forms of matter about us. Water freezes; milk sours; rocks weather and crumble; mountains and hills are eroded; wood decays; iron rusts; all the earth, in fact, appears to be in a continual process of change. These changes are either *physical* or *chemical.*

When *physical changes* occur, some of the properties of a substance may be altered for a time, but no new substances are formed. The following are examples of such changes: (1) The melting of ice and the condensation of steam; (2) the mixing of sugar with water to form a solution; (3) the change observed when a platinum wire is heated to redness. In each of these there is a change in some properties. Thus, a liquid is produced from a solid when ice melts, and a gas is changed into a liquid when steam condenses. When sugar dissolves, it changes from a solid to a liquid. The platinum wire changes when heated from a silvery, lustrous metal that reflects light to one that emits light; it becomes red-hot or white-hot. But in none of these changes is one substance converted into another substance.

A *chemical change* always produces one or more substances that are different in composition and properties from those that existed before the change. When milk sours, the sugar in the milk is converted into an acid, the properties and composition of which are very different from those of the sugar. Iron rust differs in color, density, hardness, texture or structure, and in many other ways from iron; it contains oxygen as well as iron and is, therefore, a different substance. Chlorine, a poisonous, greenish-yellow gas, and sodium, a soft and very active metal, combine to form a white, crystalline solid called sodium chloride, or salt, which is not poisonous, as ordinarily used, and has none of the marked activity of sodium. Carbon, a black solid, and sulfur, a yellow solid, combine to form carbon disulfide, a colorless and very volatile liquid. In all these and in similar transformations there is a definite and radical change in the properties and composition of the substances involved. Such changes are called chemical changes or *reactions.*

10. States of Matter

Matter exists in three states: *solid*, *liquid*, and *gas*. Some substances can be obtained readily in each of these three states. Water, for example, exists under different conditions as a solid (ice), as vapor (steam), and as a liquid. Common salt, under ordinary conditions, is a white, crystalline solid, but at a temperature of several hundred degrees it melts to form a liquid, and at a still higher temperature it is converted completely into vapor. For some substances one or more physical states may be almost unknown and very difficult to produce. Carbon, for example, is a solid ordinarily, and at extremely high temperatures it can be vaporized, but only under very unusual conditions can it be converted into a liquid.

Changes in the state of a substance are always physical. The change from water to ice does not produce a new substance; only a different form, or physical state, of the same substance results. Such changes are, however, accompanied by changes in the energy content of the substance. When one gram of ice melts, 80 calories of heat are absorbed, and when one gram of water is changed into vapor at the boiling point of water, 539 calories of heat must be absorbed. The transitions in the opposite direction — vapor to liquid and liquid to solid — are accompanied, of course, by the liberation of energy.

11. Compounds

Most substances can be decomposed into

two or more simpler substances, and they can be produced from simpler substances. Substances of this kind are called *compounds*. Each compound is composed of two or more *elements*.

Most compounds can be decomposed by heat, light, an electric current, or by other forms of energy, and some compounds are so unstable that they decompose without the addition of energy of any kind. These unstable compounds, of which explosives are examples, liberate energy during their decomposition. Water, which is relatively a very stable substance, is decomposed by the electric current into two gases, hydrogen and oxygen, when the current is passed through a solution containing a small amount of sulfuric acid. Without the acid, or some substance that will act in a similar manner, the water will not conduct electricity. The silver bromide in a photographic film is decomposed by exposure to the light. When mercuric oxide, a substance bearing the same relation to mercury that iron rust bears to iron, is heated in a test-tube, drops of mercury collect in the upper portions of the tube. The second substance produced by this decomposition is oxygen, an invisible gas, which can be detected by placing a glowing splinter of wood in the upper part of the test-tube while the powder is heated. The oxygen causes the glowing wood to burst into flame.

Water, silver bromide, and mercuric oxide can be produced directly by the combination of the substances that they form when they decompose. Thus, a mixture of hydrogen and oxygen explodes, when ignited, and produces water; silver and bromine combine to form silver bromide; and mercury, when heated in the air, is converted into the red powder, mercuric oxide, because it combines with the oxygen in the air. Some compounds, however, cannot be formed by the recombination of the substances that are formed when they decompose. Such compounds must be made in other ways.

12. Elements

There are some substances that cannot be decomposed by the methods used to decompose compounds, and they cannot be produced by the combination of other substances. These substances are *elements*. We now have knowledge of the existence of ninety-eight elements. The story of their discovery stretches across several centuries of experimental chemistry and extends even up to the present time. Only twelve substances now known as elements were known in 1630, and their recognition as elements came, of course, at a still later date. Strangely enough, only one of these twelve belongs among the twelve most abundant elements of the outer portions of the earth, including the seas and the atmosphere. The twelve elements known in 1630 were zinc, antimony, silver, tin, sulfur, gold, bismuth, nickel, lead, copper, iron, and carbon. The twelve most abundant elements are oxygen, silicon, aluminum, iron, calcium, sodium, hydrogen, potassium, magnesium, titanium, chlorine, and phosphorus (Fig. 5).

13. The Metallic Elements

Most of the well-known and important elements can be classified as *metals* or *nonmetals*. There are, however, certain elements the properties of which represent a sort of middle ground between the properties of the metals and those of the nonmetals. Some of the compounds that these elements form resemble corresponding com-

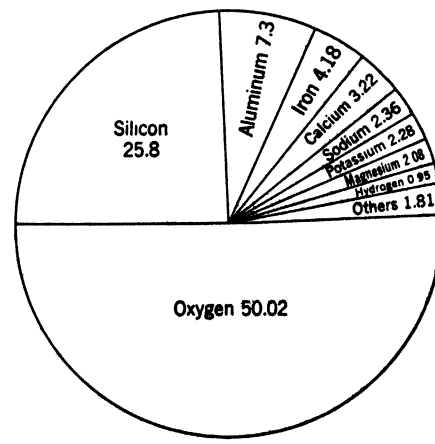


Figure 5. The Occurrence of the Elements in the Earth's Crust

pounds of the metals, and others resemble compounds formed by non-metals.

Each element has, of course, its own set of characteristics, but there are certain general properties usually — but not always — associated with the metals. Physically, they are usually solids, although mercury is a liquid metal at ordinary temperatures. They possess metallic luster when in a compact form. Most metals are white, but gold and copper are yellow and red, respectively. They can be beaten or rolled into sheets, although a few are too brittle. Most metals are denser than water, although lithium, the lightest metal, is only about one-half as heavy as water. Their melting points range from −38.9° C. for mercury to temperatures in excess of 3000° C. Tungsten melts at 3370° C. Some of the metals can be volatilized at moderate temperatures; the boiling point of mercury, for example, is 357°, potassium, 760°, and sodium, 880°. They are good conductors of electricity, as a rule, but there are great differences in the conductivity of different metals. Copper, for example, conducts much better than iron. The metals are also good conductors of heat. Metals with which the student is not likely to be familiar include lithium, potassium, sodium, bismuth, antimony, magnesium, barium, calcium, cadmium, manganese, chromium, cesium, cobalt, iridium, osmium, palladium, molybdenum, tungsten, and several others of less importance.

Chemically, these elements show little tendency to form compounds with one another. They combine more readily with the non-metals; thus, they combine, usually directly, with oxygen to form *oxides*, with chlorine to form *chlorides*, and with sulfur to form *sulfides*. The metals differ greatly, however, in the activity that they display in forming compounds with these elements. Some of the most active metals are sodium, potassium, calcium, and magnesium. These metals are not found in nature in their free states, because there are many opportunities for an active metal to combine with the oxygen of the air or to react with water and with other substances.

With a few exceptions, all of the metals that we have named occur in nature only in compounds such as oxides, sulfides, and chlorides. Iron, for example, is not found as pure iron. It occurs chiefly in ores composed of the oxide, from which metallic iron is produced by causing the oxygen in the ore to combine with some other element, such as carbon. Iron slowly changes back to the oxide by rusting. A few metals are found in the free state. Their activity is so slight that they may lie in the earth for ages without undergoing chemical change. The most familiar inactive metals are copper, gold, silver, and platinum.

14. The Non-Metallic Elements

Some of the non-metals are solids, and some of them, such as iodine, possess a luster. Sulfur and carbon are well-known solid elements, and along with them we may name boron, silicon, phosphorus, arsenic, selenium, and tellurium. Other non-metals are gases: hydrogen, oxygen, chlorine, fluorine, and nitrogen. The elements helium, neon, argon, krypton, xenon, and radon, because of their chemical inactivity, are called the *inert gases*. Bromine is a non-metal which is liquid at ordinary temperatures.

Some of the non-metals combine readily with one another. Thus, oxygen combines with carbon, sulfur, and phosphorus, when these elements burn. Chlorine, nitrogen, carbon, fluorine, sulfur, bromine, silicon, and iodine are also often found in compounds with other non-metals. Thus, we may have a carbide of silicon, a sulfide of phosphorus, and a chloride of carbon. On the whole, however, the non-metals combine more readily with the more active metals than with one another. These combinations result in the formation of chlorides, iodides, bromides, nitrides, carbides, sulfides, and

fluorides of the metals. The most active of the non-metals is fluorine, which reacts readily with almost all other elements and many compounds.

15. The Definite Composition of Compounds

A mixture of iron and sulfur can have any composition; they can be mixed in any proportion. But in the compound that results when the mixture is heated, the ratio of the weights of iron and sulfur is always the same: Iron, 63.6 per cent, and sulfur, 36.4 per cent. Common table salt always contains 39.3 per cent of sodium and 60.7 per cent of chlorine, regardless of its source. Salt from the ocean, from the Great Salt Lake, from the Dead Sea, from a salt deposit deep down in the earth, or from a laboratory preparation, all possess the same composition. *A compound always contains the same elements, and the ratio (by weight) in which these elements are combined in the same compound is always the same.* This is the Law of Definite Composition. It is one of the fundamental principles of chemistry.

16. Names of Elements and Compounds

A complete list of the names of the elements is given on the inside of the front cover of this book. Here, too, will be found the *symbols* of the elements. These are the abbreviations of the English, Latin or, in a few instances, German names. Thus, the symbol for iron is Fe, the abbreviation of the Latin name, *ferrum.* Any abbreviation of iron — I, Ir, In, etc. — would lead to confusion with the symbols for iodine, iridium, indium, etc.

We shall refer at this time to the names of only some of the simplest compounds. If the compound is composed of two elements, one of which is a metal and the other a non-metal, its name includes the name of the metal and a word built upon one or more syllables of the name of the non-metal and ending with *-ide.* Thus, compounds of oxygen with the metals are called *oxides*; of chlorine, *chlorides*; of sulfur, *sulfides*; and of nitrogen, *nitrides.* The metal magnesium, for example, forms magnesium oxide, chloride, sulfide, and nitride when it combines with oxygen, chlorine, sulfur, and nitrogen. If the metal reacts with the same non-metal to form two compounds, the name of the metal is modified by adding the ending *-ous* or *-ic.* Thus, mercury forms two chlorides and two oxides. These are called mercurous chloride and mercuric chloride, and mercurous oxide and mercuric oxide. The *-ic* ending is used to designate the compound in which there is more chlorine or oxygen for the same quantity of mercury. Sometimes the Latin, instead of the English, name of the metal is used in referring to the name of the compound. For example, iron forms two chlorides which are called *ferrous* and *ferric* chlorides, instead of ironous and ironic.

Many compounds contain a metal and two non-metals, one of which is usually oxygen, and the other is carbon, sulfur, nitrogen, phosphorus, or some other non-metal. Using sodium as the metal, we can show how such compounds are named by the following examples: *Sodium carbonate, sodium sulfate, sodium nitrate,* and *sodium phosphate.* Instead of the ending *-ate,* the ending *-ite* is used, if there are two compounds composed of the same three elements, to indicate the compound containing the smaller, relative quantity of oxygen. Thus, we have *sodium sulfite, sodium nitrite,* and *sodium phosphite.*

Many compounds also have other names that may be in more common usage than the names that chemists use. Thus, in commercial practice and in everyday uses, sodium chloride is called *salt,* calcium oxide is called *lime,* and sodium carbonate is called *soda ash, sal soda,* or *washing soda.* Some substances also have names that depend upon their properties, and the names may indicate the general group to which the substances belong. Thus, hydrogen chloride, especially when it is dissolved in water, is called *hydrochloric acid.*

CHEMICAL CHANGES OR REACTIONS

17. Examples of Different Types of Reactions

Most chemical changes, or reactions, can be classified according to the four types described below.

(1) *Combination.* Many compounds are produced by the direct combination of elements. Iron and sulfur combine to form ferrous sulfide; magnesium combines with oxygen from the air, when it burns, to form magnesium oxide; hydrogen and oxygen form water, when a mixture of the two is exploded. Many compounds are also produced by the combination of one *compound* with another compound or with an element. Thus, quicklime, which is the oxide of calcium, reacts with water to form "slaked lime," or calcium hydroxide.

(2) *Decomposition.* Most compounds can be decomposed into simpler compounds or into their constituent elements. For examples of this kind of chemical change see Section 11, page 14.

(3) *Replacement.* This is a type of chemical change in which one substance displaces another from a compound. When a piece of iron is placed in a solution containing cupric (copper) sulfate, iron is converted into ferrous (iron) sulfate, which is soluble; thus, iron displaces copper, which is then deposited from the solution as the metal.

(4) *Double Decomposition.* Some compounds, when brought together, change into different substances by a process called *double decomposition.* This change usually occurs in solution. Silver nitrate and sodium chloride, when placed in the same solution, form sodium nitrate and silver chloride by double decomposition. Because the corresponding parts of the two compounds exchange places, a reaction of this kind is frequently spoken of as an *exchange reaction.*

Silver Nitrate + Sodium Chloride ⟶ Sodium Nitrate + Silver Chloride.

The silver chloride is not very soluble in water; hence, the quantity formed in excess of that which will dissolve (this amount is only 0.00016 g. in 100 ml. of water at 18° C.) is thrown out of solution. We say that silver chloride, or any other slightly soluble substance that is formed by mixing soluble substances in a solution, is *precipitated.* The sodium nitrate, which is formed at the same time that silver chloride is precipitated, remains in solution, since it is readily soluble. The solid silver chloride is removed by *filtering* the mixture through a sheet of filter paper. When the *filtrate* is evaporated to remove most of the water, crystals of sodium nitrate form as the solution cools.

REVIEW EXERCISES

1. How could you show that a solution of sugar in water is a mixture and not a pure substance?
2. How could you show that "tap" water is not pure water?
3. What are some of the most important physical properties of gold? of salt? of water?
4. How is a chemical change different from a physical change? Give five examples of each.
5. Define: Element and compound.
6. What are some of the physical properties generally possessed by the metallic elements?
7. A mixture containing 100 g. of finely divided iron and 75 g. of sulfur is heated. Which element and what weight of it will remain unused when the reaction is complete?
8. Why is the same weight of ash not left when 10 g. samples of different grades of coal are burned?
9. The following weights of the constituent elements are combined in a sample of sulfuric acid: Hydrogen, 1.5 g., sulfur, 24 g., and oxygen, 48 g. Calculate the percentage of each element in the compound.
10. To what class of chemical change does each of the following reactions belong?
    (*a*) Hydrogen + Chlorine → Hydrogen Chloride.

(*b*) Hydrogen Chloride + Magnesium → Magnesium Chloride + Hydrogen.
(*c*) Sodium Sulfide + Hydrogen Chloride → Hydrogen Sulfide + Sodium Chloride.
(*d*) Hydrogen Sulfide → Hydrogen + Sulfur.

11. Classify the following materials as elements, compounds, or mixtures: Aluminum, egg, paint, blood, sulfuric acid, ink, europium, mercuric oxide.
12. How do the terms *mass* and *weight* differ in meaning?
13. What kind of energy is possessed by a compressed, or tightly coiled, spring? by a lump of coal? by live steam? by a moving locomotive? by water behind a dam?
14. Upon what factors does the kinetic energy of a body depend?
15. State the law that applies to the conservation of energy and then show how the law applies to an example of your own selection.
16. What weight of hydrogen can be produced by the decomposition of 100 g. of water if water contains 11.19 per cent of hydrogen?
17. Define *calorie*. How much heat, approximately, is required to raise the temperature of 10 g. of water from its freezing point to its boiling point?
18. What types of chemical changes are represented in the following series of reactions? (1) Iron and sulfur when heated form a compound. (2) When this compound is treated with a solution of hydrogen chloride, a gas is formed. (3) When this gas is heated, in the absence of air to prevent its combustion, sulfur is deposited, and hydrogen is liberated and escapes.
19. Iron is attracted by a magnet. Hence, the sulfide of iron must also be attracted by a magnet, because iron is one of the elements that compose it. Is this statement true?
20. What elements compose the following compounds: Lead bromide, potassium chlorate, calcium arsenite, mercuric iodide, sulfur dioxide, sodium silicate?
21. How can a substance that is slightly soluble be separated by a substance that is very soluble?
22. How does a compound of two elements differ from a mixture of the same elements?
23. How does a change in the physical state of a substance differ from a chemical change in which the same substance is involved?

REFERENCES FOR FURTHER READING

Dampier-Whetham, W. C., *A History of Science*. New York: The Macmillan Company, 1929.
Findlay, A., *The Spirit of Chemistry*. New York: Longmans, Green and Company, 1930.
Findlay, A., *A Hundred Years of Chemistry*, 2nd ed. New York: The Macmillan Company, 1948.
Foster, W., *The Romance of Chemistry*.
J. Chem. Ed., **10,** 227 (1933).
Moore, F. J., *History of Chemistry*, 3d ed. New York: McGraw-Hill Book Company, 1939.
Nechaev, I., *Chemical Elements*, translated by B. Kinkead. New York: Howard-McCann, Inc., 1942.
Taylor, F. Sherwood, *The Alchemists*. New York: Henry Schuman, 1949.
Weeks, M. E., *The Discovery of the Elements*, 5th ed. Easton, Penna.: Chemical Education Publications, 1944.

2

PARTICLES OF MATTER

ATOMS AND MOLECULES

1. Introduction

As soon as some of the physical and chemical characteristics of different forms of matter were known, interest was aroused in the structures of these forms and especially in the differences in structure that would explain the behavior and properties of different substances. For example, what differences in structure make iron a metal and sulfur a non-metal? Why is oxygen, under ordinary conditions, a gas while carbon is a solid? Such questions cannot always be answered easily, but many of the behaviors, or actions, of substances that were first observed were rather simple and called for simple explanations, or at least they would appear to be simple to the student of science today. Air is a mixture of several gaseous substances, but these substances do not settle out into layers. How is this possible? Why do these substances remain mixed? And how can all of these gases occupy the same space at the same time?

Such questions as these led to others that were more fundamental. Does the matter of which a body is composed occupy all the space within the body? Or is this matter composed of particles with some empty space among them? In other words, is the matter of a body "all in one piece," and can it be divided indefinitely into smaller and smaller portions, with each portion always retaining the composition and properties of the original body? Or is it possible to attain, finally, particles that cannot be divided further without destroying the identity of the form of matter with which we started?

From the beginning and down through the history of chemistry and physics the preponderance of evidence has been on the side of the "particle," or corpuscular, theory of the structure of matter. Modern chemistry and most of its accomplishments have been made possible by the acceptance of this explanation of the nature of matter and by its use as a guide in the study of substances, their uses, and the ways in which they can be produced. According to this theory there is for every substance an ultimate particle, called the molecule, which is the smallest particle of a substance that can exist alone and which, if further divided, produces particles of other substances.

2. Atoms and Molecules

The smallest portion of *either an element or a compound* that can exist alone is a molecule. As we study the composition of compounds, however, we soon reach the conclusion that the smallest particle of an ele-

ment found in a molecule of a compound of that element *is not a molecule of the element;* it is not the same as the smallest particle of the element that can exist alone. And, hence, we find that there is need to define a particle of an element which is smaller than the molecule. This particle we call an *atom.*

To summarize we may define atoms and molecules as follows: *Atoms are the smallest portions, or particles, of elements that combine to form compounds. Molecules are the smallest particles of any substance — element or compound — that can exist alone and which have the characteristic composition and properties of the substance.* We cannot say, of course, that a single molecule of a substance has all the properties that a relatively large mass of the substance possesses. It would be absurd, for example, to speak of the boiling point of a single molecule. However, the essential chemical character — its possible reactions and the substances that can be made from it — is the same for one molecule and for a pound of a substance.

The chemist, therefore, speaks of *atoms of oxygen* when he refers to the particles of oxygen that *react* with hydrogen to form water, or with carbon to form carbon dioxide, or with any other element to form an oxide of that element. The smallest particles of free oxygen — of the oxygen in the air around us, for example — are spoken of as *molecules of oxygen.*

Some compounds are not composed of molecules. Certain crystalline compounds, for example, are made up of two separate electrically charged atoms or groups of atoms arranged in definite crystalline patterns. In these compounds the component particles (atoms or atom-groups) are not combined in pairs or otherwise, and, although they do exist as more or less independent particles, they are definitely located in the crystal with reference to other particles. We may, therefore, in a certain sense regard the whole crystal as one "giant" molecule.

3. Evidence Supporting the Atomic-Molecular Theory

There are many facts that support the view which we have just presented, namely that all substances are composed of particles, to which we have assigned the names atoms and molecules. Some of the supporting evidence has required long, tedious, and rather complicated investigations, and to some of these studies and their results we shall shortly turn our attention. There are, however, many observations that all of us have made many times and which lead inevitably, if we consider the probable causes of the effects we observe, to the conclusion that different forms of matter must be composed of particles. Let us recall a few of these observations.

The flow of liquids suggests that they are composed of particles, which can move with respect to one another in somewhat the same fashion that particles of sand slip and slide over and around one another when they are poured out of a vessel. The fact that metals can be bent and can be beaten into thin sheets can be explained in a similar manner. The tendency of one gas to pass into the space occupied by another can be explained if we assume that both gases are composed of particles, and that neither gas occupies all the space. If all the gases which make up the mixture that we call air are composed of particles, and if these particles are moving, the motion of the particles will tend to keep them mixed and will prevent the separation of the different substances into layers. In a similar manner, we can explain a solution of sugar in water as a mixture of the particles of these two substances. If we should assume, instead, that they are each "all in one piece," the formation of a solution would be difficult, indeed, to explain. The compressibility of gases can also be explained by assuming that they are composed of particles that are crowded closer together by pressure. The evaporation of a

liquid would be difficult to explain if the substance were continuous — if it were all "in one piece." The liquid evaporates a little at a time. If it were continuous in character, we might expect all of it to pass into the vapor state at the same time. If, on the other hand, the liquid is made up of particles which are more or less independent, the more rapidly moving ones that strike the surface may pass through, while those traveling more slowly remain behind.

4. The Early History of the Atomic Theory

The notion that matter is atomic, or discontinuous, can be traced back as far as 1000 B.C. Some of the Greek philosophers favored the atomic concept, and one of them, Democritus, is sometimes credited with the first atomic theory. He believed that there are as many kinds of atoms as there are varieties of matter, and he made no distinction, therefore, between the particles of elements, of compounds, and even of mixtures. He called all of these atoms; there were atoms of wood, stone, water, iron, gold, blood, flesh, bone, air, earth, and the soul. The atoms of Democritus, therefore, were not very much like the atoms with which chemistry deals today.

On the other hand, Aristotle, and certain others of the Greek philosophers, thought of bodies as combinations of a fundamental substance, called *hyle*, and certain *qualities* such as wetness, dryness, cold, and heat. Atoms played no part in their explanations of the nature and behavior of matter. Because of the great influence of Aristotle and the widespread practice of alchemy, which was founded in part upon his teachings, the atomic theory was abandoned for at least the first fifteen centuries of the Christian era. During this period, the study of matter, along with all other scientific studies, failed to make any important advances. Instead of observing facts as they are revealed in nature and by experiment, the alchemists were devoted to beliefs based upon superstition, fraud, magic, and ideas of the supernatural.

The atomic concept was revived at the time of the Renaissance. Robert Boyle and Isaac Newton were particularly prominent in bringing about this revival. But it was not until the early years of the nineteenth century that a generally acceptable and soundly substantiated atomic theory made its appearance. The man who contributed most to the establishment of this theory was John Dalton.

5. Dalton's Atomic Theory

Dalton's theory, which he outlined during the period of 1802–1808, is summarized below. We have changed and added to his original statements in some instances to make the theory agree with our present knowledge. Our summary, in a certain sense, is, therefore, Dalton's theory brought partially up-to-date.

(1) Every substance, whether element or compound, consists of ultimate particles. Dalton called all these particles atoms, from a Greek word meaning *undivided*, but, as now used, atoms (page 20) refer only to the smallest particles of elements that react to form compounds, and we shall so use the term in all of our discussion.

(2) The atoms of any one element are identical in weight and in other characteristics.

(3) Atoms cannot be divided, created, or destroyed; they are permanent, unchanging bodies.

(4) The molecules (Dalton called these, also, atoms) of a compound are produced when atoms of two or more elements combine.

(5) Atoms of elements combine in simple numerical ratios, such as one to two, or two to three, or one to one, and for any one compound this ratio is always the same.

(6) The atoms of two elements may combine in different ratios to form more than one compound. Thus, one atom of

element A may combine with one atom of element B to form a molecule of the substance AB; if one atom of A combines with two atoms of B, a molecule of the compound AB_2 is formed.

(7) Dalton also believed that the *most stable and the most abundant compound* of two elements consisted of particles that contained *one atom of each of the two elements*. This opinion was not based upon facts, and later evidence proved that it was completely unreliable.

In the absence of adequate information upon which to determine the relative numbers of atoms of each of two elements that combine to make a definite compound, Dalton made a reasonable, but erroneous, assumption. He thought it reasonable to assume that the compound most likely to result from the combination of two kinds of atoms would be the one formed when the atoms combined in the ratio of one to one.

THE CHEMICAL EVIDENCE UPON WHICH DALTON'S THEORY WAS FOUNDED

Let us now turn our attention to certain experimental evidence that Dalton used in developing the different concepts of the atomic theory as we have stated them above. Here we have an excellent example of the use of the scientific method (page 4).

6. The Atomic Theory and the Laws of Chemical Change

During the late years of the seventeenth and the first few years of the eighteenth centuries, considerable information was obtained experimentally concerning the composition of compounds and concerning the relative weights of different substances that react in a few rather simple kinds of chemical changes, such as the combination of elements to form compounds. The careful review and analysis of the facts thus obtained led to certain general conclusions concerning elements, compounds, and the chemical changes in which they are involved. These conclusions came to be considered as laws, or general principles, because it was evident that they were applicable, each in its own way, to all substances and to all reactions. After the laws had been recognized and were generally accepted, chemists began to wonder why elements and compounds behaved in accordance with these laws rather than in other ways. What physical characteristics of structure and composition caused elements and compounds to act as these laws showed quite clearly they did act? When we go beyond the laws and the experimental evidence upon which they are founded, and seek explanations of them, we are building theories. Dalton's theory of atoms was built in this way, as we shall see in the paragraphs that follow.

7. The Law of the Conservation of Mass

In 1785, Lavoisier proved that *the sum of the weights of all the substances that enter a chemical reaction is equal to the weight of all the substances produced by the reaction.*

This statement is true, within the limits of accuracy of our methods of measuring mass, for ordinary chemical processes that occur in nature or in the laboratory. In certain unusual processes that we shall discuss later some energy is converted into matter, and in others matter is converted into energy.

This is called the Law of the Conservation of Mass. Lavoisier established this law by experiments in which he weighed as accurately as possible the substances involved in chemical changes, such as combustion. He found that mercury, for example, could be made to combine with a certain portion of air to form the red powder now known as mercuric oxide. When this powder was heated, it decomposed to give the same weight of mercury that originally had been consumed in producing the red powder. There was no change in the total weight during the formation and decomposition of the compound. We now know

that the substance in the air that changes mercury into a red powder is the element oxygen. In fact, it was Lavoisier, himself, who first recognized the existence of this element and gave it a name. The weight of oxygen liberated in the decomposition of the red powder was found, also, to be equal to the weight of air originally consumed when the compound of mercury and oxygen was produced.

8. The Relation of the Law of the Conservation of Mass to the Atomic Theory

How does this law support Dalton's concepts of atoms? In all the changes in which different forms of matter are involved, matter itself is permanent, and its quantity is unchanging. We can carry one gram of iron, for example, through a hundred chemical changes, first forming a compound of iron, then decomposing this compound and using the liberated iron to form another, and so on through one reaction after another. At the end, unless there are losses in handling some of the materials, there will be the same weight of iron as in the beginning.

What is the explanation? Perhaps, the elements *are* composed of particles which we may call atoms if we like. Let us assume, also, that the change of one form of matter into another consists only of grouping different atoms to make certain patterns, or arrangements, or in separating the atoms of such groups and rearranging them to make new patterns.

Since there is no change in mass when elements combine, or when compounds are decomposed, atoms must be unchanging in the mass that they contain. If they lost or gained mass during a chemical change, or if some of the atoms were destroyed or consumed in some manner, or if more were created, the total quantity of matter — the mass of the reacting system of substances — could not remain unchanged during a reaction. Reasoning in this manner, Dalton decided (part 3 of this theory, page 21) that atoms cannot be "divided, created, or destroyed."

9. The Law of Definite Proportions

The composition of a compound is definite. It follows, therefore, that the weights of the elements that combine to form a certain compound are always in the same ratio, or proportion. If, for example, 1 g. of A reacts with 2 g. of B to make a certain compound of A and B, then the weights of A and B that react to form *any amount* of the same compound are always in the ratio of 1 to 2. Thus, 4 g. of A reacts with 8 g. of B, 40 tons of A with 80 tons of B, 3 g. of A with 6 g. of B, and so on.

Let us consider a few actual examples of the ratios of the weights of different elements in their compounds.

(1) Iron and sulfur always combine in the ratio of 63.6 per cent of iron to 36.4 per cent of sulfur to form ferrous sulfide.

(2) Magnesium oxide contains 60.3 per cent of magnesium and 39 per cent of oxygen.

(3) Whenever water is produced from its elements, the ratio of the weights of the hydrogen and oxygen that produce it are in the ratio of 1.008 to 8. The weight of water produced is always in the ratio of 9.008 to 1.008 to the weight of hydrogen, and in the ratio of 9.008 to 8 to the weight of oxygen, from which it is made.

The examples cited above indicate the kinds of experimental results that led to the establishment of the Law of Definite Proportions: *The proportions by weight of the substances involved in a specific chemical change are definite.* This law applies to the weights of different elements and compounds that react with each other and to the weights of the products of all kinds of reactions as compared to the weights of any or all of the substances from which they are made.

This law does not exclude the possibility that two elements can combine in more than one proportion by weight. If they do

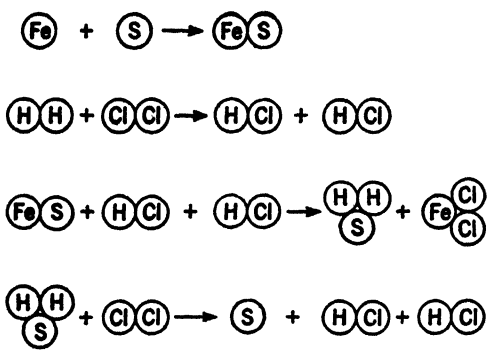


Figure 6. The Law of Conservation of Mass and the Law of Definite Proportions

The atoms of iron, sulfur, hydrogen, and chlorine are permanent and the number of each is unchanged in the reaction. All that happens is a rearrangement of the atoms to form new compounds. All of the atoms of iron are identical. So, too, are the atoms of sulfur, hydrogen, and chlorine. Furthermore, the same atoms always combine in the same ratio to make the same compounds. These statements being true, it is easy to see that the weights of iron sulfide and hydrogen chloride that react to produce iron chloride and hydrogen sulfide will always be in the same ratio to each other. We see, too, that the weight of iron chloride produced from a certain weight of iron sulfide, e.g. 1 g., will always be the same.

combine in different proportions, different compounds are produced.

10. The Law of Definite Proportions and the Atomic Theory

How did this law aid Dalton? Assuming that elements are composed of atoms, he was forced to the conclusion that all the atoms of any one element have the same weight. If this were not true, the weight of hydrogen that combines with 8 g. of oxygen would not always be 1.008 g., but it would vary, depending upon whether lighter or heavier atoms of hydrogen were used. For the same reason the ratio of the weights of hydrogen and oxygen would vary unless all oxygen atoms had the same weight.[1]

[1] There was one other possibility that Dalton could not foresee in his day. All the oxygen atoms need not have the same weight, if the different varieties are mixed always in the same proportions. The *average* weight of the atoms of oxygen would be constant, and the weight of oxygen that combined with a fixed weight of hydrogen would, also, always be the same weight. As we shall show later, we now know that this is the condition that actually exists.

The atoms of an element must, thought Dalton, also be identical in all other ways, because, if they were not, the properties of the compound that they form with atoms of another element would vary as different atoms of different characteristics were used to make the compound. This law was responsible, therefore, for Part 2 of Dalton's theory (page 21).

11. The Combining Proportions of the Elements

The next law that we shall discuss concerns the weights of different elements that combine with one another to form compounds. For example, is there any relation between (1) the weights of carbon and nitrogen that combine with the same weight of oxygen and (2) the weights of carbon and nitrogen that combine with each other?

To answer this question we must first decide upon some definite, or fixed, weight of oxygen to be used in the study. Let us select 16 g. of oxygen as this fixed weight.

In one of the oxides of carbon there are 12 g. of carbon for 16 g. of oxygen, and in one of the oxides of nitrogen for every 16 g. of oxygen there are 14 g. of nitrogen. When we examine the compounds of carbon and nitrogen we find some in which the weights of carbon and nitrogen are in the ratio of 12 to 14. In such compounds the weight of the two elements that combine with 16 g. of oxygen are the same weights that combine with each other!

But we must not forget that there are many compounds containing two or all three of these elements — and, perhaps, other elements as well. There is another oxide of carbon in which 6 g. of carbon are combined with 16 g. of oxygen. In another compound there are 24 g. of carbon for 16 g. of oxygen (hydrogen is also present). In all such compounds we find that the combining proportions of the two elements can be expressed by using 12 or a multiple of

12 g. of carbon and 16 or a multiple of 16 g. of oxygen. Thus, $\frac{24}{16}$ is the same ratio as $\frac{2 \times 12}{1 \times 16}$. Likewise if 3 g. of carbon is found combined with 12 g. of oxygen the combining proportion can be expressed (multiplying each quantity by 4) as $\frac{12}{48}$, or $\frac{1 \times 12}{3 \times 16}$, and so on.

In all the compounds containing nitrogen and oxygen the combining proportions of the two elements can be expressed as the ratio of 14 or some multiple of 14 g. of nitrogen to 16 or some multiple of 16 g. of oxygen. Thus in the five oxides of nitrogen the combining proportions are:

Nitrogen	Oxygen	Weight of nitrogen combined with 16 g. of oxygen
2×14	16	28
14	16	14
2×14	3×16	$9\frac{1}{3}$
14	2×16	7
2×14	5×16	$5\frac{3}{5}$

In all the compounds containing carbon and nitrogen the combining proportions of the two elements can be expressed as the ratio of 12 or a multiple of 12 g. of carbon to 14 or a multiple of 14 g. of nitrogen. Thus, we might find the proportions in certain compounds to be 12 to 14; 2×12 to 14; 2×12 to 3×14; and so on.

In short, the proportion, or ratio, of the weights of carbon and nitrogen in their compounds can be expressed by using the same numbers as are used in expressing the ratios of their weights to 16, or some multiple of 16, parts by weight of oxygen in the compounds that each of them forms with oxygen.

12. The Law of Combining Proportions

If we should investigate the compounds of all the elements, as we have studied those of carbon, nitrogen, and oxygen, we would find the following general principle to be true: *In all their compounds the combining proportions by weight of the elements can be represented as ratios of experimentally determined numbers, one number for each element, or by small integral (whole number) multiples or sub-multiples of these numbers.* Thus, in any compound containing carbon and oxygen, as we have shown previously, the ratio

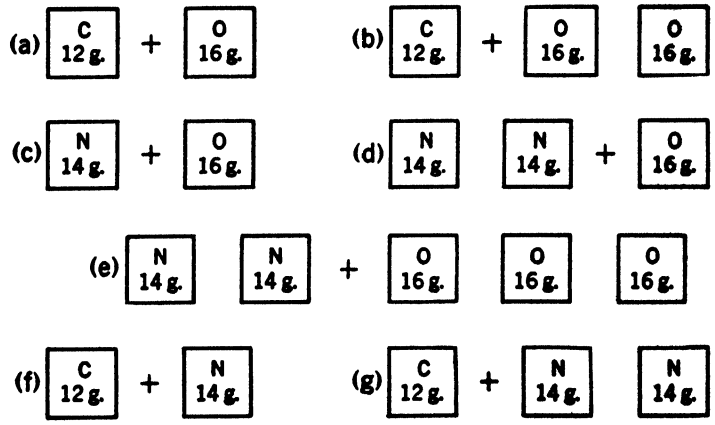


Figure 7. The Law of Combining Proportions

A few examples are shown to indicate that the ratio of the weights of carbon and nitrogen that combine, also the weights of carbon and oxygen and of nitrogen and oxygen, can be expressed by using one number for each element in all its compounds. If the weights of carbon, nitrogen, and oxygen atoms are in the proportion of 12, 14, and 16, respectively, then any weights of these elements that react will be in the ratio of 12 to 16, 14 to 16, 12 to 14, or in the ratio of multiples of these numbers, depending upon the relative numbers of atoms of each element that combine.

of the weights of the two elements may be expressed as:

$$\frac{\text{12, or a multiple of 12, parts of carbon}}{\text{16, or a multiple of 16, parts of oxygen}}$$

As the result of the analysis of any one compound of an element, it may be impossible to determine the number to be used in stating the combining proportions of that element, but after several of the compounds containing the element have been analysed it should be fairly easy to select the number to be used. Thus, we might find that the weights of carbon and oxygen in different compounds are in the following ratios:

$$\frac{\text{Weight of carbon}}{\text{Weight of oxygen}} = \frac{24}{32}, \frac{6}{4}, \frac{2.4}{3.2}, \frac{3}{8}, \text{ and } \frac{2}{2\frac{2}{3}}$$

The numbers 12 and 16 do not appear in these ratios, but each ratio can be written without changing its value as a ratio of 12 to 16, as a ratio of a multiple of 12 to 16, or as a ratio of a multiple of 12 to a multiple of 16. Thus,

$$\frac{24}{32} = \frac{12}{16}; \frac{6}{4} = \frac{24}{16} = \frac{2 \times 12}{16}; \frac{2.4}{3.2} = \frac{12}{16};$$

$$\frac{3}{8} = \frac{12}{32} = \frac{12}{2 \times 16}; \text{ and } \frac{2}{2\frac{2}{3}} = \frac{12}{16}$$

13. Relation of the Law of Combining Proportions to the Atomic Theory

How shall we explain this law? Certainly, one conclusion is very clearly indicated, namely that in forming compounds the elements act as if they are composed of definite units, or — to draw a rather crude analogy — as if they "are put up in packages," and that a definite number of "packages" of one element combines with a definite number of another, e.g., one with one, one with two, or two with three. The "packages" of one element weigh the same, but those of different elements have different weights. In short, the law strongly suggests that the elements are composed of particles — atoms if we wish to give them that name.

Let us assume, then, that in forming compounds a certain number of atoms of one element combines with a certain number of atoms of another. Let us represent the weight of an atom of oxygen by the number 16. Let us also assume that the weight of an atom of carbon is $\frac{12}{16}$ that of the oxygen atom; i.e., as compared to 16 for the weight of an atom of oxygen, the weight of a carbon atom can be represented by the number 12. The number 12 is selected for carbon because it is the number that has been found experimentally (page 25) as the correct number to use in expressing the combining proportions of carbon with other elements in accordance with the Law of Combining Proportions.

We arrive, therefore, at the conclusion that, when the weights of carbon and oxygen in a compound are in the ratio of 12 to 16, equal numbers of atoms of the two elements combine, i.e., one atom of one for each atom of the other. If the ratio is 24 to 16, then two atoms of carbon are combined with one of oxygen, and for compounds in which the ratio is 24 to 48, there are two atoms of carbon for three of oxygen.

Let us consider the five compounds of nitrogen and oxygen. We shall assume that the weight of the atom of nitrogen can be represented by the number 14 as compared to the number 16 for the weight of an atom of oxygen. The relative numbers of atoms of the two elements in the five compounds can then be expressed as follows:

Ratio of Weights of Nitrogen and Oxygen in Grams			Number of Atoms Combining
2×14	to	16	2 atoms + 1 atom
14	to	16	1 atom + 1 atom
2×14	to	3×16	2 atoms + 3 atoms
14	to	2×16	1 atom + 2 atoms
2×14	to	5×16	2 atoms + 5 atoms

14. The Law of Multiple Proportions

Many pairs of elements form two or more compounds in which, of course, the ratios of the weights of the elements are

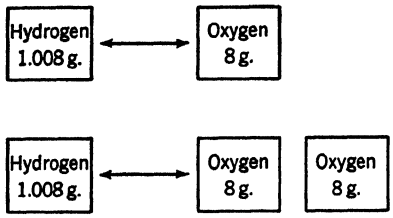


Figure 8. The Law of Multiple Proportions as Illustrated by Water and Hydrogen Peroxide

different. In the two oxides of carbon we find that the weights of carbon that combine with 16 g. of oxygen are 12 g. and 6 g., respectively. These weights of carbon are in the ratio of 2 to 1. Such observations as this led John Dalton, in 1804, to formulate the Law of Multiple Proportions: *If two elements form more than one compound, the weights of one that combine with a fixed weight of the other can be represented by a ratio of whole (usually small) numbers.* For example, the ratio of the weights of the element *A* which combine with the same weight of element *B* to form two compounds is a ratio of two small numbers, such as 1 to 2 or 2 to 3, or if more than two compounds are formed, the weights of *A* are related in the same manner as small whole numbers, such as 1, 2, 3, 4, 5. Let us take 14 g. of *nitrogen as the fixed weight* and *compare the weights of oxygen* that combine with it in the five oxides.

	Weight in Grams of	
	Nitrogen	Oxygen
(Nitrous Oxide)	14	8
(Nitric Oxide)	14	16
(Nitrogen Trioxide)	14	24
(Nitrogen Dioxide)	14	32
(Nitrogen Pentoxide)	14	40

The different weights of oxygen are thus shown to be equal to 1, 2, 3, 4, and 5 times 8.

15. The Law of Multiple Proportions and the Atomic Theory

If the different weights of oxygen combined, in different compounds, with a fixed weight of nitrogen are in the same proportion to one another as the numbers 1, 2, 3, 4, and 5, a reasonable explanation is that twice as many atoms of oxygen combine with a certain number of atoms of nitrogen in the second compound as in the first, three times as many in the third, four times as many in the fourth, and five times as many in the fifth. In water and hydrogen peroxide, 8 g. and 16 g., respectively, of oxygen are combined with 1.008 g. of hydrogen. Since the weight of hydrogen is the same,

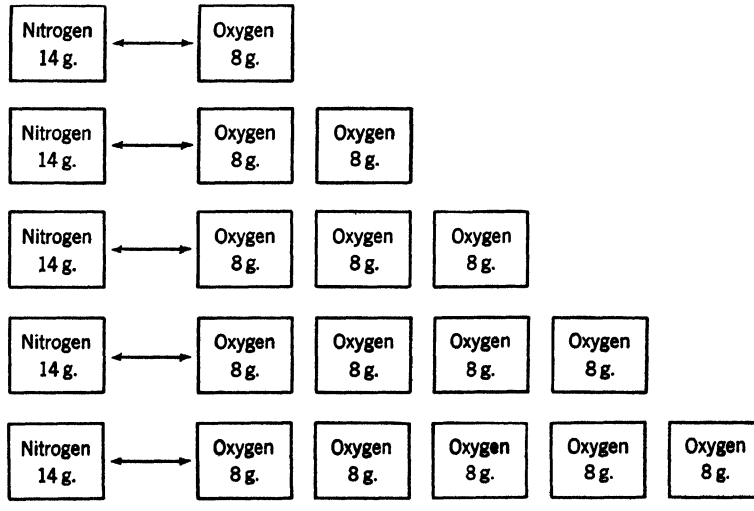


Figure 9. The Law of Multiple Proportions as Applied to the Five Compounds of Nitrogen and Oxygen

the number of atoms of this element is the same in both instances if all hydrogen atoms have the same weight, but there must be twice as many atoms of oxygen in 16 g. as in 8 g. Hence, the facts are satisfactorily explained if we assume that twice as many atoms of oxygen combine with a given number of hydrogen atoms in hydrogen peroxide as in water. We could also assume that, for the same number of atoms of oxygen, there are twice as many hydrogen atoms in water as in hydrogen peroxide.

This law suggested to Dalton Part 6 (page 21) of the atomic theory.

16. Atomic Weights

Single atoms cannot be weighed, because they are too small. The chemist, however, has methods that can be used to determine the relative weights of different atoms as compared to the weight of the atom of one element. Thus, as we have previously suggested (page 26), the weight of the atom of oxygen may be represented by the number 16, thus establishing a scale on which different numbers represent the weights of different atoms, not the absolute weights, but the relative weights of atoms as compared with 16 for the weight of the oxygen atom. These numbers are called the *atomic weights* of the elements.

The atomic weight of an element may, therefore, be defined as *a number that represents the weight of an atom of the element as compared with 16, which is arbitrarily selected as the number to represent the weight of an atom of oxygen.*

17. The Scale of Atomic Weights

To explain the scale of atomic weights, and the use of 16 as the number representing the atomic weight of oxygen, let us consider a similar scale based upon a similar standard. If we wish to compare the weights of a large number of persons, we might select one person whose weight, regardless of the number of pounds, might be indicated simply by the number 16. Now on this scale, the weight of a second person, who is twice as heavy as the first, would be represented by the number 32; the weight of another who is $\frac{1}{16}\frac{2}{}$, or $\frac{3}{4}$, as heavy would be represented by 12; and so on. Our scale of atomic weights is such a scale; the number assigned to represent the weight of the oxygen atom is 16; it serves the same purpose as the number 16 in the scale of weights of different persons.

It must be understood, of course, that the selection of 16 for oxygen as the basis of atomic weights is purely arbitrary. We might have selected *any* element and *any* number to represent the weight of one of its atoms. The selection made is justified only by its *convenience.* First, oxygen is a convenient element for the comparison of atomic weights because it combines readily with many elements, and its compounds are easily studied. In the second place, 16 is a convenient number, because upon this basis the atomic weights of all the other elements are neither very small nor very large. The atomic weight of hydrogen, the lightest, is greater than one, and the atomic weight of the heaviest, is about 240. In the third place, the atomic weights of many of the elements turn out on this scale to be whole numbers or very nearly whole numbers.

Dalton's atomic weights for many of the elements were not those that we accept today. He assumed that the compound of two elements that was most stable and was most abundant in nature, and was, perhaps, most easily produced from its elements, must contain the atoms of these elements in equal numbers. It must have appeared logical to him that one atom of A, for example, was more likely to meet and combine with one atom of B than that one of A would meet and combine with two of B. However, the assumption that he made was in error, and it led him to estimate incorrectly the atomic weights of many of the elements. This situation was not entirely clarified until about the middle of the nineteenth century.

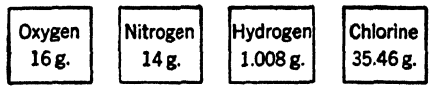


Figure 10

These weights of the four elements contain the same number of atoms. Hence, the relative weights of oxygen, nitrogen, hydrogen, and chlorine atoms are 16, 14, 1.008, and 35.46.

18. Gram-Atomic Weights

The chemist, frequently, must be able to determine the weight of one element that he must use with a definite weight of another to produce a certain compound. Let us say, for example, that he is producing an oxide of nitrogen in which he knows that the atoms of the two elements are present in equal numbers — one for one. If he uses 16 g. of oxygen, what weight of nitrogen must be used so that the reaction will be complete, i.e., there will be one atom of nitrogen for each atom of oxygen? Since the atoms combine in equal numbers — one for one — he must use that weight of nitrogen which contains the same number of atoms as 16 g. of oxygen. Otherwise, there would not be one atom of nitrogen for each atom of oxygen. Since the atomic weight of nitrogen is 14, he uses, therefore, 14 g. of that element. This weight of nitrogen is the gram-atomic weight of the element. *The gram-atomic weight of any element is the weight in grams of that element that contains the same number of atoms as 16 g. of oxygen.*

19. Gram-Molecular Weights

The weights of molecules can also be represented by numbers on the same scale that is used for the atomic weights of the elements. Thus, the molecular weight of oxygen is 32, which indicates that a molecule of oxygen weighs twice as much as an atom of the same element. On the same scale the molecular weight of nitrogen is 28, water 18.016, hydrogen 2.016, and carbon dioxide 44.

The gram-molecular weight of a compound or element is the weight in grams of the substance that contains the same number of molecules as the number of atoms in 16 g. of oxygen.

20. Avogadro's Number

The number of molecules in one gram-molecular weight is the same for all substances; it is called Avogadro's number and can be determined by several indirect methods. Molecules and atoms cannot be counted directly, of course, because they are not visible, and even if they were visible they still could not be counted one by one, because the number in a gram-molecular weight is too great. The value of Avogadro's number now generally accepted is 6.023×10^{23} or 602,300,000,000,000,000,000,000. If one could count two molecules per second, worked 8 hours per day, worked 365 days per year, and lived 60 working years, one would count only 1,261,440,000 molecules, leaving 602,299,999,999,998,738,560,000 uncounted.

21. Some Suggestions Concerning Methods by Which Atomic Weights Can Be Calculated

Although we have now for several pages acted on the knowledge that the atomic weight of nitrogen is 14, we have not shown why it cannot be some multiple or submultiple of 14? Why 14 instead of 28, 42, 7, or 3.5? Before the correct decision concerning the atomic weight can be made, certain additional information must be available.

If we could study and analyze *single molecules of all the compounds that contain any element*, we would find that some of these molecules contain one atom, some two, some three, and some still other numbers of atoms of the element. This we cannot do, but we can obtain the same information by a less direct method. Just as the molecule of a compound contains a certain number of atoms of each of the elements that

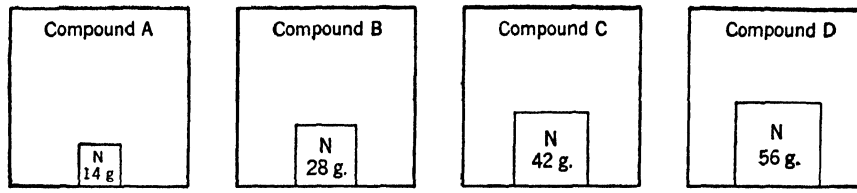


Figure 11. Weights of Nitrogen in Gram-Molecular Weights of Four Nitrogen Compounds

In a gram molecular weight of any compound of nitrogen there is 14 g., or some multiple of 14 g. of nitrogen. The gram-atomic weight of nitrogen, therefore, is 14 g.

compose the compound, *the gram-molecular weight of the compound contains a certain number of gram-atomic weights of each of the elements of the compound.* Therefore, if we analyze gram-molecular weights of all the compounds that contain an element, we should find one gram-atomic weight of the element in some, two in others, three in others, and so on. The smallest weight of the element thus found should be one gram-atomic weight, and the other weights of the same element in gram-molecular weights of other compounds should be multiples of this smallest weight.

If, for example, we analyze all the compounds that contain nitrogen, we find that the smallest weight of the element that occurs in a gram-molecular weight of any of these compounds is 14 g. Furthermore, in the gram-molecular weights of other compounds we find only multiples of 14 g. of nitrogen — 28 g., 42 g., 56 g., and so on. Hence, 14 g. must be the gram-atomic weight of this element, and as compared with 16 for oxygen the weight of one of its atoms can be represented by 14, the atomic weight. The atomic weight cannot be 7, because 7 g., 21 g., 35 g., or any other multiple of 7 g. that is not also a multiple of 14 g. of nitrogen are never found in a gram-molecular weight of any nitrogen compound.

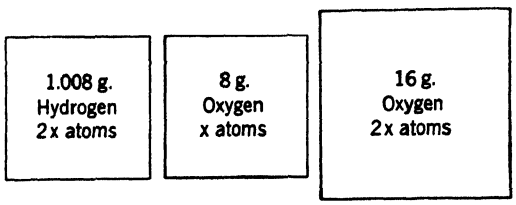


Figure 12. The Atomic Weight of Hydrogen

If two atoms of hydrogen combine with one atom of oxygen, then we can say that x atoms of oxygen weigh 8 g. and 2 x atoms of hydrogen weigh 1.008 grams. Then, if we arbitrarily assign 16 as the number to represent the relative weight of an oxygen atom, we see that 2 x atoms of oxygen weigh 16 g. The weights of equal numbers (2 x) atoms of hydrogen and oxygen are thus shown to be in the ratio of 1.008 to 16. The same ratio expresses the relative weights of single hydrogen and oxygen atoms.

22. Of What Value are Atomic Weights?

The chemist uses his knowledge of the atomic weights of the elements in many ways. Let us consider at this time some of these.

(1) How much oxygen must be used to convert 12 g. of carbon into carbon dioxide? The chemist knows that this compound contains two atoms of oxygen for each atom of carbon. He also knows that the gram-atomic weights of carbon and oxygen are 12 g. and 16 g., respectively. Therefore, he finds that for 12 g. of carbon he must use 32 g. of oxygen. If he labors under the erroneous impression that the atomic weight of carbon is 6, then he would make the mistake of using twice as much oxygen as he should use, because in that case he would assume that 64 g. of oxygen would be required to provide twice as many atoms as are contained in 12 g. of carbon.

(2) In building up, or synthesizing, new compounds the chemist must know the composition and structure of the molecules of the compounds that he wishes to make. He must know the elements that compose the compound, the number of atoms of each in a molecule of the compound, and the arrangement of these atoms in the molecule.

To determine the number of each kind of atom in the molecule he must know the molecular weight of the compound and the atomic weight of each of the elements. For example, let us assume that methyl (wood) alcohol is to be synthesized. It is known that its gram-molecular weight is 32.032 g., and that this weight contains 12 g. of carbon, 4.032 g. of hydrogen, and 16 g. of oxygen. The chemist knows that the gram-atomic weights are 12 g. for carbon, 1.008 g. for hydrogen, and 16 g. for oxygen. It is easy for him to see, therefore, that for each atom of oxygen in a molecule of the compound there are four atoms of hydrogen and one atom of carbon. If, however, he labored under the mistaken impression that the atomic weight of carbon is 6 instead of 12, he would conclude that the molecule contains two atoms of carbon.

23. Conclusion

We have attempted in this chapter to present the principal concepts which considered together constitute the atomic theory of matter, and we have also presented some of the experimental evidence that leads us to accept this theory. From time to time we shall consider other evidence, much of which is more convincing than that which was available at the time that Dalton introduced the theory into the science of chemistry. So overwhelmingly in favor of the atomic view of matter is the total accumulation of evidence that the reality of the atom is considered no longer as a theoretical possibility but as an accepted fact.

REVIEW EXERCISES

1. Distinguish between a molecule and an atom of an element.
2. Summarize the evidence which indicates that matter is discontinuous rather than continuous.
3. Summarize the main points in Dalton's atomic theory.
4. Show how each of the laws of chemical change supports the atomic theory.
5. With the help of the atomic theory, explain each of the laws of chemical change.
6. Upon what evidence are parts 2, 4, and 5 (page 21) of Dalton's atomic theory based?
7. Show that the following data are in accord with the Law of Combining Proportions:
   (*a*) 6 g. of carbon combines with 8 g. of oxygen to form carbon monoxide.
   (*b*) 4 g. of carbon combines with 10⅔ g. of oxygen to form carbon dioxide.
   (*c*) 3 g. of hydrogen combines with 24 g. of oxygen to form water.
   (*d*) 20 g. of carbon is combined with 6⅔ g. of hydrogen in methane.
   (*e*) 8 g. of carbon is combined with 2 g. of hydrogen in ethane.
   (*f*) 12 g. of carbon is combined with 1 g. of hydrogen in benzene.
   (*g*) 5 g. of carbon, 1¼ g. of hydrogen, and 3⅓ g. of oxygen are combined in ethyl alcohol.
   Assume that the numbers assigned to carbon, oxygen, and hydrogen are 12, 16, and 1, respectively.
8. Show that the data of (*a*) and (*b*) of question 6 are in accord with the Law of Multiple Proportions.
9. Using data of your own selection, illustrate each of the laws discussed in this chapter for reactions of the hypothetical elements A and B.
10. Copper forms two oxides. One of these contains 88.83 per cent of copper and the other 79.90 per cent. Show that the Law of Multiple Proportions applies to these compounds.
11. Show that the combining proportions (by weight) of nitrogen and oxygen in the following compounds can be represented (without changing the values of the ratios) by using 14 parts for nitrogen and 16 parts for oxygen or integral multiples of these numbers:

Combining Proportions	
Nitrogen	Oxygen
7	8
14	24
7	16
28	80

12. Arrange the data in (11) (without changing

the values of the ratios) to illustrate the Law of Multiple Proportions

13. Dalton believed that in water there was one oxygen atom for each atom of hydrogen. With what statement in his theory did this opinion agree?
14. If this assumption (question 13) were correct, what would be the atomic weight of hydrogen, if 16 were accepted as the atomic weight of oxygen? What would be the atomic weight of oxygen if the atomic weight of hydrogen were arbitrarily fixed at 1?
15. We now know that two atoms of hydrogen combine with each atom of oxygen in forming water. Show the line of reasoning that may be followed in finding the present accepted atomic weight of hydrogen, if 16 is taken as the atomic weight of oxygen.
16. Why is 16 for oxygen a convenient basis for the atomic weights of all the elements?
17. What do we mean when we say that the atomic weight of an element is 32?
18. What would be the atomic weight of this element (question 17) if the atomic weight of oxygen had been fixed at 64 instead of 16?
19. Why is 16 preferred to 64 as the atomic weight of oxygen in establishing a scale for the atomic weights of other elements?
20. Define: Atomic weight and gram-atomic weight of an element; molecular and gram-molecular weight of a compound.
21. Is there any reason why Dalton should have considered point (7) in the atomic theory as a likely assumption?
22. Why is 14 rather than 7 or 28, accepted as the atomic weight of nitrogen?
23. Of what value is information concerning the atomic weights of the elements?
24. Any weights of two elements that are in the same ratio as the atomic weights of the elements, contain the same number of atoms. Is this statement true? Justify your answer.
25. Do 3.5 g. of nitrogen and 4 g. of oxygen contain the same number of atoms? Justify your answer.
26. What weight of nitrogen is combined with 50 grams of oxygen in a compound in which there are two atoms of nitrogen for each atom of oxygen?
27. What is the gram-molecular weight of a compound if a molecule of it contains 2 atoms of carbon, 6 atoms of hydrogen and one atom of oxygen?
28. If 1000 g. of oxygen and 800 g. of Element E contain the same number of molecules of oxygen and E, respectively, the atomic weight of E is 12.8. Point out the possible inaccuracy in this statement. When would it be true?
29. If gram-molecular weights of compounds of element A were found to contain 32, 64, 80, 112, and 128 g. of A what would be the probable gram-atomic weight of A?
30. The atomic weight of silicon is approximately 28. What weight of this element would react with 4 g. of oxygen to make silicon dioxide in which there are two atoms of oxygen for each atom of silicon?
31. Is it possible that a compound of carbon and oxygen might contain one gram of carbon for each gram of oxygen? If so what would be the relative numbers of atoms of these two elements in the compound?

REFERENCES FOR FURTHER READING

Dalton, J., *Foundations of the Atomic Theory*, Alembic Club Reprint, No. 2. Edinburgh: E. and S. Livingstone, 1808.

Findlay, A., *A Hundred Years of Chemistry*. New York: The Macmillan Company, 1937.

Freud, I., *The Study of Chemical Composition*. London: Cambridge University Press, 1904.

Holmyard, E. J., *Chemistry to the Time of Dalton*. New York: The Oxford University Press, 1925.

J. Chem. Ed., **10,** 21 (1933); **22,** 300 (1945).

Moore, F. J., *History of Chemistry*.

Muir, W. M. P., *History of Chemical Theories and Laws*. New York: John Wiley and Sons, Inc., 1907.

3

THE STRUCTURE OF THE ATOM

1. Introduction

In the preceding chapter we were concerned, principally, with the view that all matter is composed of particles and with the evidence that shows atoms and molecules to be real particles of matter. In this chapter we shall be concerned with changes that have been made in Dalton's theory and which we must now add to bring our discussion of the atomic theory up-to-date. All theories are subject to modification as more information becomes available, and the atomic theory is no exception. However, the changes that have been made in it have not destroyed the theory, and they have not altered its principal contentions. Indeed, they have expanded and strengthened the theory and have made atoms appear more nearly real than they possibly could have appeared to anyone in Dalton's time. For the most part, the changes that have been made concern the nature of the atom, its composition, and its structure, rather than the question of its existence and the part that it plays as a fundamental unit of an element in forming compounds.

For the present, we shall be content to summarize rather briefly modern views about the composition and structure of atoms and molecules without attempting to describe or to explain the evidence and information upon which all of the views are based or the experimental methods that have been used to collect this information. The complete story is a long one, and, therefore, we shall return to it in a later chapter after we have studied certain other fundamental concepts and principles of chemistry that cannot be postponed.

2. Atoms Can Be Decomposed

In certain changes that are much more profound than ordinary chemical reactions, and which involve the absorption, and sometimes the liberation, of quantities of energy far in excess of the changes of energy associated with reactions, atoms can be, and are, decomposed. The atoms of the *radioactive elements* disintegrate spontaneously, losing by emission some of the energy and matter that they contain and, at the same time, forming other atoms which may disintegrate still further. An atom of *radium*, for example, changes into an atom of *radon*, when it emits a certain quantity of energy and ejects an *alpha particle*, which is a positively charged atom of helium. The atom of radon later disintegrates and loses another alpha particle, and the atom that is left then disintegrates in a similar manner. A series of radioactive elements thus results. *Uranium*, for example, is the first element in a series of radioactive elements, which change from one member of the series to the next by the disintegration of their atoms. The disintegration of the atoms of

some of these elements involves the emission of an alpha particle from each atom, but each of the atoms of other elements in the series lose one *electron*, or *beta particle*, when they disintegrate. The atoms of elements that are not radioactive can be disintegrated in the laboratory by bombarding them with swiftly moving particles, such as the alpha particles that are emitted by some of the radioactive elements, or with particles such as electrons and electrically charged atoms of hydrogen, that have been given very high velocities by means of special devices.

Discoveries of the kind mentioned above have altered the concept of an atom as a particle once thought to be solid and permanent. We now recognize that the atom is composed of smaller particles, which differ in number and in arrangement for different kinds of atoms. The different arrangements, or structures, are responsible for different behaviors and characteristics of atoms, and of the elements that they compose, and of the compounds that they form. However, the principal concept of atoms remains unchanged, because we can still regard them as the smallest portions of elements that combine to form compounds, and there is still no reason to believe that elements are decomposed into simpler substances or are produced by the combination of simpler substances in the ordinary chemical reactions by which compounds are decomposed and produced. The fundamental concept of an element as distinguished from a compound is not, therefore, altered from the form in which it has previously been stated (page 14).

If the atoms of an element are disintegrated, then the compounds that can be produced from that element can no longer be made from them, but the atoms that result from the disintegration can form compounds of some other element.

It is likely, also, that atoms can be, and probably are, built-up from smaller particles in certain parts of the universe in which unusual conditions prevail. In the interior of the sun, for example, probably few if any of the atoms that we know on the earth exist. Only the particles that compose all atoms — particles similar to those emitted by atoms during radioactive disintegration — probably can exist at the very high temperature of the sun's interior. The temperature is lower, however, in the outer portions of the sun, and in that region some of these smaller particles appear to have combined to form atoms of some of the elements with which we are acquainted.

3. The Atoms of an Element Are Not Necessarily Identical

Dalton was certain, when he formulated the atomic theory, that all the atoms of any one element were identical in every way. We are now aware, however, that all the atoms that are designated, usually, by one name, oxygen for example, do not have the same mass, and that their properties, although very similar, do show some differences. The study of radioactive substances has revealed atoms of lead that have different masses — 206, 207, 208 — as compared with 16 for the mass of an atom of oxygen. There are also two varieties of atoms of chlorine, two of neon, three each of hydrogen and oxygen, and two or more of many other elements.

What we have usually considered as a single form of matter and have called an element is thus seen to consist, at least for some elements, of more than one kind of atom. Each kind of atom should probably be designated by a different name. Only for hydrogen and uranium has it thus far been possible to separate completely two varieties of atoms of the same element, or of what has for a long time been regarded as a single element, and to study each variety separately. One of the kinds of hydrogen, now called *deuterium*, has been found to consist of atoms that weigh twice as much as atoms of ordinary hydrogen and to possess properties that are slightly differ-

ent. A third variety of atoms which have a mass of about three times that of ordinary hydrogen atoms is called *tritium*.

4. Questions Unanswered by Dalton's Theory

Dalton's theory left unanswered several questions concerning the manner in which elements combine to form compounds. His theory stated that atoms of different elements combined to form molecules — or compound atoms as he called them — but it did not explain the following:

(*a*) Why one element does not react with all other elements, and why among elements that form the same general kinds of compounds there is a great difference in activity.

(*b*) Why one atom of hydrogen, for example, reacts with one atom of chlorine, while two atoms of hydrogen react with one of oxygen, three with one of nitrogen, and four with one of carbon.

(*c*) How atoms react to form compounds and what forces hold the atoms of elements together in the compounds that they form.

(*d*) How atoms are arranged in relation to one another in molecules of the compounds that they form.

Fairly satisfactory but not always complete answers to these and similar questions are made possible by our knowledge of atoms and by theories of their structures that are based upon this knowledge.

THE STRUCTURE OF THE ATOM

5. The Particles that Compose Atoms

In Dalton's day, and throughout the nineteenth century, an atom was regarded as a "simple, solid, hard, impenetrable, durable particle." All information now available clearly indicates, however, that the atom has a complex structure, and that it is composed of small particles distributed within the space that it occupies in a fashion somewhat similar to the arrangement of the sun and the planets of the solar system.

The three principal kinds of particles that compose atoms are *electrons*, *protons*, and *neutrons*. No one can say just what an electron *is*. To be able to do so would mean that one could say, also, what electricity and matter are. It can be said, however, that the electron is a constituent of all atoms, and that its electrical charge is the *unit of negative electrical charge*, i.e., all other charges are multiples of its charge. The positively charged atom of hydrogen is a proton; the atom contains one electron and one proton, and, when the electron is separated from the atom, only the proton remains. The mass of a proton is very nearly the same as the mass of an atom of hydrogen — 1.0076 as compared with 16 for the mass of an atom of oxygen. The mass of the electron is only about $\frac{1}{1838}$ as great, or 0.00055 as compared with 16 for an atom of oxygen. The electrical charge of the proton is of the same magnitude as the charge of the electron, but it has the opposite sign (+ instead of −).

The neutron has no charge, and its mass is about the same as that of a proton — 1.009 as compared with 16 for the oxygen atom.

6. The General Plan of Atomic Structure

The nucleus at the center of the atom (Figure 13) contains all the protons and neutrons, and all atomic nuclei contain both kinds of particles, with the exception of the hydrogen nucleus, which is a single proton. The nucleus, therefore, is always positively charged, and the number of units of charge that it possesses is equal to the number of protons that it contains.

The number of electrons in an atom, under normal conditions and when the atom is uncombined, is equal to the number of protons in the nucleus of the atom. This condition must be true, because the atom as a whole is electrically neutral. The elec-

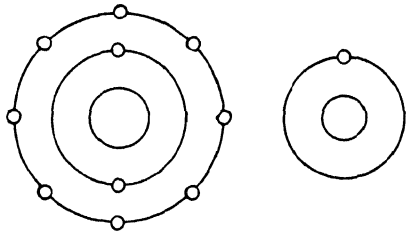


Figure 13. The Structure of an Atom of Neon (*left*) and of an Atom of Hydrogen (*right*)

The circle in the center represents the nucleus The small circles represent planetary electrons Those electrons in the same ring revolve in similar orbits

trons are thought to revolve about the nucleus in orbits of various sizes and forms, some circular and some elliptical. According to this view, the atom resembles a miniature solar system with the nucleus acting as the sun and the electrons as planets. The electrons and the nucleus are very small as compared with the size of the atom, which, therefore, must have within its boundaries a great deal of empty space.

Actually, it is not quite true that the space around the nucleus of an atom is empty. Most of this space probably is empty at any one instant, but the electrons do not always move in the same orbits. Rather, they move in all directions around the nucleus and at different distances from it. Because they move very rapidly, they may be thought of as filling all the space. Over a period of time, each electron is most likely to be found at a rather definite distance from the nucleus. This most probable distance, extending in every direction from the nucleus, corresponds to what we have called, sometimes, the normal orbit of the electron. For the hydrogen atom this "orbit" has a diameter of about 0.00000002 cm., which, therefore, is an approximation of the diameter of an atom of hydrogen.

7. Atomic Numbers

The number of units of positive charge [1] associated with the nucleus of any atom is determined solely by the number of protons that the nucleus contains. There are methods by which the charge of the nucleus can be found — one of these will be described in a later chapter — and, therefore, the number of protons in the nuclei of different atoms can also be determined. It is found that this number ranges from one in the hydrogen atom to 98 in the atom of californium. Hence, the elements can be arranged in a series that begins with hydrogen and ends with californium, and in which the atoms of any element contain one more proton each than the atoms of the preceding element. The number of an element in this series is called its *atomic number*. Numerically, the atomic number of any element is the same as the number of protons in the nucleus of an atom of that element and, also, the same as the number of electrons in an atom, since the number of protons is equal to the number of electrons.

[1] It will be recalled that the electron carries one unit of negative charge. The charge of a proton is also one unit, but it has a + instead of a − sign.

8. Atomic Weights; Numbers Representing the Relative Masses of Atoms

The electrons of an atom contribute only a very small part of the total mass of the atom, because the mass of a single electron is only 0.00055 as compared with 16 for the mass of an atom of oxygen. Therefore, the atomic mass must depend almost entirely upon the number of protons and neutrons in the nucleus of the atom. Furthermore, the mass of each proton or neutron is approximately 1, as compared with 16 for the oxygen atom; and hence, the mass of any atom — its atomic weight — can be represented by a number equal, approximately, to the sum of the numbers of protons and neutrons in its nucleus. When we take into account the atomic weights of different kinds of atoms which we are inclined to call by the same name (see hydrogen, page 34), we find that all atomic weights differ from whole numbers by only slight fractions. The whole number nearest the exact atomic weight is sometimes called the *mass number* of the element.

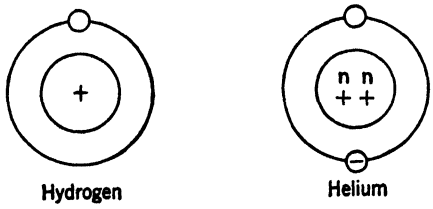


Figure 14. The Structures of Atoms of Hydrogen and Helium

It is thought that there must be a slight loss in mass when neutrons and protons are packed very closely, as they must be, within the nucleus of an atom. Otherwise, the atomic weight would always be equal to the number of protons times the weight of a proton, plus the number of neutrons times the weight of one neutron. Because of differences in packing, or in the arrangement of protons and neutrons in the nucleus, the loss of mass differs for different atoms. The mass that disappears is probably converted into energy.

9. The Composition of the Nuclei of Different Atoms

Hydrogen, deuterium, and tritium have the same atomic number, and atoms of all three contain one proton each. They differ in atomic weights because of differences in the numbers of neutrons in their nuclei. Ordinary hydrogen has none; deuterium, which has an atomic weight that is about twice that of ordinary hydrogen, has one neutron per atom; and the tritium atom contains two neutrons. Each of these three kinds of atoms also contains one electron.

Ordinary hydrogen, deuterium, and tritium are *isotopes. The isotopes of an element have the same atomic number but different atomic weights.*

The nucleus of the helium atom contains two protons; and hence, this element's atomic number is two. Its atomic weight is four, and, therefore, the nucleus must contain two neutrons. The atomic number of lithium is 3, and the atomic weight, since there are two isotopes of this element, is 6 or 7, depending upon whether the nucleus contains 3 or 4 neutrons. The two isotopes are mixed in nature so that the average atomic weight is always 6.94, a fact that indicates the much greater abundance of the isotope having an atomic mass of 7 than that of the isotope of mass 6. The three isotopes of oxygen each have an atomic number of 8, and their atomic weights are 16, 17, and 18, respectively; hence, the nuclei of the atoms of the three isotopes contain 8, 9, and 10 neutrons. The two isotopes of chlorine have an atomic number of 17, and atomic weights of 35 and 37. Their atoms, therefore, must contain 18 and 20 neutrons, respectively.

Generally speaking, the greatest degree of stability of the atomic nucleus appears to be attained when the number of protons is the same as the number of neutrons. In this connection one may note that the oxygen isotope in which this condition exists — the one having an atomic weight of 16 — is the one that is most abundant.

10. The Arrangement of Electrons in the Atom

The electrons of an atom possess different amounts of energy and, therefore, revolve around the nucleus in orbits of different sizes and shapes. In the normal condition of the atom all the electrons revolve in orbits that correspond to the minimum amount of energy that they can possess. If an electron absorbs energy — from a beam of X-rays, for example — it can then revolve in a larger orbit, but the resulting state is an unstable condition of the atom. The electron that has moved into a larger

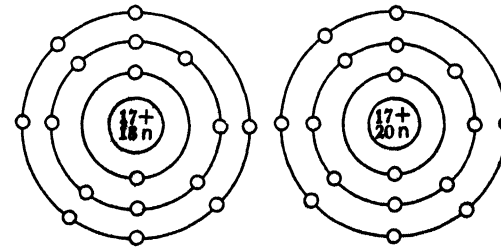


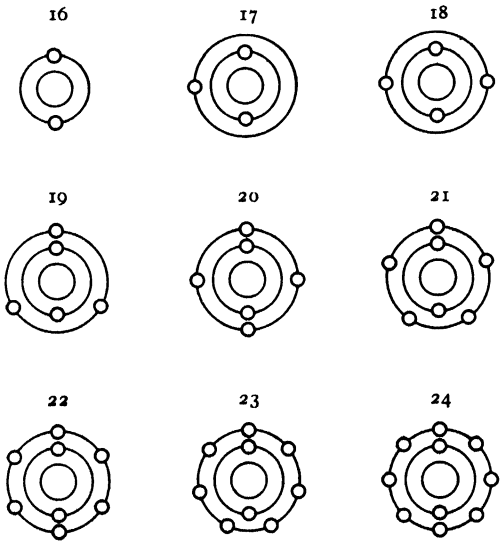
Figure 15. Atoms of the Two Isotopes of Chlorine

Because of different numbers of neutrons in the nuclei of the two atoms the atomic weights are 35 and 37.

orbit and, therefore, now lies farther away from the nucleus, will tend to move back again into its original orbit, and when it does so it will release its surplus energy as light or as some other form of radiant energy.

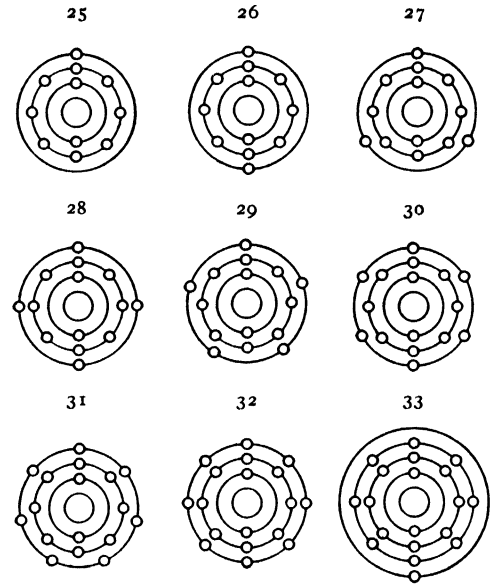
The orbits in which the electrons of an atom rotate appear to be divided into very definite groups more commonly called *shells*. These shells are indicated by numbers beginning with the shell nearest the nucleus (1, 2, 3, 4, 5, 6) or by letters (K, L, M, N, O, P).

Every atom, except the atom of hydrogen, contains two electrons that revolve in orbits of the first or K shell, and not more than two electrons can occupy orbits of this shell at the same time. These are the orbits that lie closest to the nucleus, have the smallest diameters, and contain electrons that possess the smallest amounts of energy. When we consider the atoms of lithium, which contain three electrons each, we find that the third electron is more easily removed from an atom than either of the other two. It must, therefore, lie farther away from the nucleus, and it must rotate in a larger orbit. Since it already possesses more energy than the other two electrons, less energy is required to separate it completely from the atom and it is, therefore, more easily removed. We say that it rotates in an orbit of the second or L shell.



Figures 16–24. Structures of Atoms

Helium (16); lithium (17); beryllium (18); boron (19); carbon (20); nitrogen (21); oxygen (22); fluorine (23); neon (24)



Figures 25–33. The Structure of Atoms

Sodium (25); magnesium (26); aluminum (27); silicon (28); phosphorus (29); sulfur (30); chlorine (31); argon (32); potassium (33).

Atoms of the next seven elements, in the order of atomic numbers, contain, respectively, 2, 3, 4, 5, 6, 7, and 8 electrons in the second or L shell; and, of course, each also contains two in the first shell. (See Figures 16–24.) The second shell appears to be filled when it contains eight electrons, as it does in the atom of neon, because in the atom that contains one more electron — sodium, Figure 25 — the additional electron appears to enter an orbit that belongs to a third shell. It is much more easily removed from the atom than any of the eight electrons of the second shell or either of the two in the first shell.

As more and more electrons are added in the heavier atoms, other shells are filled. See Figures 16–33. The number of elec-

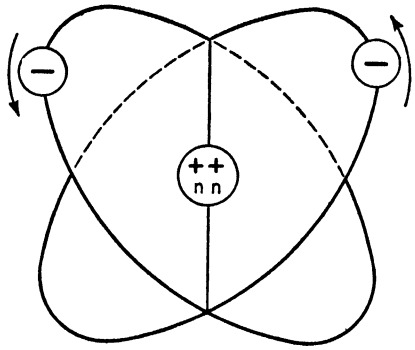


Figure 34. Structure of Helium
Each electron occupies its own orbit.

trons required to *fill* each of the first groups is shown below:

Shell	Maximum No. of Electrons in the Shell
1 or K	2
2 " L	8
3 " M	18
4 " N	32

For convenience only, it is customary to show the electrons that rotate around the nucleus in similar orbits — that belong to the same shell — as small circles located on a common ring, or circle, as shown in Figure 15. We should keep in mind, however, that each electron rotates in its own orbit, and that these orbits lie in different planes. The actual condition is better illustrated in Figure 34. The reader should not draw the conclusion, however, that any of these diagrams actually represent a true picture of an atom. They have proven to be of great value in explaining and predicting the behavior of atoms.

11. Distribution of Electrons in Atoms Containing More than Two Shells

For the first or K shell, it appears that the maximum number of electrons that may be present is two. For shell two, the maximum number is eight. A group of eight electrons appears to have a high degree of stability, and the behavior of atoms and all other available information indicates that *the outermost shell of electrons of any atom cannot contain more than this number.*

Hence, as soon as the outside shell has eight electrons in it, as it does in neon, the next electrons go into the next higher shell (Figures 16 to 33). It will also be noted (Figure 33) that, as soon as the third shell contains eight electrons, the next electron goes into an orbit of shell four, although the third shell is not filled completely until it contains eighteen electrons. The next electron (calcium) also goes into the fourth shell, but in the atoms of the next several elements (scandium to zinc) the additional electrons go into shell three until the number in that shell reaches eighteen, and the shell is filled. The next six electrons (gallium to krypton) join the two electrons already located in the fourth shell until the total number in that shell is eight, the maximum number that can be located in an outermost shell. The next two electrons go into orbits of the fifth shell (rubidium and strontium).

In a later chapter we shall discuss more fully the distribution of electrons in atoms containing more than two shells and with a view of presenting at least some of the evidence upon which this theory of distribution is based.

12. One Way in Which Atoms React to Form Compounds

When an atom reacts with other atoms to form compounds, it is the outermost electrons of the atom that are involved in the change.[1] In these reactions the atom tends to change in such a way that a stable outermost group will be produced. This stability may be obtained by some atoms if they lose to others all the electrons in their outermost group, thus leaving as the exterior portion of their structures the stable arrangement of electrons already existing in the next

[1] For some elements, such as copper for which the distribution is 2–8–18–1, an electron in the group next to the outside one may be involved.

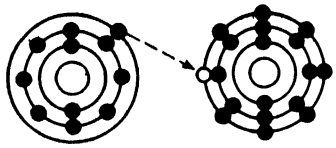


Figure 35. The Reaction of an Atom of Sodium with an Atom of Chlorine
One electron is transferred.

lower group. Thus, an atom of lithium can attain stability by losing the single electron that it has in group two, thus leaving on its external surface the two electrons of group one. Similarly, the sodium atom will lose its single electron of group three, leaving exposed to external influences the stable group of eight electrons in group two. Lithium and sodium, therefore, might be expected to have similar properties.

If one atom in a reaction loses electrons, it must do so because some other atom takes them away from it; and hence, we must assume that certain atoms can attain stability by acquiring electrons. These are the atoms that already have almost enough electrons to produce a stable outermost group. The fluorine atom, for example, contains seven electrons in group two. It can attain stability if it acquires one more — from an atom that has only one in its outermost group, for example — and thus produces a group of eight. The hydrogen atom with only one electron can produce a stable group containing two electrons by removing an electron from some other atom; usually, however, the hydrogen atom loses its electron to some other atom. Helium with two electrons in group one, neon with eight in group two, and argon with eight in group three already possess stable outermost groups, and their atoms, therefore, show almost no tendency to react with others.

An atom that gains or loses electrons acquires an electrical charge. If one electron is removed from an atom in the manner described above, the atom will contain one more proton than the number of electrons remaining and, therefore, will have as a whole one unit of *positive* charge. The atom that acquires the electron will possess as a whole one unit of *negative* charge, because it will contain one more electron than the number of protons in its nucleus. The two charged particles resulting from the transfer of an electron from one atom to another will attract each other because of their unlike charges. This attraction explains one way in which the atoms of elements can be held together in compounds.

The number of units of charge acquired by atoms as a result of electron-transfers depends upon the number of electrons that the atom gains or loses. For example, if an atom of element A, which can lose two electrons — because it has only two in its outside group — reacts with atoms of element B, which contain seven in the outside group and, therefore, can acquire only one more, the two electrons from one atom of A must go to two atoms of B. Thus, an atom of A carrying two units of positive charge and two atoms of B, each carrying one unit of negative charge, result from the reaction. We can represent the compound formed as $A^{++}B_2^-$ or $(A^{++} + 2\ B^-)$. See Figure 36.

13. Metals and Non-Metals

The atoms of hydrogen and the metallic elements tend to lose electrons, because their outermost electron-groups contain only one, two, or three electrons, which are only weakly held by the nucleus. Atoms of

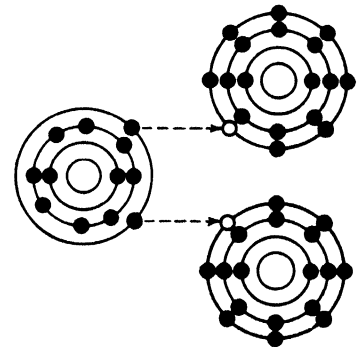


Figure 36. The Reactions of One Atom of Magnesium with Two Atoms of Chlorine

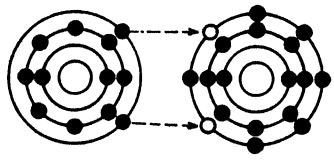


Figure 37. The Reaction of One Atom of Magnesium with One Atom of Sulfur

these elements tend to form compounds in which they are positively charged. To acquire such charges they must lose electrons to atoms that attract electrons more strongly than themselves. The latter are the non-metallic elements, such as oxygen, chlorine, bromine, and sulfur. The atoms of these elements possess outermost electron-groups that are already nearly filled, and their nuclei exert relatively strong attraction for electrons in even the outermost portions of their structures.

We find, therefore, in this theory of the atom's structure a reasonable basis for explaining the changes by which some elements are converted into compounds. We understand, also, why an atom of one element reacts with one atom of a second element, but with two of a third and, perhaps, with three of a fourth.

14. Compounds Composed of Ions

Compounds produced by the transfer of electrons from one atom to another consist of electrically charged atoms or groups of atoms. Such particles are called *ions*, and the compounds that contain them are spoken of as *ionic compounds*. There are no molecules of these substances. *The compounds that belong to this group of substances are, for the most part, compounds consisting of the positive ion of a metal and a negative ion made up of one or more non-metals.*

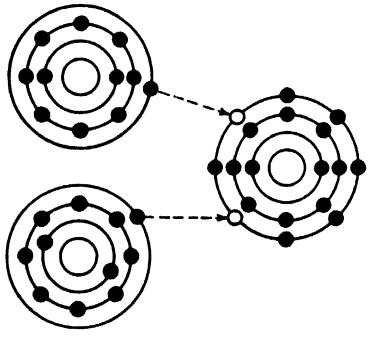


Figure 38. The Reaction of Two Atoms of Sodium with One Atom of Sulfur
Two electrons are transferred.

In some compounds of this kind one or both of the ions are composed of a group of atoms, such as the sulfate ion, $SO_4^{=}$, the nitrate ion, NO_3^{-}, the ammonium ion, NH_4^{+}, and the carbonate ion, $CO_3^{=}$. Ions formed from single atoms are represented by the sodium ion, Na^{+}, the chloride ion, Cl^{-}, the magnesium ion, Mg^{++}, and the sulfide ion, $S^{=}$. The letters used in these statements concerning ions refer to the elements; the numbers (subscripts) show the number of atoms of each element in the ion; and the + and − signs indicate the nature of the electrical charge and the number of units of charge per ion, i.e., the number of electrons lost or gained.

15. A Typical Ionic Compound

Sodium chloride, common salt, is a good example of compounds composed of ions. (See Figure 39.) It contains the positively charged ion of sodium, Na^{+}, and the negatively charged non-metallic ion of chlorine, Cl^{-}. Therefore, it is desirable to indicate the composition of this substance as $Na^{+} + Cl^{-}$. This expression does not mean that the two ions are joined together as a molecule; it means, instead, that in every crystal of salt, in fused salt, or in a solution, there is present *one sodium ion for each chloride ion*. In other words, when sodium and chlorine form sodium chloride, equal numbers of the two kinds of atoms react. In a crystal of sodium chloride these ions are arranged in an orderly pattern, the general structure of which is shown in Figure 39. Other ionic compounds crystallize in equally definite patterns of different forms.

The removal of each electron from an

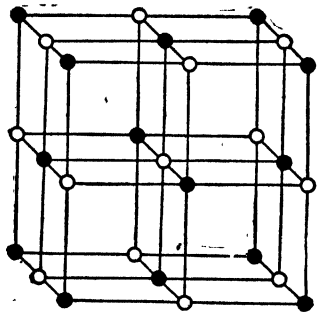


Figure 39. The Structure of a Crystal of Sodium Chloride

White circles represent sodium ions; black circles represent chloride ions.

atom leaves a positive charge upon the atom, and, since unlike charges attract, it becomes increasingly difficult to separate another electron from the atom which carries a positive charge and which, therefore, has an increased attraction for electrons. Likewise, an atom that has a negative charge will have less attraction for an additional electron; and hence, after two electrons have been taken up by an atom, its negative charge will cause it to have little if any attraction for a third electron. Hence, atoms that lack three or more electrons (carbon, for example) of having a group of eight in their outermost shell will not be likely to gain that number. Those atoms that have more than three in their outermost shell are not likely to lose these, thus forming positive ions; carbon, for example, does not lose four electrons to form a C^{++++} ion.

16. Compounds not Composed of Ions

Elements sometimes react in such a way that electrons are not transferred from one atom to another. Let us consider, for example, the compound of carbon and hydrogen called *methane*, CH_4. Now each hydrogen atom has a single electron, and the carbon atom has four electrons, in its outermost group. When they combine, the four atoms of hydrogen could, theoretically, give up one electron each to the single atom of carbon, which would then have a stable group of eight electrons in its outermost group. We cannot believe that this transfer of electrons occurs, however, because, if it did, ions would be produced, and all the properties of methane indicate that it does not contain any ions. How, then, are the five atoms of the methane molecules held together? Although we cannot be certain of the true answer to this question, the following explanation has been suggested and has been very useful.

In forming the molecule of methane, perhaps atoms of carbon and hydrogen *share* electrons with each other. Each atom of hydrogen could share its single electron with the carbon atom and, in turn, could share one of the four electrons of carbon. This arrangement would give the carbon atom eight electrons in its outermost group and each hydrogen atom two, but neither atom would actually gain or lose any, because for each electron of its own that it shares, an atom would share an electron belonging to another atom; and hence, the atoms would not be electrically charged. We may assume that many compounds that are composed of two non-metals are produced by the sharing of electrons between atoms. In a like manner, two or more atoms of the same element may form molecules of the element by sharing electrons. Thus, two atoms of hydrogen form the molecule H_2:

$$H^{\cdot} + H^{\cdot} \longrightarrow H:H$$

Compounds of this kind are composed of molecules, and are called *covalent compounds*. To this class of substances belong (1) oxides of the non-metals; (2) other compounds containing two or more non-metals, e.g., CS_2, CH_4, NH_3 and CCl_4; (3) compounds commonly called acids that contain hydrogen and one or more non-metallic elements, e.g., HCl, H_2CO_3, H_2S, and H_2SO_4; and (4) most of the compounds of organic chemistry, such as the alcohols, the sugars, starch, fats, and proteins.

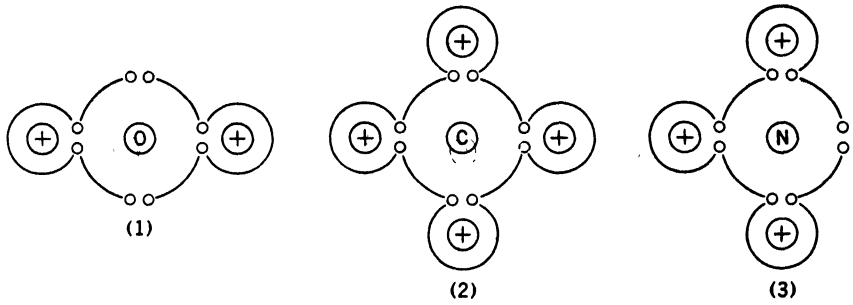


Figure 40. Compounds Formed by Atoms that Share Electrons

(1) Water; (2) Methane, CH_4; (3) Ammonia, NH_3. When we write CH_4 we mean that one molecule contains one carbon and four hydrogen atoms.

17. Valence Numbers

The valence of an element refers to the combining capacity of its atoms. For binary ionic compounds the valence number of an element depends upon the number of electrons that an atom of the element gains or loses when it reacts with other atoms. In sodium chloride, NaCl, the sodium atom loses one electron, and the chlorine atom gains one. Therefore, the valence number of each element is 1. To indicate the difference — one atom gains and the other loses an electron — we frequently refer to the valence number of sodium as + 1 and to that of chlorine as − 1. In calcium chloride, $CaCl_2$, the valence number of calcium is + 2, and that of aluminum in $AlCl_3$ is + 3.

For the simple covalent compounds, such as those shown in Figures 40 and 41, the valence number of an element depends upon the number of pairs of electrons that an atom of the element shares with other atoms. In water, H_2O, the valence number of oxygen is 2, because the atom of this element *shares* electrons with two atoms of hydrogen. The valence number of hydrogen is one, because each atom shares one pair of electrons with oxygen. In carbon tetrachloride, CCl_4, one carbon atom shares a pair of electrons with each of four chlorine atoms, and, therefore, carbon's valence number is 4.

One cannot assign positive and negative valence numbers to the elements in covalent compounds, because there are no positively and negatively charged particles in such compounds; and, hence, the words positive and negative would be without real meaning if used in this way.

Since it has not gained, lost or shared any electrons, we regard the atom of a free element as having a valence number of 0.

The electrons in the outermost group of an atom are the ones that are involved in reactions. Since they determine the combining capacity of the atom, they are sometimes spoken of as the *valence electrons* of the atom, and the shell to which they belong is called the valence shell.

SYMBOLS, FORMULAS, AND EQUATIONS

18. How the Chemist Represents Elements and Compounds in Written or Printed Statements

As indicated in the preceding discussion and in Figure 40, two atoms of hydrogen combine with one atom of oxygen to produce one molecule of water. This is a statement of certain facts concerning the reaction of these two elements. When a chemist describes in written or printed expression a reaction of this kind he frequently uses an *equation* consisting of certain *symbols* and *formulas*. The symbol represents one atom, or more frequently, one gram-atomic weight of the element; thus, H

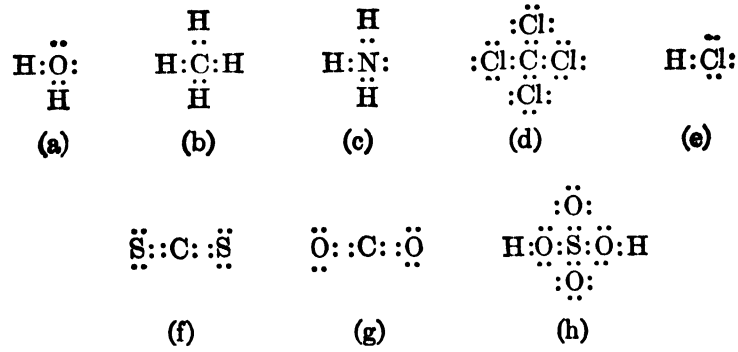


Figure 41. Structures of Covalent Compounds

Structures of molecules are sometimes shown by indicating the electrons in the outermost groups, or shells, of atoms as dots. It will be noted that some atoms can share more than one pair of electrons, e.g., carbon and oxygen in CO_2, (a) water; (b) methane; (c) ammonia; (d) carbon tetrachloride; (e) hydrogen chloride; (f) carbon disulfide; (g) carbon dioxide; and (h) sulfuric acid.

stands for one atom, or one gram-atomic weight (1.008 g.), of hydrogen. The symbols of all the elements will be found on the inside of the front cover of this book. One atom of hydrogen is represented by H and two atoms by 2 H. A formula represents a molecule, or a gram-molecular weight, of some substance. Thus, H_2 is the formula for a molecule of hydrogen; it shows that a molecule is composed of two atoms. The formula, H_2O, shows that each molecule of water is composed of two atoms of hydrogen and one atom of oxygen.

In expressing the composition of different compounds we shall use the following system. (1) For those compounds in which atoms share electrons, we shall write formulas showing the number of atoms of each element in a molecule, e.g., H_2O for water. (2) Compounds composed of ions will be represented by the formulas of the ions, instead of molecules, when the compounds are dissolved in water, e.g. ($Na^+ + Cl^-$). (3) When we deal with solid compounds composed of ions we shall place the formulas of the ions together and omit the signs, e.g., NaCl.

In equations, the formulas of the molecules or ions of the reacting, or original substances, are placed on the left and those of the products of the reaction are placed on the right of an arrow. The number of molecules of each substance (left and right) must be such that there will be the same number of atoms of each element on both sides. We might write an equation to show the formation of water from hydrogen and oxygen as follows:

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

But the molecules of hydrogen and oxygen contain two atoms each: H_2, O_2. The equation, therefore, must show such particles of oxygen and hydrogen, rather than single atoms:

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

By writing the 2 before H_2 and also before H_2O, we show that two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. This equation is *balanced*, because there is the same number of atoms of each element on both sides of the equation. If this were not true, the statement would be contrary to the Law of the Conservation of Mass.



Figure 42. The Reaction of Two Molecules of Hydrogen (H_2) with One Molecule of Oxygen (O_2) to Form Two Molecules of Water, (H_2O)

REVIEW EXERCISES

1. Show that the facts and theories discussed in this chapter do not affect our definition of an atom.
2. Summarize the errors and weak points in Dalton's atomic theory.
3. In what ways is the modern concept of an atom different from Dalton's concept?
4. According to the theory of the atom's structure, upon what factor does the atomic weight of an element depend?
5. What is the relation of a proton to a hydrogen atom?
6. Define or identify: Electron, nucleus, isotopes, neutron, radioactive element, beta particle, alpha particle.
7. In what ways is the modern theory of the atom more satisfactory than Dalton's theory?
8. What is an ion? How does it acquire its electrical charge?
9. In what structural features do atoms of metals differ from atoms of non-metals?
10. In what ways may atoms react to form compounds?
11. What conditions determine whether or not the atoms of an element will react more readily with the atoms of a metal than with atoms of a non-metal?
12. What conditions determine the maximum number of electrons that an atom loses or gains in a chemical reaction?
13. Describe the general plan of atomic structure.
14. What are isotopes? Give examples.
15. How do the structures of the atoms of isotopes differ?
16. What is meant by the atomic number of an element?
17. Describe the general plan of arrangement of electrons in the first four shells of atoms.
18. Why should we not expect the carbon atom to gain or lose four electrons?
19. Describe the arrangement, or distribution, of electrons by shells in atoms containing 2, 6, 10, 12, 16, 18, 19, 23, and 35 electrons.
20. Which of the atoms mentioned in Number 19 are likely to form compounds (1) by losing electrons: (2) by gaining electrons: and (3) by sharing electrons? Which are not likely to form any compounds?
21. Distinguish between ionic and molecular, or covalent, compounds. Give examples.
22. Define: (1) Valence and (2) the valence number of an element.
23. Why is it logical to say that the valence number of a free element is 0?
24. Name at least one possible valence number for each of the elements having the following atomic numbers: 1, 4, 7, 8, 9, 11, 12, 16, 17, 19, 20, 26, 34, 35, 37.
25. Atoms of chlorine, oxygen, nitrogen, and carbon form compounds by sharing electrons with 1, 2, 3, and 4 atoms of hydrogen, respectively. Account for the differences in the number of atoms of hydrogen that combines with one atom of each of these elements.
26. What is the meaning of the following statement? The four elements mentioned in Number 25 have valence numbers of 1, 2, 3, and 4, respectively.
27. From the atomic weights of the elements that compose carbon tetrachloride (*d*, Figure 41) and from the formula calculate the gram-molecular weight of this compound.
28. What is the atomic weight of an element if its atomic number is 13 and if the nucleus of one of its atoms contains 14 neutrons?
29. Why do we represent the composition of salt as $(Na^+ + Cl^-)$ and water as H_2O?
30. In what way is a chemical equation different from a mathematical statement, such as $16 \div 8 = 2$?
31. Which of the following statements are true? Point out all errors.
    (*a*) The numbers of protons and neutrons in the nucleus of any atom are the same.
    (*b*) The numbers of electrons and protons in any atom are the same.
    (*c*) The mass number of an element is equal to the sum of the numbers of protons and neutrons in the nucleus of an atom of that element.
    (*d*) The atomic number of an element is equal to the number of electrons in an atom of that element.
    (*e*) No shell of any atom can contain more than eight electrons.
    (*f*) The first shell of any atom, except the

hydrogen atom, can contain only two electrons.

REFERENCES FOR FURTHER READING

Campbell, John W., *The Atomic Story.* New York: Henry Holt and Company, 1947.

Darrow, K. K., *The Renaissance of Physics.* New York: The Macmillan Company, 1936.

Hecht, Selig, *Explaining the Atom.* New York: The Viking Press, 1947

Jaffe, B., *Crucibles,* Chaps. XIV–XVI.

J. Chem. Ed., **3,** 1110, 1254, 1426 (1926); **4,** 73, 220, 1008, 1335 (1927); **5,** 1135, 1473, 1639 (1928); **6,** 906 (1929); **7,** 138 (1930); **10,** 233 (1933); **11,** 313, 476 (1934); **12,** 76 (1935); **13,** 303 (1936); **15,** 575 (1938); **16,** 283 (1939); **17,** 481 (1940); **18,** 515 (1941); **23,** 356 (1946); **24,** 20 (1947).

Millikan, R. A., *Electrons* (+ and −), *Protons, Photons, Neutrons, and Cosmic Rays.* Chicago: The University of Chicago Press, 1935.

Robertson, J. K., *Atomic Artillery.* New York: D. Van Nostrand Company, 1937.

Tilden, Sir W. A., and S. Glasstone, *Chemical Discovery and Invention in the Twentieth Century,* Chap. VIII, 6th ed. New York: E. P. Dutton and Company, 1936.

4

OXYGEN

1. Introduction

In the study of an element the following subjects are usually considered: (1) The occurrence and general importance of the element and its compounds; (2) the history of the element; (3) methods of producing it in the laboratory and also for commercial purposes; (4) its physical and chemical properties; and (5) its uses.

In this chapter, chemical equations are used for the first time. Statements of the reactions are also given in words, and these are more important at this stage in our study than the equations. One's ability to use equations, however, must be developed by experience in using them; hence, the more familiar you become with the equations in this chapter, the easier to understand will be your next experience with them.

2. The Occurrence and Importance of Oxygen

Oxygen, although invisible, is probably the most familiar of the elements, because this element and its compounds play important parts in the life and environment of every living thing. For animals, it is the vitally necessary substance in the air, and for both plants and animals, it is one of the elements of which almost every compound in their structures is composed. Free oxygen plays an important part in many processes, such as the rusting of metals, decay, and the hardening of paints. The combustion of fuel to warm our houses, cook our food, and generate the energy required in industry also depends upon the reactions of this element.

About one-half of the earth's crust, including the atmosphere, consists of oxygen. Approximately sixty-five per cent of the weight of our bodies is oxygen. Rocks contain, on the average, about fifty per cent of the element, and cellulose, of which the woody structure of plants is largely composed, contains about the same percentage. Except for the free oxygen in the atmosphere, all of the element in these materials is in the form of compounds. It also occurs in combination with other elements in many ores and minerals, in all foods, and in cotton, wool, wood, water, and many other natural and synthetic materials.

HISTORY

3. Early Explanation of Combustion

Although oxygen is the most abundant of all the elements, many others were known long before it was discovered. The properties of the element, and even the fact that it is an element, have been known only since about the time of the American Revolution. However, some of the Chinese philosophers appear to have known as long

ago as 700 A.D. that air contains an active, and also an inactive, substance. Mayow, in 1669, explained combustion and respiration by assuming that air contains some gas that is actively involved in these processes. In the same year, however, Becher announced a theory to explain combustion in an entirely different manner, and in 1702, Stahl renewed and extended this theory. According to the opinions of these men, combustible substances contain "phlogiston," which is liberated during burning. It was argued that the residue left after the burning of a piece of wood, for example, weighs less than the unburned wood, and, therefore, that something *must* escape when a substance burns.

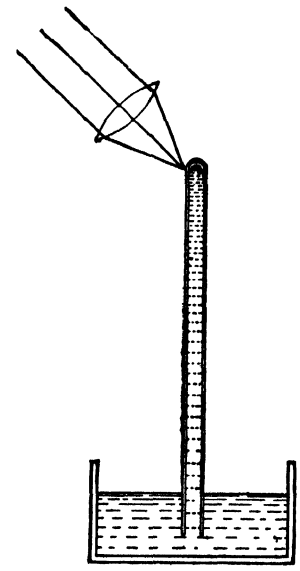


Figure 43. The Apparatus Used by Priestley in the Experiments by Which He Discovered Oxygen

4. The Discovery of Oxygen

Joseph Priestley, of England and later of America, is usually given the credit for the discovery of oxygen. About 170 years ago, he was interested in the gases that are liberated when different substances are heated. Priestley did not regard these gases as essentially different substances, but he thought of them as different kinds of air, or as samples of air possessing different properties. To liberate gases from the substances that he studied he employed a tube closed at one end, filled with mercury, and inverted in a dish or trough filled with the same liquid. The substance to be heated was introduced and made to float upon the surface of the mercury in the upper part of the tube (Figure 43). Here it was heated by converging upon it the rays of the sun by means of a lens. One of the substances that he heated in this manner was mercuric oxide. The gas liberated by heating this substance caused a candle to burn much more brilliantly and vigorously than ordinary air.

In preparing this gas, Priestley had discovered oxygen (1774), but he did not recognize the discovery. He explained the properties of the gas by saying that it was "dephlogisticated air." He believed that, the smaller the quantity of phlogiston already present in air, the more readily and vigorously the air would absorb phlogiston and, therefore, the more actively it would promote the burning of combustible materials. Priestley was an ardent believer in the phlogiston theory to the end of his life in 1804.

Scheele prepared the same gas from several substances in 1771. Although his discovery predates Priestley's, the latter is usually given the credit for discovering oxygen, because Scheele's results were not published until 1777. In the meantime, Priestley's discovery had been recognized.

5. Lavoisier's Explanation of Combustion

Lavoisier saw in Priestley's "dephlogisticated air" the probable explanation of combustion. He reasoned that, if a candle burns in the gas that is liberated when mercuric oxide is heated with the same effects as when the candle burns in air, then this gas is present in the air and is the component that causes substances to burn. He believed that this component of air *combines* with substances during combustion.

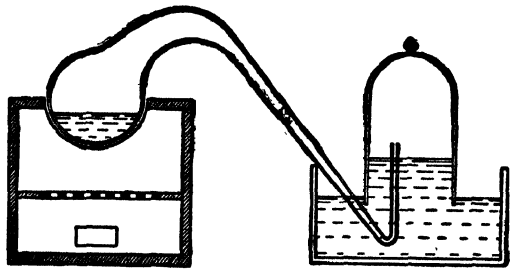


Figure 44. Lavoisier's Apparatus

According to this view, therefore, an *increase* in weight should be expected when one compares the weights of the products with the weights of the materials that burn.

To prove that his explanation was correct, Lavoisier heated mercury in a retort with air (Figure 44) for twelve days. The neck of the retort extended into a bell-jar, which was filled with air and inverted in a trough filled with water. It was found that the volume of air in the bell-jar and retort finally decreased by an amount equal to one fifth of the original volume, and that the surface of the mercury became covered with a red powder. The gas left in the bell-jar did not possess the properties of air; it did not support combustion and it did not sustain life. Furthermore, Lavoisier found that the red powder that formed on the surface of the mercury liberated a volume of gas, when it was heated, that was equal to the volume of air which disappeared when the powder was made. At the same time, sufficient mercury was produced to make up the loss in weight of the mercury when it was heated. The gas that was liberated possessed the properties lost by the sample of air during the heating of the mercury, but these properties were much more strongly manifested by the gas than by air. Lavoisier concluded, therefore, that in addition to this active gas, air contains another substance that is inactive in combustion and in similar chemical changes. He showed that air is a mixture, one part of which combines with certain metals, supports combustion, and is necessary for life.

There could no longer be any doubt that Priestley's "dephlogisticated air" was the same substance as this active component of air, which Lavoisier recognized as an element. Because he thought that all acids must contain this element, Lavoisier gave it the name of *oxygen*, which means "acid former." This view of acids is erroneous, but the name of the element has remained. Lavoisier called the inactive component of the air *azote*, a French word signifying the inability to support life. Its English name is *nitrogen*.

PRODUCTION

6. Preparation of Oxygen from the Air

When air is cooled to about −190° C. at the usual pressure of the atmosphere, or to somewhat higher temperatures under increased pressure, it can be condensed to a liquid. Cooling to this extremely low temperature is accomplished by allowing highly compressed air to expand through a small valve *E* (Figure 45) into a chamber where the pressure is lower. In expanding, a gas absorbs heat. In the apparatus used to liquefy air the heat absorbed comes from the coils that carry the compressed air, since the apparatus is thoroughly insulated to prevent the absorption of heat from the outside. The air that escapes from the valve at the end of the coil is returned through *D* to the compressor *A*, where it is again subjected to high pressure. It is then passed through coils *B* in a cold mixture of ice and salt to remove the heat resulting from the compression and, finally, is allowed to expand again. In this way, the air that escapes through the valve is gradually cooled, until at last it becomes a liquid.

When the temperature of liquid air is increased, the different substances that it contains change back again to the gaseous state. As the temperature rises, all the substances present in the liquid evaporate (change to vapor) but not at the same rate. Those that boil at the lower temperatures

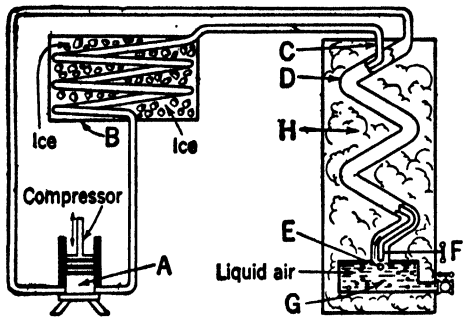


Figure 45. The Liquefaction of Air

A, compressor; B, cooling coils; C, pipe carrying compressed air; D, pipe carrying cold air back to compressor; E, expansion valve; F, valve handle; G, liquid air; H, insulation.

evaporate more rapidly than those that have higher boiling points. Approximately four-fifths of the air is nitrogen, the inactive component, which boils at − 195.8°. Oxygen boils at − 183°. Hence, as the temperature rises, the liquid loses nitrogen more rapidly than it does oxygen, and the residue becomes richer and richer in oxygen until, finally, it is nearly pure. Some nitrogen and small amounts of other components of air are still present. The oxygen thus prepared is nearly enough pure for most commercial purposes. It is allowed to evaporate, and the gas is compressed in steel cylinders. More nearly pure oxygen can be obtained by liquefying the gas once again and further separating the nitrogen by the evaporation process.

7. Preparation of Oxygen from Water

Water can be decomposed into oxygen and hydrogen by means of a direct current of electricity. Since pure water does not conduct the current, a small amount of sulfuric acid is added to make an excellent conductor. The two terminals of the electrical circuit, in the solution, are made of some inactive metal, such as platinum; they are called *electrodes* (Figure 46). Oxygen collects at the *anode* (positive electrode) of the cell, and hydrogen collects at the *cathode* (negative electrode). This reaction is called the *electrolysis* of water. It is a type of chemical decomposition in which electrical energy, instead of heat, is used. As the cell is operated, the sulfuric acid is not consumed, but water must be added to replace that which is converted into oxygen and hydrogen. The two gases are collected in separate containers and are, therefore, obtained in a nearly pure state. This method of producing oxygen is profitable when there is a good market for both hydrogen and oxygen. In general, it is not as extensively used as the production of oxygen from liquid air.

8. Preparation of Oxygen from Certain Substances Which Decompose when Heated

When small quantities of oxygen are desired in the laboratory, certain substances that contain oxygen can be decomposed, partially or completely, by heating. We have already noted Priestley's preparation of the element by heating the red powder called *mercuric oxide.* This substance con-

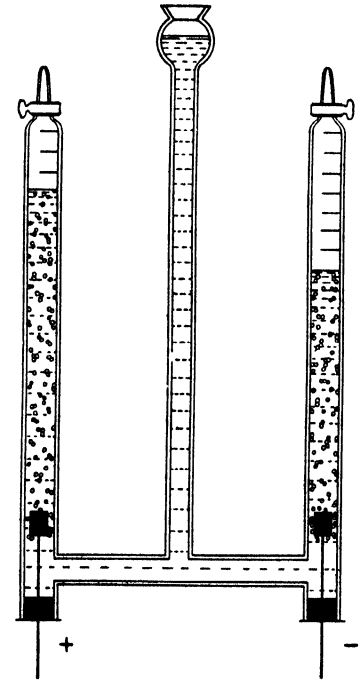


Figure 46. The Electrolysis of Water

tains 7.385 per cent of oxygen by weight.

Mercuric oxide ⟶ Mercury + Oxygen
2 HgO ⟶ 2 Hg + O_2.

Other oxides which do liberate all or a portion of the oxygen that they contain when they are heated, are barium peroxide, BaO_2, red lead, Pb_3O_4, and silver oxide, Ag_2O.

If potassium or sodium nitrate is heated, some oxygen is liberated and the nitrite of the metal is formed.

Potassium nitrate ⟶ Potassium nitrite + Oxygen
2 KNO_3 ⟶ 2 KNO_2 + O_2.

Only one third of the total oxygen content of potassium nitrate is liberated in this reaction. Potassium nitrate contains 47.52 per cent of oxygen, and potassium nitrite contains 37.7 per cent.

9. Preparation of Oxygen from Potassium Chlorate

Potassium chlorate contains 31.9 per cent of potassium, 39.2 per cent of oxygen, and 28.9 per cent of chlorine. It decomposes when it is heated to a temperature above its melting point (357° C.):

Potassium Chlorate ⟶
2 $KClO_3$ Potassium Chloride + Oxygen
2 KCl + 3 O_2.

Oxygen is liberated, and a white solid containing potassium and chlorine is left. This solid is potassium chloride, KCl. The reaction occurs at noticeable speed only when a moderately high temperature is reached. At temperatures below the melting point of potassium chlorate, oxygen may be liberated, but the speed of the reaction is very slow. The usual method of preparing and collecting samples of oxygen from potassium chlorate is shown in Figure 47. Since oxygen is only slightly soluble in water, it is collected by the displacement of water in a cylinder or bottle, which is first filled with water and placed in an inverted position on the shelf of the trough.

10. Manganese Dioxide as a Catalyst

If a little manganese dioxide, MnO_2, is mixed with the potassium chlorate and the mixture is heated, oxygen is liberated readily at a temperature (200°) considerably below the melting point of potassium chlorate. We may be certain that the oxygen liberated does not come from the manganese dioxide, because this substance can be heated at this temperature without decomposition. Furthermore, after the reaction is completed, the manganese dioxide can be separated from the potassium chloride in the residue by taking advantage of the fact that the latter is very soluble in water while the former is not; the quantity of manganese dioxide recovered in this way is equal to the amount originally added. We reach the conclusion, therefore, that manganese dioxide only increases the speed of the decomposition of potassium chlorate at relatively low temperatures and is not, itself, consumed during the reaction. A

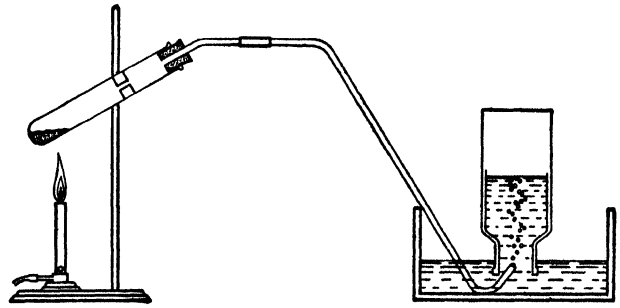


Figure 47. The Preparation of Oxygen from Potassium Chlorate

substance which influences the speed of the reactions of other substances, without undergoing any permanent chemical change itself, is called a *catalyst.*

11. Preparation of Oxygen from Sodium Peroxide

When sodium peroxide, Na_2O_2, is treated with water, oxygen is liberated by the following reaction:

Sodium peroxide + Water ⟶
$2\ Na_2O_2 + 2\ H_2O$
Sodium hydroxide + Oxygen
$4(Na^+ + OH^-) + O_2.$

Small samples of oxygen are sometimes prepared by this method.

12. A Note on the Equations Used Above

In discussing the preparation of oxygen from different compounds, we have used equations for the first time to express chemical facts. A few remarks concerning these equations may be appropriate at this time.

In the first of these equations — that dealing with mercuric oxide — the formula of this substance is written as HgO to indicate that it contains one atom of mercury for each atom of oxygen. Likewise, the formulas $KClO_3$, KCl, KNO_3, KNO_2, Na_2O_2, and NaOH show the relative numbers of atoms of the different elements that compose these compounds. Thus, in potassium chlorate there are three atoms of oxygen and one of chlorine for each atom of potassium. The number *2* written before the formula HgO indicates that twice as much of this substance as is indicated by the formula must be used to balance the equation. We also place the number *2* before the symbol of mercury (2 Hg), because two atoms of this element are liberated when we use 2 HgO. We do not write these atoms as Hg_2, because there are not two atoms of mercury in a molecule. It is necessary to write 2 HgO on the left-hand side of the equation, because two atoms of oxygen must be liberated; these are required to form one molecule, O_2, of oxygen, which is the smallest quantity of this substance that can exist in the free state. Similar explanations will account for the numbers of molecules or atoms of the different substances indicated in the other equations.

PROPERTIES AND USES

13. Physical Properties

Gaseous oxygen is 1.105 times as heavy as air. One liter, measured at 0° C. and at a pressure equal to the average pressure of the atmosphere at sea level, weighs 1.429 g.

Oxygen is colorless, tasteless, and odorless. In very thick layers it appears to be slightly blue in color. It can be liquefied at − 118° C. under a pressure fifty times greater than the pressure of the atmosphere and at lower temperatures by applying correspondingly lower pressures. Liquid oxygen is blue in color and, at atmospheric pressure, boils at − 182.97° C. It is attracted by a magnet. Solid oxygen, a light blue, snow-like substance, can be produced by special cooling methods. Its melting point is about − 218°.

Oxygen is only slightly soluble in water. At 20° C. and at atmospheric pressure, about 2 ml., and at 0° C., 5 ml., of oxygen dissolve in 100 ml. of water. Since oxygen is more soluble than nitrogen, dissolved air contains a larger percentage of it than ordinary air. Animals that live in water depend upon dissolved oxygen to supply their needs for this element.

14. Chemical Properties

At low temperatures, oxygen is only moderately active, i.e., it reacts only slowly, and often imperceptibly, with most substances with which it reacts very readily at higher temperatures. At higher temperatures, it combines with many of the elements. It does not combine directly with fluorine, chlorine, bromine, iodine, or with some of the least active metals, such as gold, silver, and platinum, but oxides of some of these elements can be made indirectly by decomposing compounds containing them and oxygen, or by using ozone (page 54) in place of ordinary oxygen.

The oxygen atom has six valence electrons (Figure 22, page 38) and therefore forms some compounds by acquiring two electrons, thus attaining the stable arrangement of the neon atom; i.e., an outside shell of eight electrons. It also forms other compounds by sharing electrons with other atoms. As an ion, oxygen exists as $O^{=}$ in oxides of some metals. It forms covalent compounds with hydrogen and other non-metals, such as carbon and sulfur. It does not exist as positively charged ions in any of its compounds.

15. Reactions with Metals

The most active metals, such as sodium and calcium, combine rather slowly with oxygen at low temperatures, but they burn brilliantly when heated in pure oxygen:

Sodium + Oxygen ⟶ Sodium Peroxide
$2\,Na + O_2 \longrightarrow Na_2O_2$
Calcium + Oxygen ⟶ Calcium Oxide
$2\,Ca + O_2 \longrightarrow 2\,CaO.$

Iron, which combines only very slowly with oxygen in the air to form ferric oxide (iron rust), Fe_2O_3, burns in pure oxygen, if it is heated to the required initial temperature, to form magnetic oxide of iron:

Iron + Oxygen ⟶ Magnetic Oxide of Iron
$3\,Fe + 2\,O_2 \longrightarrow Fe_3O_4.$

16. Hydroxides and Bases

The oxides of many of the metals dissolve only slightly, or not at all, in water, but some react with water to form *hydroxides*, which act as *bases* if they are soluble:

Sodium Peroxide + Water ⟶
$2\,Na_2O_2 + 2\,H_2O$
Sodium Hydroxide + Oxygen
$4(Na^+ + OH^-) + O_2$
Calcium Oxide + Water ⟶ Calcium Hydroxide
$CaO + H_2O \longrightarrow (Ca^{++} + 2\,OH^-).$

Solutions of both of these substances have a bitter taste, and they cause one's finger to feel "soapy," when the fingers are placed in the solutions and rubbed together. These properties are characteristic of solutions containing hydroxides of the active metals. Such solutions are frequently described as *alkaline*. They change the color of *litmus* from red to blue. Litmus is an *indicator*. Its color is blue in the presence of a basic substance, such as sodium hydroxide, and red in the solution of an acid, such as vinegar.

17. Reactions of Oxygen with the Non-Metals

Many of the non-metals, also, combine directly with oxygen. Sulfur, if it is first heated in a flame until it ignites, burns more brilliantly in pure oxygen than in air. Red phosphorus burns with a very brilliant flame, forming phosphorus pentoxide, P_4O_{10}, which appears as a dense white cloud of smoke. If carbon, in the form of charcoal, is first ignited, it continues to burn in pure oxygen and does so at a much faster rate than in air. Whenever carbon is completely burned, carbon dioxide (CO_2) is produced.

Sulfur + Oxygen ⟶ Sulfur Dioxide
$S + O_2 \longrightarrow SO_2$
Phosphorus + Oxygen ⟶ Phosphorus Pentoxide
$4\,P + 5\,O_2 \longrightarrow P_4O_{10}$
Carbon + Oxygen ⟶ Carbon Dioxide
$C + O_2 \longrightarrow CO_2.$

18. Acids

The oxides of the non-metals react with water to form *acids*.

$CO_2 + H_2O \longrightarrow H_2CO_3$, carbonic acid
$SO_2 + H_2O \longrightarrow H_2SO_3$, sulfurous acid
$P_4O_{10} + 6\,H_2O \longrightarrow 4\,H_3PO_4$, phosphoric acid.

The solutions formed when these oxides react with water show all the typical properties of acids. They change the color of blue litmus to red, and they possess a sour taste. Not all acids, however, contain oxygen.

19. Reactions of Oxygen with Compounds

In addition to its direct combination with elements to form oxides, oxygen also reacts with many *compounds*, sometimes to form the oxides of the elements contained in the compounds, and sometimes to produce other substances. Thus, many oxides are converted into "higher" oxides. The reactions of some of these oxides are shown in the following equations. These equations are left in an incomplete (unbalanced) form, so that the student may balance them (Exercise 7, page 57).

$$NO + O_2 \longrightarrow NO_2$$
$$Cu_2O + O_2 \longrightarrow CuO$$
$$FeO + O_2 \longrightarrow Fe_2O_3$$
$$SO_2 + O_2 \longrightarrow SO_3$$
$$P_4O_6 + O_2 \longrightarrow P_4O_{10}.$$

Oxygen also reacts with many other substances. The linseed oil in paint hardens partially because of a reaction of the oil with the oxygen in the air. Gasoline, which we may represent as heptane (C_7H_{16}), although it contains also several other compounds of similar composition, burns to form carbon dioxide and water in the presence of an excess of oxygen.

Gasoline + Oxygen ⟶ Carbon Dioxide + Water
$C_7H_{16} + 11\ O_2 \longrightarrow 7\ CO_2 + 8\ H_2O.$

When paper and wood, which are composed essentially of cellulose, burn, carbon dioxide and water are produced.

Cellulose + Oxygen ⟶ Carbon Dioxide + Water
$C_6H_{10}O_5 + 6\ O_2 \longrightarrow 6\ CO_2 + 5\ H_2O.$

20. The Uses of Oxygen

Pure oxygen has many uses, and its production constitutes an industry with an annual capacity of several billion cubic feet. Most of the oxygen — 95 to 97 per cent — used commercially is produced by the distillation of liquid air, and the remainder by the electrolysis of water.

Oxygen is used in the medical profession in treating cases of impaired respiration as in pneumonia. The oxygen tent is familiar equipment in many hospitals. It is also administered to patients who have breathed poisonous gases and whenever certain anaesthetics are used. Oxygen is used with acetylene in the oxyacetylene blowpipe for welding iron and steel during the construction of the steel framework of buildings, bridges, etc. The oxygen-hydrogen blowpipe is used for cutting steel beams and plates when structures are demolished. The metal is heated to incandescence by the blowpipe, the hydrogen is then shut off, and oxygen alone is used to burn the metal. Tanks of oxygen are carried in submarines to renew the oxygen in the air, and oxygen is also used by aviators who fly to very high altitudes, where the pressure is low, and the concentration of oxygen is small. Liquid oxygen and also liquid air are mixed with carbon dust and oil to produce an explosive used in coal mining and in certain other operations. Bombs containing liquid oxygen and charcoal, magnesium, and other combustible materials have been used in warfare with devastating effects.

OZONE

21. An Allotropic Modification of Oxygen

Shortly after the discovery of oxygen, experiments in which electric sparks were passed through the gas at ordinary temperatures resulted in the production of a new substance. In many respects this substance resembled oxygen; for example, it was found to form the same compounds. However, it possessed a peculiar odor; it was not stable; and it manifested much greater activity in chemical reactions than ordinary oxygen. It was named *ozone*, a name derived from the Greek word meaning "to smell." Careful study of its composition showed that this substance contained no other element, and it was decided, therefore, that ozone is merely a different form of oxygen. *Different*

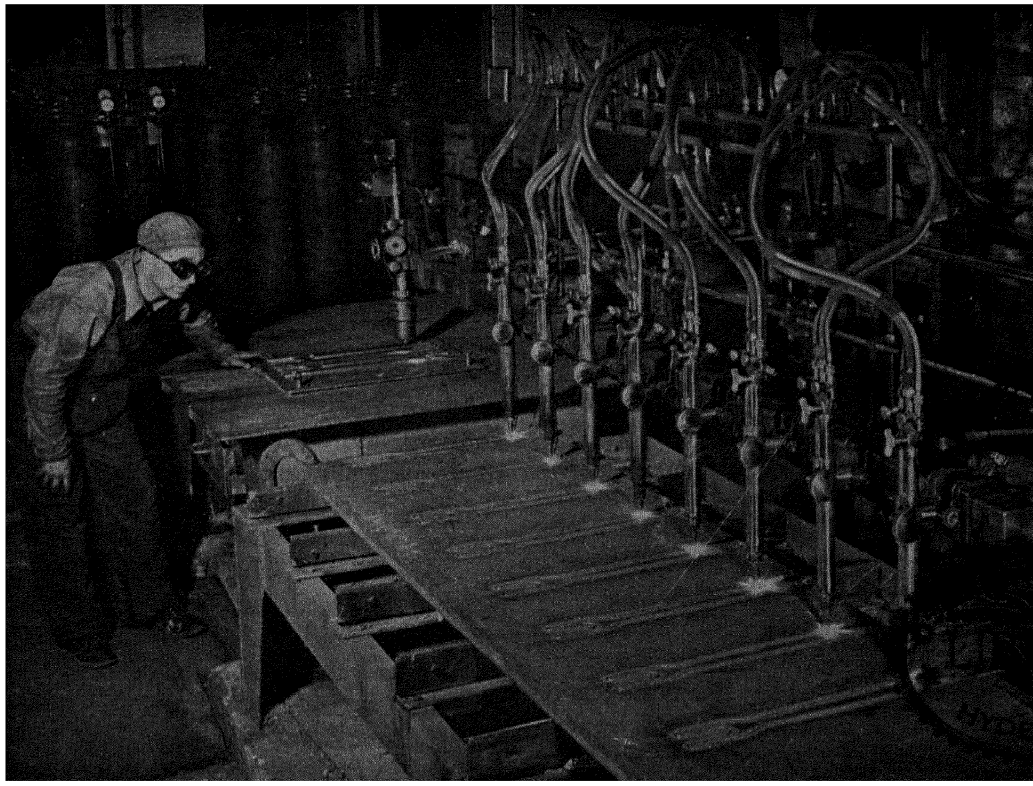


Figure 48. Eight Torches Mounted on a Bar for Cutting Purposes in a Multiflame Machine
(Courtesy of Air Reduction Sales Company)

forms of the same physical state of a substance are called allotropic modifications.

The molecule of ozone is represented by the formula O_3, while the molecule of ordinary oxygen is O_2. The change from oxygen to ozone involves, therefore, the addition of an atom of oxygen to each molecule. The behavior of ozone indicates that the added atom is rather loosely held.

22. Preparation

The equation for the reaction by which ozone is produced may be written as

$$68{,}440 \text{ calories} + 3\ O_2 \longrightarrow 2\ O_3.$$

The energy required for this reaction cannot be supplied in the form of heat, because ozone is not stable at elevated temperatures. Some other form of energy, therefore, must be used. The method ordinarily employed is one that involves the passage of oxygen or air between two plates or sheets of metal which are highly charged electrically. A silent electrical discharge takes place between the plates and across the space that is filled with oxygen or air. A common form of ozonizing apparatus is shown in Figure 49. The inner surface of the inner tube and the outer surface of the outer tube are covered with tin foil. These two layers of tin foil act as the metallic plates between which the discharge occurs. They are connected to an induction coil. The electrical discharge can be observed in a dark room as a pale blue glow within the apparatus. Only a small percentage of the oxygen passed through the apparatus is changed, ordinarily, into ozone. More is produced at lower temperatures. By using cold, dry oxygen yields of 6 to 20 per cent can be obtained.

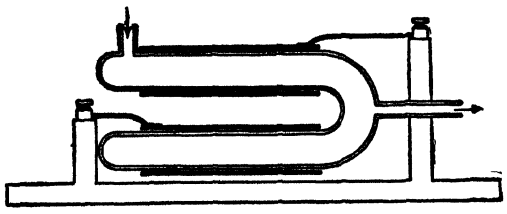


Figure 49. Apparatus Used to Produce Ozone by Means of an Electrical Discharge

23. Properties

Ozone is heavier than oxygen, one liter weighing 2.144 g. The gas has a pale blue color, and the liquid, which boils at − 112.3° C., is deep blue. The solid is black and melts at − 250° C. The chemical properties of ozone are similar to those of oxygen, except for its greater chemical activity. Some of the metals, such as silver and mercury, which are not affected by oxygen, are tarnished rapidly by the formation of their oxides when they are exposed to ozone. When ozone decomposes, it liberates some oxygen in the atomic form — as single atoms instead of molecules:

$$O_3 \longrightarrow O_2 + O.$$

Unless consumed in reactions with other substances, the single atoms immediately combine with others of their own kind to form molecules of O_2.

The rate at which ozone decomposes is greatly increased by elevated temperatures and by moisture. It is not likely, therefore, that the amount of ozone produced by lightning flashes during a storm ever becomes more than a mere trace in the atmosphere. Some of the ozone formed by the action of ultra-violet light in the upper regions of the atmosphere may penetrate to the earth's surface, but it is not likely that appreciable quantities often do so. Near the earth's surface there are about two parts of ozone per hundred million parts of air.

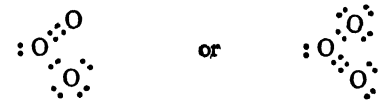
Ozone is usually detected by its characteristic odor. It is also detected by means of a strip of filter paper that has been moistened with a solution of potassium iodide and starch. Ozone reacts with potassium iodide to liberate iodine (displacement of iodine by oxygen). The free iodine then gives a blue color with the starch.

24. Uses

Ozone, or air containing varying amounts of ozone, has a number of uses, all of which depend upon its action as an oxidizing agent. When ozone reacts with certain colored materials, it changes them into colorless products. This action is called *bleaching*. Cloth, flour, waxes, starch, and other materials are sometimes bleached in this manner. Ozone is sometimes used to improve the taste and to sterilize drinking water. It is also used as a disinfectant and deodorant. Because of the difficulty of producing it, the cost is high, and its uses are limited. It is sometimes used in "curing" or "seasoning" wood, leather, and tobacco and in the manufacture of certain organic compounds, such as synthetic, or artificial, camphor.

25. Structures of Different Forms of Oxygen

If we neglect the electrons of the oxygen atom, except the six that lie in the outermost group, we may represent the atom as $:\dot{\underset{\cdot\cdot}{O}}\cdot$, and the molecule as $\dot{\underset{\cdot\cdot}{O}}::\dot{\underset{\cdot\cdot}{O}}\cdot$. There is, however, stronger justification for $:\dot{\underset{\cdot}{\overset{\cdot\cdot}{O}}}:\dot{\underset{\cdot\cdot}{O}}:$ as the structure of the molecule, because the unpaired electrons of this arrangement explain the activity of oxygen and certain of its properties more satisfactorily than the other arrangement of electrons. Ozone is thought to have the structure



26. Resonance

Two possible structures are shown for ozone in the paragraph above because it appears that there is no difference between

the bonds that join the two end-atoms of oxygen to the one in the middle. It is thought that in a given molecule first one arrangement exists and then the other, i.e., the oxygen bond consisting of two electron pairs changes to a bond consisting of one electron pair and *vice versa*. This change occurs very rapidly; and hence, in a sample of ozone at a given instant one half of the molecules have one structure, and the other half have the second structure. It is said that the bond consisting of two pairs of electrons *resonates* between the two possible positions that it may occupy. Similar examples of resonance are found in the structures of many other substances.

REVIEW EXERCISES

1. Describe the contributions of Priestley, Scheele, and Lavoisier to the early history of oxygen.
2. Why did Priestley call the gas that he prepared "dephlogisticated air"?
3. How did the phlogiston theory differ from the modern explanation of combustion?
4. Name four compounds from which oxygen can be prepared, and describe the method used in each case.
5. How does the presence of manganese dioxide influence the production of oxygen from potassium chlorate? How could you show that it produces no oxygen itself during the reaction?
6. What weight of oxygen could be obtained from 1000 g. of potassium chlorate? What volume would this weight of oxygen occupy? (The data required for this and other problems in this list will be found in this chapter. The density of oxygen, page 52, is the weight of a liter of the gas, measured at 0° and the average pressure of the atmosphere at sea level. This value varies with the temperature and pressure, but we shall not consider such variations at this time.)
7. Complete the equations on page 54.
8. Following the examples given on page 54, write equations for the combustion of the following substances (in the air): nonane, C_9H_{20}; methyl alcohol, CH_3OH; and acetone, C_3H_6O. Check each equation to see that it is balanced correctly.
9. What difference between the metallic and the non-metallic elements has been described in this chapter.
10. Since oxygen combines with so many elements, how do you account for the large amount of it that remains uncombined in the atmosphere?
11. Compare the weights of mercuric oxide, potassium nitrate, and potassium chlorate that would be required to produce 100 liters of oxygen. (Consider the weight of one liter of oxygen as 1.429 g.)
12. If mercuric oxide costs $1.75 per pound, potassium nitrate $0.20, and potassium chlorate $0.25, which compound would be the cheapest source of oxygen for laboratory experiments?
13. A mixture consisting of 10 g. of manganese dioxide and 50 g. of potassium chlorate is heated until the liberation of oxygen by potassium chlorate is complete. What is the weight of the residue in the container? Of what substances is it composed?
14. What volume of oxygen can be produced by the electrolysis of 50 g. of water?
15. Why will water not burn?
16. How does ozone differ from ordinary oxygen in composition and properties?
17. Define: allotropic modifications of an element.
18. How is nearly pure nitrogen obtained from liquid air?
19. How would you determine whether a sample of a gaseous substance was oxygen *or* ozone?
20. Why is potassium chlorate not used as a commercial source of oxygen?
21. The basis of our scale of atomic weights is 16 for the weight of an atom of oxygen. Why does the use of 16 for this purpose give slightly inaccurate values for the atomic weights of all the other elements?

REFERENCES FOR FURTHER READING

Dampier-Whetham, W. C., *A History of Science.*
Findlay, A., *The Spirit of Chemistry.*
Jaffe, B., *Crucibles.*

Leonard, W., *Crusaders of Chemistry*. New York: Doubleday, Doran and Company, 1930.
Moore, F. J., *History of Chemistry*.
Priestley, J. B., *The Discovery of Oxygen*, Alembic Club Reprint, No. 7, part 1. Edinburgh: E. and S. Livingstone, 1775.
Scheele, C. W., *The Discovery of Oxygen*, Alembic Club Reprint, No. 8, part 2. 1777.
Weeks, M. E., *The Discovery of the Elements*.
History of Oxygen: *J. Chem. Ed.*, **4,** 141 (1927); **13,** 403 (1936); **27,** 83 (1950).
Liquid Air: *J. Chem. Ed.*, **8,** 1027 (1931).
Liquid Oxygen Explosives: *Ind. and Eng. Chem., News Ed.*, **18,** 1114 (1940).
Manganese Dioxide: *J. Chem. Ed.*, **9,** 1111 (1932).
Ozone: *J. Chem. Ed.*, **8,** 2429 (1931); **9,** 291 (1932); *Ind. and Eng. Chem., Analytical Ed.*, **17,** 8 (1937).
Production of Oxygen: *Chem. and Met. Eng.*, **29,** 276 (1923); **30,** 181 (1924); Bureau of Standards, *Jour. of Research*, **22,** 301 (1939).
Uses: *Chem. and Met. Eng.*, **29,** 264, 272, 276 (1923); *J. Chem. Ed.*, **19,** 91 (1942); **24,** 145 (1947).

5

COMBUSTION, OXIDATION, AND REDUCTION

1. Introduction

This chapter is concerned with the nature of the chemical changes that occur in combustion and with other slower, but similar, reactions, such as the rusting of a piece of iron, or the decay of a piece of wood. These reactions are changes with which all of us have some acquaintance, even before we begin the study of chemistry. Many other reactions, less familiar in everyday life, but even more familiar to the worker in a chemical laboratory than combustion, rusting, and decay, involve similar changes in the atoms, molecules, and ions of different substances.

2. Oxidation and Combustion

All the reactions in which oxygen combines with other elements, or in which compounds react with oxygen, may be included under the general term of *oxidation*, and some of them, if sufficiently vigorous, may be classified as *combustion*. Oxidation is a more general term than combustion. Thus, iron is slowly oxidized when it rusts, and it is also oxidized when it burns brilliantly in pure oxygen. *Combustion may be defined as rapid oxidation attended by the emission of heat and light.* Slow oxidation also results in the liberation of heat in some reactions, although in others energy may actually be absorbed; if heat is evolved it is not liberated rapidly enough to heat the burning substance to incandescence.

The terms oxidation and combustion may also be applied to many reactions in which oxygen does not participate. If iron is exposed to the action of moist chlorine, it combines with that element to form ferrous chloride or ferric chloride, $FeCl_2$ or $FeCl_3$. If heated and if finely enough divided, it may even *burn* in pure chlorine, forming the same compounds. Finely divided zinc and sulfur react vigorously to form zinc sulfide when a mixture of them is heated. The reaction liberates heat and light and closely resembles the burning of paper or wood in air or pure oxygen. A stream of hydrogen gas, when ignited, burns in chlorine to form hydrogen chloride just as it does in oxygen to form hydrogen oxide (water). These reactions involve oxidation as truly as the combinations of iron and zinc with oxygen to form oxides.

In arriving at a proper definition for oxidation, we must note, also, that certain compounds in which an element is already combined with oxygen, or with some other non-metallic element such as chlorine or sulfur, may combine with more of the same element. Thus, carbon reacts with oxygen, when the supply of oxygen is limited, to form carbon monoxide (CO). This substance may react with more oxygen to form carbon dioxide (CO_2). Similarly, iron reacts with chlorine to form ferrous

chloride ($FeCl_2$) and, in the presence of sufficient chlorine, this compound is converted into ferric chloride, $FeCl_3$.

We must note, too, that the oxygen, chlorine, or some other non-metal that takes part in the oxidation need not be in the free state; it may be already combined with other elements. Thus, magnesium, if heated in the presence of steam, burns brilliantly. In this reaction magnesium reacts with the oxygen of water to form magnesium oxide, MgO, and the hydrogen of the water is set free.

3. Definition of Oxidation in Terms of Electron Transfers; Oxidizing Agent

As the term was first used, oxidation referred to all reactions in which oxygen combined with other elements, or in which it reacted with compounds (page 54). As indicated in the preceding paragraphs, its use has been greatly extended, however, to include many reactions in which oxygen has no part. There are certain respects in which all these reactions that are now classified as oxidation are similar. What one change, or kind of change, occurs in each of them?

Let us consider two simple reactions of calcium (1) with oxygen and (2) with chlorine. When this metal is slightly heated and placed in pure oxygen, its atoms react readily with atoms of oxygen in the ratio of one to one, forming calcium oxide:

$$(1) \qquad 2\,Ca + O_2 \longrightarrow 2\,CaO.$$

Now to understand exactly what atomic changes are involved in this reaction let us picture the reaction, as we have similar changes (page 40), to show the transfer of electrons from the calcium atom to the oxygen atom, because calcium oxide is an ionic compound. We note that two electrons are transferred from the calcium atom to the oxygen atom:

$$Ca + O \longrightarrow Ca^{++} + O^{=}.$$

A similar change occurs when calcium reacts with chlorine:

$$(2) \qquad Ca + Cl_2 \longrightarrow Ca^{++} + 2\,Cl^{-}.$$

The only difference is that the chlorine atom with seven electrons already in its outermost group can accept but one more electron, and, therefore, two atoms of chlorine are required to remove both of the electrons from the atom of calcium.

Both of these reactions are examples of the oxidation of calcium. Now what single change occurs in each reaction? Evidently, it is *the removal of electrons from the calcium atom.*

Other examples of oxidation are represented by the following equations:

$$(3)\ Fe + (Cu^{++} + 2Cl^{-}) \longrightarrow (Fe^{++} + 2Cl^{-}) + Cu.$$
$$(4)\qquad Fe + S \longrightarrow (Fe^{++} + S^{=}).$$
$$(5)\ Ca + 2\,(H^{+} + Cl^{-}) \longrightarrow (Ca^{++} + 2\,Cl^{-}) + H_2.$$

In these reactions iron and calcium are oxidized, because electrons are removed from their atoms by copper (3), sulfur (4), and hydrogen (5). Iron is also oxidized in the following reaction:

$$(6)\ 2\,(Fe^{++} + 2\,Cl^{-}) + Cl_2 \longrightarrow 2\,(Fe^{+++} + 3\,Cl^{-}),$$

because each iron atom, although it has already lost two electrons, loses another one to chlorine.

In all these reactions the element whose atoms or ions lose electrons is oxidized, and the element whose atoms or ions acquire electrons acts as the oxidizing agent.

4. Reduction and Reducing Agents

Reactions in which atoms or ions acquire electrons are classified as *reduction.* In all such reactions other atoms must lose electrons; and hence, every reaction that involves the reduction of one substance also involves the oxidation of another. The substances that supply the electrons acquired by the reduced atoms or ions are called the *reducing agents.* In the reaction with oxygen, (1) above, calcium is the reducing agent, because each atom of it that

reacts supplies two electrons to an atom of oxygen. Oxygen is reduced. In reactions (3), (4), (5), and (6) of Section 3, Cu^{++}, S, H^+, and Cl_2 are reduced, and Fe, Fe, Ca, and Fe^{++} are the reducing agents, respectively.

5. Oxidation and Reduction in Terms of Changes in Oxidation Numbers

In dealing with reactions in which the same element has different valence numbers, or exists in different states of oxidation, it is common practice to use the term *oxidation number* in place of valence number. This is a positive number if atoms of the element lose electrons and negative if they gain electrons. Thus, in reactions (1), (2), and (5) (page 60), calcium acquires an oxidation number of +2. In reactions (3) and (4) iron acquires an oxidation number of +2, and in (6) this number is increased to +3.

The valence number and, likewise the oxidation number of a free, or uncombined element is 0 (page 43). Therefore, the oxidation number of oxygen in the reaction

$$2\ Ca + O_2 \longrightarrow 2\ (Ca^{++} + O^{=})$$

is *reduced* from 0 to − 2, and in the reaction

$$Ca + Cl_2 \longrightarrow (Ca^{++} + 2\ Cl^-)$$

the oxidation number of chlorine is reduced from 0 to − 1. In the following reaction, however, chlorine is oxidized:

$$2(Na^+ + Cl^-) + F_2 \longrightarrow 2(Na^+ + F^-) + Cl_2.$$

The oxidation number of chlorine is increased from − 1 to 0, and that of fluorine is reduced simultaneously from 0 to − 1.

Refer once more to reaction (3), page 60,

$$Fe + (Cu^{++} + 2\ Cl^-) \longrightarrow (Fe^{++} + 2\ Cl^-) + Cu.$$

In this reaction the oxidation number of iron is increased from 0 to + 2; that of copper is reduced from + 2 to 0; and chlorine's number is unchanged. Iron is oxidized and copper (more exactly, cupric ion) is reduced;

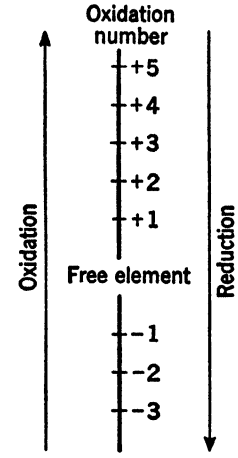


Figure 50. Changes in Oxidation Numbers by Oxidation and Reduction

iron is the reducing agent and copper (ion) is the oxidizing agent.

We may define oxidation as a reaction in which the oxidation number of an element is increased in the positive direction, as from +2 to +3, 0 to +2, −2 to 0, −2 to +2, and so on; reduction on the other hand occurs when the oxidation number changes in the opposite direction, i.e., in the direction of smaller positive or larger negative numbers as from +3 to +2, +2 to 0, 0 to −1, −1 to −2, and so on.

The elements of compounds in which atoms are held together by covalent, or electron-pair, bonds can also be assigned positive and negative oxidation numbers but only in a somewhat arbitrary manner, since the parts of such compounds are not positively and negatively charged. Positive numbers are assigned to the elements whose atoms have the weaker attraction for electrons (page 41), and negative numbers to those that have stronger attraction for electrons. In general, we may say that, in a compound of two elements that are combined by atoms sharing electrons, the element whose atoms contain the larger number of electrons in the outermost group has greater attraction for electrons and a negative oxidation number. Thus, in CCl_4, the chlorine atom contains seven

and the carbon atom four electrons in this group; and hence, the oxidation number of carbon is +4 and that of chlorine is −1. In SO_2 and SCl_4 the number for sulfur is + 4; in H_2S it is −2; in SO_3 it is + 6; and in CS_2 it is − 2. Therefore, when H_2S is converted into free sulfur (1), sulfur dioxide (2), or sulfur trioxide (3), the oxidation number of sulfur is increased from − 2 to 0, + 4, and + 6, respectively, and in each reaction sulfur is oxidized:

$$(1)\ 2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$
$$(2)\ 2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$
$$(3)\ H_2S + 2\,O_2 \longrightarrow H_2O + SO_4.$$

COMBUSTION

6. Kindling Temperature

Different substances must be heated to different temperatures before they ignite and continue to burn without further supply of heat from an outside source. Gasoline ignites at a lower temperature than kerosene, and kerosene at a lower temperature than motor oil. Ether ignites at a lower temperature than alcohol. Matches coated with paraffin, which ignites at a lower temperature than wood, are more easily ignited than matches not thus treated. The paraffin ignites soon after the head of the match is "struck"; heat is liberated; the temperature rises; and finally the *kindling temperature* of the wood is reached. The kindling temperature, *at which a substance bursts into flames and combustion proceeds without further application of heat,* is not a definite temperature. It varies considerably depending upon the state of division of the substance.

7. Spontaneous Combustion

When a substance oxidizes slowly, just as much heat is liberated as when the same weight of the substance burns quickly. The temperature of substances that undergo slow oxidation usually does not become very high, however, because heat is liberated slowly, and the surroundings absorb it as rapidly as it is released. If slow oxidation occurs, however, under conditions that do not allow the heat to be removed as rapidly as it is liberated, the temperature slowly rises. With the rise in temperature, the oxidation rate also increases, and heat is liberated more rapidly. Eventually, the kindling temperature of the substance is reached and *spontaneous combustion* results. Rags soaked in linseed oil or in certain other oils often ignite spontaneously. The oil is oxidized slowly, and because of the poor thermal conductivity of the rags, especially if they are in a heap, the temperature of the mass increases. At higher temperatures, the oil oxidizes more rapidly, raising the temperature of the rags to a still higher point, and so on, until the mass reaches the kindling point and, suddenly, bursts into flame.

The slow oxidation of coal results in great losses. This is especially true of finely divided bituminous, or soft, coal. If the coal is stored in thin layers, the heat is lost rapidly. Under improper storage conditions, however, heat accumulates, and spontaneous combustion frequently results. To prevent spontaneous combustion, fine coal should not be mixed with lump coal, and it should be stored in thin layers.

8. Flame

The combustion of many, but not all, substances is accompanied by flames. Wood and coal, especially bituminous or soft coal, produce flames when they burn, but charcoal and coke do not. Flames are burning gases. When wood or soft coal is heated to the kindling point, or even before that temperature is reached, combustible gases, or vapors, are liberated. These substances usually ignite at a lower temperature than the residue of wood or coal, and their combustion produces the effect that we call flame. Charcoal is made from wood, and coke from coal, by heating wood

or coal in the absence of air to prevent combustion. During the period of heating, volatile substances escape, and a residue consisting, in each instance, principally of carbon remains. When charcoal and coke burn, therefore, no combustible vapors are liberated, and there is no flame.

CONDITIONS WHICH INFLUENCE THE RATE OF OXIDATION AND OTHER TYPES OF REACTIONS

9. The Conditions

Warm milk becomes sour more quickly than milk in a refrigerator. Powdered coal oxidizes more rapidly than lumps. Substances burn in pure oxygen more vigorously and more rapidly than in air. Finely divided platinum will cause a mixture of hydrogen and oxygen at ordinary temperatures to react explosively. These four statements call attention to four conditions that affect the speed of oxidation and other reactions: *Temperature*, *concentration*, *catalysts*, and the *state of division* or amount of surface exposed. Warm milk becomes sour more rapidly than cold milk, because the chemical change that is involved occurs much more rapidly at the higher temperature; powdered coal oxidizes more rapidly than lumps, because more surface is exposed to the action of the oxygen in the air by the fine particles than by the lumps; platinum catalyzes the oxidation of hydrogen by oxygen; and oxidation is more rapid in pure oxygen than in air, because the former is more concentrated than the latter. In addition to the four conditions mentioned, the chemical nature of substances — the structures of their atoms and molecules and the quantities of chemical energy that they contain — also play important parts in determining the velocities of their reactions.

10. Effect of Temperature

In general, the speed of a reaction is doubled for a rise of 10° in the temperature of the reacting substances. If the same rule holds for very low temperatures, a reaction that is completed in two minutes at 20° would require about seven and one half years for completion at − 180°, a temperature which can be reached by means of liquid air. At least a part of the change in velocity is easy to understand, if the reacting substances are made up of moving molecules. The velocities of the molecules are increased as the temperature rises; and hence, at a higher temperature the molecules meet more frequently, and more molecules participate in the reaction in a given period of time than do at a lower temperature. The whole effect of temperature cannot be explained in this manner, but we shall postpone a fuller discussion of the subject until a later chapter.

11. Effect of Concentration

Pure oxygen supports combustion more rapidly than air, because four fifths of the air is nitrogen, which takes no part in the reaction. We say that the *concentration* of oxygen is smaller in air. Concentration is a measure of the number of molecules of a substance in a definite unit of volume, such as the cubic centimeter or the liter. Naturally, the more molecules of a reacting substance in a given volume, the greater will be the number of these molecules that react with the molecules of another substance in a definite period of time.

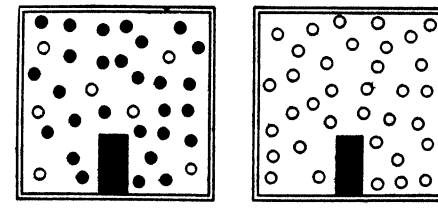


Figure 51. The Effect of the Concentration of Oxygen Upon the Rate at Which a Substance is Oxidized

In air (left) only one fifth of the molecules surrounding the oxidizable substance are molecules of oxygen; in the other case, all the molecules are capable of supporting oxidation.

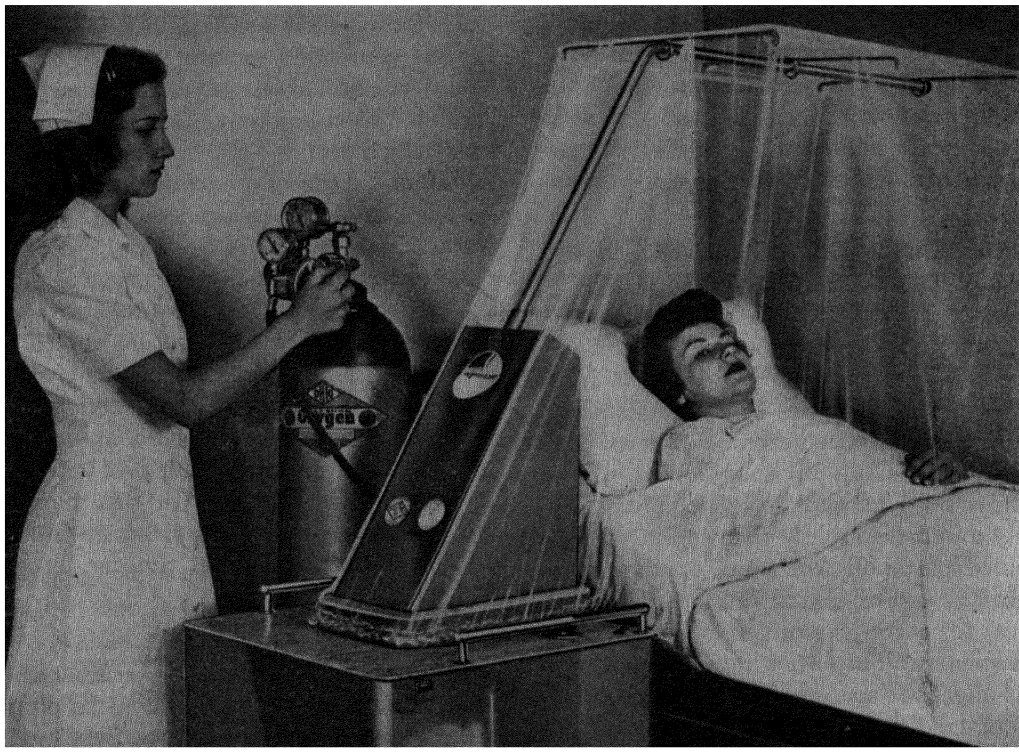


Figure 52. An Oxygen Tent
(Courtesy of the Ohio Chemical and Manufacturing Company)

12. Effect of Catalysts

The effect of platinum upon the reaction of hydrogen and oxygen, and similar effects of other substances on other reactions, is called *catalysis*, and the agent producing the effect is a *catalyst* (page 51). A catalyst does not start a reaction; it merely changes the reaction's velocity. Many reactions occur so slowly at low temperatures, however, that no change is perceptible. By use of the proper catalyst, such a reaction may be increased in velocity, without changing the temperature or other conditions, and the effects of a reaction that otherwise does not appear to occur, because it is so slow, become very noticeable.

Some substances retard certain reactions and are, therefore, called ***inhibitors*** or ***retarders***. Thus, certain substances added to rubber articles retard the oxidation of rubber and prevent the effects of oxidation — hardness and brittleness.

13. Effect of State of Division

When substances — liquids and solids — are finely divided into small grains, threads, or drops, the amount of surface is greatly increased. This increase in surface permits better contact and, hence, more chances of reaction than are possible when the same substances are used in coarser states of division. Many examples can be cited to show this effect. Shavings, splinters, or kindling burn much more rapidly than the same quantity of wood in the form of a log. Lumps of coal burn slowly, but a mixture of coal dust and air can be exploded with a spark or small flame. This is the cause of

many mine explosions. Similar explosions sometimes occur in flour mills, or wherever finely divided combustible materials of any kind are mixed with air.

14. How Oxygen is Used and Transported in the Body

Much of the energy of the human body is derived from the oxidation of various substances. Some of the food taken into the body may be oxidized directly, some may be stored for future use, and the remainder may be used to build up tissues to replace those that have grown old and have been broken down. Waste tissues, also, are oxidized to form soluble substances that can be eliminated readily from the body. A large part of the energy that is released during these oxidation processes is used to maintain the proper temperature of the body.

Oxygen passes into the blood in the lungs, first dissolving in the water that wets the membranes. In the blood, oxygen combines with *hemoglobin*, producing red *oxy-hemoglobin*, which is responsible for the color of the blood in the arteries. In this form it is carried to the various parts of the body, where it is consumed in oxidation reactions, and the blood now containing hemoglobin, carbon dioxide, and other products of oxidation returns, through the veins, to the lungs. There it liberates carbon dioxide and collects another supply of oxygen. Water and other oxidation products are eliminated through the kidneys.

Sugar and fat must be heated to a temperature far above that of the body before they ignite and burn in the air or, indeed, before any observable change occurs. Within the body, they are oxidized at a temperature of 37°–38° C. It is believed that certain substances which occur in small amounts in the animal body accelerate the speed of oxidation at the relatively low temperature of the body.

REVIEW EXERCISES

1. Define: Oxidation, reduction, combustion, kindling point, spontaneous combustion.
2. Paper is composed largely of cellulose, $C_6H_{10}O_5$, in which the carbon and hydrogen are already combined with oxygen. How can paper burn, if burning means that these elements combine with more oxygen?
3. Why can this reaction (question 2) properly be called oxidation?
4. Using the term oxidation as it is defined in this chapter, show that each of the following reactions is an example of oxidation:
   Steam (H_2O) + Carbon (C) → Carbon monoxide (CO) + Hydrogen (H_2).
   Iron (Fe) + Cupric Chloride (Cu^{++} + 2 Cl^-) → Ferrous Chloride (Fe^{++} + 2 Cl^-) + Copper (Cu).
   Iron (Fe) + Sulfur (S) → Ferrous Sulfide (FeS).
5. Name the oxidizing agent and the reducing agent in each of the reactions of question 4.
6. How do fires sometimes originate spontaneously in barns filled with hay? Why will hay that is very wet not ignite in this way?
7. State the meaning of the term concentration and show how the concentration of oxygen affects the rate of combustion.
8. Why does powdered coal when mixed with air burn more rapidly than large lumps of coal?
9. For what purpose and in what manner is oxygen used in the body? Where do the chemical changes involving oxygen occur?
10. How is oxygen transported from the lungs to the different parts of the body?
11. Discuss the accuracy of the following statement: Oxidation is a reaction in which oxygen combines with a substance.
12. When tin, Sn, reacts with chlorine, stannic chloride is produced; tin is oxidized by chlorine. How does this statement agree with the general definition of oxidation?
13. Oxidizing agents are added as ingredients in fireworks and matches. What purpose do they serve?
14. Why does coke burn without a flame? What is a flame?

15. Refer to Figures 22 and 30. Which element should be designated as the one that is oxidized when sulfur and oxygen react to form sulfur dioxide, SO_2?
16. How can the spontaneous combustion of powdered coal or oily waste be prevented?
17. When wood burns, energy is released as heat. What was the original source of this energy?
18. Why does fanning a fire cause combustion to proceed more vigorously?
19. How does water aid in extinguishing a fire?
20. Why does closing the damper below a fire in a stove reduce the rate of combustion of fuel?
21. When gas is ignited at the end of a tube, why does the gas in the tube not burn?
22. Why is an electric lamp a safer source of light in a dusty coal mine than a candle flame?
23. What increase in surface would result from splitting a block of wood measuring 3 in. by 3 in. by 3 in. into two blocks each measuring 3 in. by 3 in. by $1\frac{1}{2}$ in.?
24. What changes in oxidation numbers, if any, occur in the following reactions?

    (*a*) $H_2S + I_2 \rightarrow 2\,(H^+ + I^-) + S$.
    (*b*) $2\,Sb + 3\,Cl_2 \rightarrow 2\,(Sb^{+++} + 3\,Cl^-)$.
    (*c*) $(2\,Na^+ + S^=) + 2\,(H^+ + Cl^-) \rightarrow 2\,(Na^+ + Cl^-) + H_2S$.
    (*d*) $(Sn^{++} + 2\,Cl^-) + Cl_2 \rightarrow (Sn^{++++} + 4\,Cl^-)$.
    (*e*) $2\,H_2S + 4\,O_2 \rightarrow 2\,H_2O + 2\,SO_3$.
    (*f*) $(Fe^{++} + 2\,Cl^-) + H_2S \rightarrow Fe\,S + 2\,(H^+ + Cl^-)$.
    (*g*) $2\,(Fe^{+++} + 3\,Cl^-) + 3\,H_2S \rightarrow 2\,FeS + S + 6\,(H^+ + Cl^-)$.

REFERENCES FOR FURTHER READING

Faraday, M., *Chemical History of a Candle.* New York: E. P. Dutton and Company, 1933.
Foster, W., *The Romance of Chemistry.*
Catalysts: *Ind. and Eng. Chem.*, **32,** 1189 (1940).
Dust Explosions: *J. Chem. Ed.*, **3,** 1108 (1926).
Spontaneous Combustion: *Ind. and Eng. Chem.*, **17,** 115 (1925).

6

HYDROGEN

1. Introduction

This chapter deals with the history, occurrence, methods of preparation, properties and uses of hydrogen. In addition, three other topics of considerable importance are introduced in this chapter: (1) The differences in activity of the metals and the table in which they are arranged to show these differences; (2) additional examples of reduction and the difference between oxidation and reduction; and (3) a reversible reaction.

2. History

It is sometimes said that hydrogen was discovered by Henry Cavendish, who produced it in 1766 by the action of acids upon certain metals and by the action of steam upon iron. It can scarcely be said, however, that he discovered the element, because the reactions of metals and acids had been observed many times by the alchemists, who looked upon the gas produced by these reactions as a special kind of air. Paracelsus, for example, in the early part of the sixteenth century, treated iron with sulfuric acid and observed that "air" arose from the mixture and "burst forth like a wind." In the early eighteenth century, hydrogen was thought to be phlogiston, the "substance" that was said to escape from materials during combustion.

The gas produced in his experiments was called "inflammable air" by Cavendish. He recognized that it was different, in many respects, from other kinds of "air," but he did not realize that he had prepared an element. Lavoisier showed that Cavendish's "inflammable air" is a constituent of water and that it is an element. He suggested the name *hydrogen*, which signifies "water former."

3. Occurrence

Unlike oxygen, hydrogen is seldom found free in nature, at least not on or near the earth. Only minute traces are found in the lower atmosphere. The gases from volcanoes contain small amounts, and some, usually 0.5 per cent or less, is found in natural gas. It is believed that considerable quantities of hydrogen are present in the extreme upper altitudes of the earth's atmosphere. It also appears in the sun and in many of the stars. At the time of an eclipse, long streamers of flaming hydrogen can be observed around the sun. These extend out from the sun's atmosphere one hundred thousand miles or more into space.

The compounds of hydrogen are relatively abundant, although only about one per cent of the weight of the earth's crust consists of the element. The small percentage (by weight) of hydrogen is explained by the very small mass of the hydrogen atom. Water contains approximately one gram

of hydrogen for every 8 grams of oxygen. Hydrogen is found in combination with carbon in natural gas, in petroleum, and in products, such as gasoline, kerosene, and motor oils, which are obtained from petroleum. It is also found in combination with carbon, oxygen, and a few other elements in substances produced by, or associated with, living things. Cellulose, $C_6H_{10}O_5$, and sucrose (sugar), $C_{12}H_{22}O_{11}$, are examples of such compounds. It is present in all the tissues of our bodies and in all our foods. In organic compounds, it is almost as important as carbon, and is found, therefore, in almost all fats, oils, alcohols, proteins, soaps, dyes, drugs, explosives, perfumes, and flavors. Hydrogen is also present in acids and in hydroxides (page 53).

PREPARATION OF HYDROGEN

4. Action of Metals upon Acids

All acids contain hydrogen, and from aqueous solutions of some of them hydrogen is liberated by the action of certain metals. Typical reactions of this kind are shown by the equations below.

$$2\ Na + 2\ (H^+ + Cl^-) \longrightarrow 2\ (Na^+ + Cl^-) + H_2$$
$$Zn + 2\ (H^+ + Cl^-) \longrightarrow (Zn^{++} + 2\ Cl^-) + H_2$$
$$Mg + (2\ H^+ + SO_4^{=}) \longrightarrow (Mg^{++} + SO_4)^{=} + H_2.$$

The only actual reaction occurring in these mixtures is the reaction between the metal and the hydrogen ions:

$$Mg + 2H^+ \longrightarrow Mg^{++} + H_2.$$

In this reaction magnesium is oxidized and hydrogen is reduced. The hydrogen ions remove electrons from atoms of the metal, thus forming positively charged metallic ions. The negative ions of the acids (Cl^- or $SO_4^{=}$) are not actually involved and can be omitted from the equation.

To produce hydrogen in the laboratory zinc and hydrochloric acid are most often used. The generator (Figure 53) consists of a flask or bottle fitted with a stopper in which a thistle tube and a short, glass tube bent at a right angle are inserted. The thistle tube should extend almost to the bottom of the bottle. Several pieces of granulated zinc are placed in the bottle, and sufficient water is added to cover the end of the thistle tube. Hydrochloric acid is then added through the thistle tube, and hydrogen is collected by the displacement of water in the same manner as oxygen (Figure 47, page 51). A Kipp generator (Figure 54) may also be used.

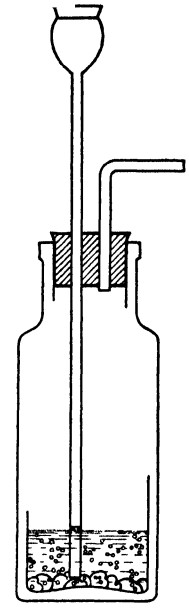


Figure 53. A Hydrogen Generator

Only certain acids can be used. Some of the acids fail to react noticeably with the metals, while others react to give products other than hydrogen. Nitric acid, for example, reacts with many metals, but it forms water and one or more oxides of nitrogen instead of hydrogen. The metals that are most active in liberating hydrogen from an acid, such as hydrochloric, are sodium, potassium, and calcium, magnesium, aluminum, zinc, and iron. The least active metals, such as gold, copper, mercury, silver, and platinum, do not displace hydrogen from acids. The atoms of these metals have stronger attraction for electrons than hydrogen; and hence, hydrogen ions do not remove electrons from them.

5. The Activity Series of the Metals

The metals may be arranged in an activity series, in which their positions depend upon the ease with which their atoms give

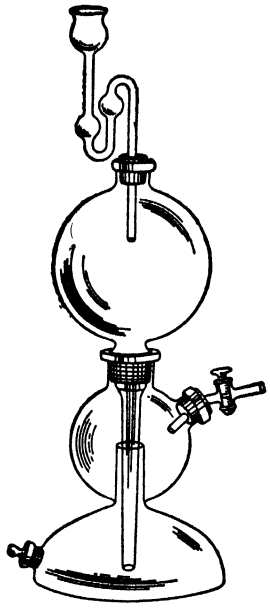


Figure 54. A Kipp Generator

A metal, usually zinc, is placed in the middle compartment. Dilute hydrochloric acid is added through the thistle tube at the top.

(Courtesy of Arthur H. Thomas Company)

up electrons to other atoms, thus becoming positive ions. From the point of view of our study at this time we may say that the positions of the metals in this series indicate (1) the rate at which they cause hydrogen to be liberated from the same acid, (2) their activity in reacting with oxygen and other non-metallic elements, and (3) other metals which each will displace from compounds. Hydrogen, itself, may be placed in this series. The metals above hydrogen will displace it from acids; those below hydrogen in the series will not.

ACTIVITY SERIES OF SOME OF THE COMMON METALS

1. Potassium	8. Tin
2. Calcium	9. Lead
3. Sodium	10. Hydrogen
4. Magnesium	11. Copper
5. Aluminum	12. Mercury
6. Zinc	13. Silver
7. Iron	14. Gold

This table is sometimes referred to as the *electrochemical series*. Later in our study we shall discuss more exact methods by which the order of the elements in this series can be determined.

Any metal in the series will displace a metal that lies below it from solutions containing ions of the lower metal; conversely, any metal is displaced from solutions of its ions by a metal that lies above it in the series. Thus, iron displaces copper from a solution containing cupric chloride:

$$(Cu^{++} + 2\,Cl^-) + Fe \longrightarrow (Fe^{++} + 2\,Cl^-) + Cu\downarrow,$$
$$\text{or,} \quad Cu^{++} + Fe \longrightarrow Fe^{++} + Cu\downarrow.$$

In this reaction, the atom of iron gives two electrons to the cupric ion, thus changing it to a neutral atom of copper. By losing the electrons, the iron atom becomes an ion, Fe^{++}. Iron is oxidized, and copper is reduced.

6. The Action of Metals upon Water

The metals at the top of the activity series decompose cold water. When sodium, for example, is placed in water, sufficient heat may be generated to cause the ignition of the hydrogen that is liberated.

$$2\,Na + 2\,H_2O \longrightarrow 2\,(Na^+ + OH^-) + H_2.$$

To show the shift of electrons we may write this equation as

$$2\,Na + 2\,H:\ddot{O}:H \longrightarrow 2\,(Na^+ + :\ddot{O}:H^-) + H:H.$$

In this reaction, the sodium atom gives one electron to the atom of hydrogen, which is thereby set free from its combination with oxygen and becomes a neutral atom.

Magnesium readily liberates hydrogen from water only if the water is hot; with cold water the speed of the reaction is too slow to give noticeable results. Magnesium hydroxide is only slightly soluble and, in the equation below, is shown by the downward pointing arrow as a *precipitate*:

$$Mg + 2\,H_2O \longrightarrow Mg(OH)_2\downarrow + H_2.$$

Magnesium, evidently, does not give up electrons to hydrogen as readily as sodium does; hence, the reaction between magnesium and water is slow. If the magnesium is heated strongly and steam is passed over it, a vigorous reaction occurs with the liberation of large quantities of energy as heat and light. Because of the temperature attained, the oxide of magnesium rather than the hydroxide is formed, because the hydroxide is not stable at this temperature:

$$Mg(OH)_2 \longrightarrow MgO + H_2O.$$

Certain other metals react less spectacularly when heated and treated with steam. Thus, steam passed over red-hot iron liberates hydrogen by the following reaction:

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

7. The Action of Certain Elements upon Hydroxides of the Active Metals

A few of the metals, which possess some of the characteristics of non-metals (page 15) react with an aqueous solution of sodium hydroxide or other alkalies to liberate hydrogen. This reaction may be demonstrated by warming a solution of sodium hydroxide, NaOH, to which finely divided zinc or aluminum has been added:

$$Zn + 2\ (Na^+ + OH^-) + 2\ H_2O \longrightarrow (2\ Na^+ + Zn\ (OH)_4^=) + H_2.$$

In this reaction the zinc atom replaces two atoms of hydrogen. The compound resulting is called *sodium zincate*, and its formula is usually written as Na_2ZnO_2. The actual formula, however, is probably more nearly correctly written as $Na_2Zn(OH)_4$, which may be regarded as Na_2ZnO_2 combined with 2 H_2O.

The compound produced by the reaction of aluminum with sodium hydroxide is called *sodium aluminate:*

$$2\ Al + 2\ (Na^+ + OH^-) + 6\ H_2O \longrightarrow 2\ (Na^+ + Al(OH)_4^-) + 3\ H_2.$$

The reaction of the non-metal, silicon, and sodium hydroxide is of a similar character. To furnish the hydrogen required for the inflation of balloons used in military operations, an alloy of iron and silicon, called *ferrosilicon*, is sometimes used with a 20 per cent solution of sodium hydroxide.

$$Si + H_2O + 2\ (Na^+ + OH^-) \longrightarrow (2\ Na^+ + SiO_3^=) + 2\ H_2.$$

The compound, Na_2SiO_3, is *sodium silicate* or *water glass.*

8. Industrial Methods of Production

(*a*) *Electrolysis.* The electrolysis of a dilute solution of sulfuric acid in water has been discussed in the chapter dealing with oxygen. This is also an important method of producing hydrogen. Hydrogen is also liberated at the cathode when a solution of sodium chloride is electrolyzed. A fuller discussion of electrolysis will be found in Chapter 16.

(*b*) *Water Gas.* When steam is passed over hot coke (1000° C.), the following reaction occurs:

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

The products are carbon monoxide, CO, and hydrogen, H_2. The mixture, called *water gas*, is an important fuel. In practice, the coke is heated by means of an air blast that causes some of it to burn. The heat liberated raises the temperature of the remainder of the coke to about 1000° C. Steam is then turned on, and the reaction forming water gas takes place. Since the reaction requires heat, the coke is soon cooled below the required temperature. The steam is then cut off, and the mass is reheated by another blast of air, thus preparing it for further reaction with steam.

Hydrogen is usually recovered from water gas by the *Bosch process.* The mixture of gases is passed, with steam, over a catalytic mass, which consists of the oxides of certain metals (oxides of iron, chromium, and thorium are used), at a moderately high

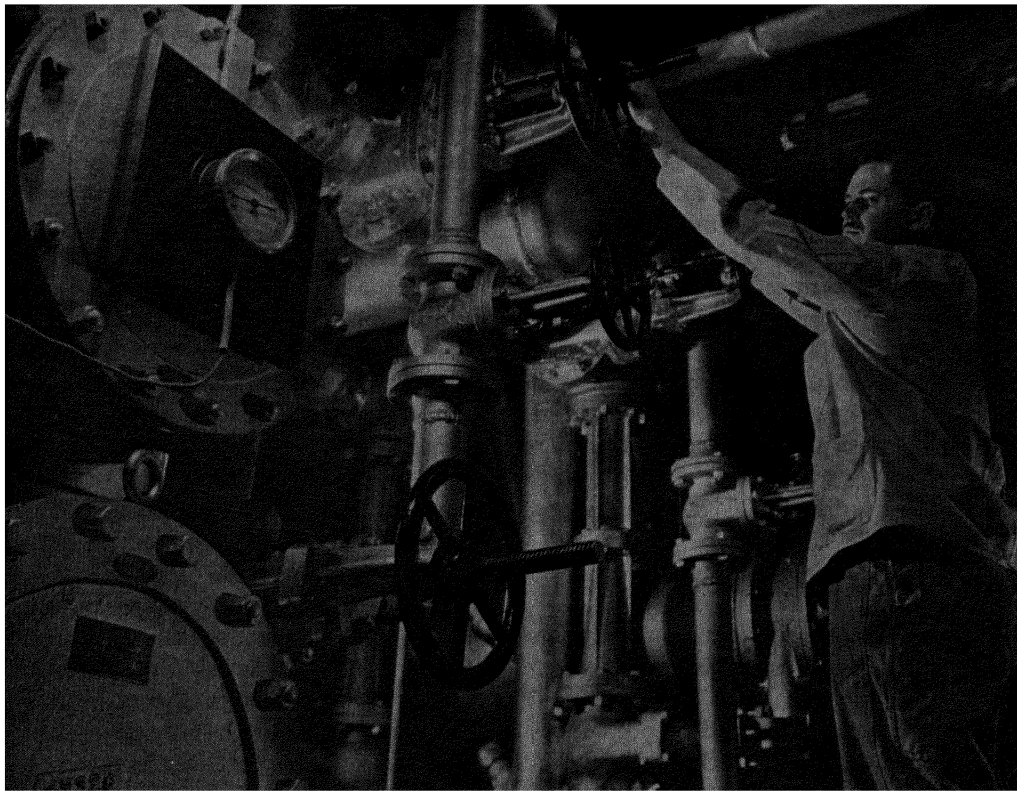


Figure 55. A Section of a Plant in Which Liquid Fats Are Converted into Solid Fats by Hydrogenation
(Courtesy of Lever Brothers)

temperature (about 500°). Under these conditions the steam oxidizes carbon monoxide to carbon dioxide:

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

The carbon dioxide is soluble in cold water and even more soluble in a solution of sodium carbonate, especially, if it is placed under increased pressure. Hydrogen is not very soluble and, hence, may be obtained in a fairly pure state. About one-half of the hydrogen used commercially is produced by this or similar methods.

(*c*) *Gas from Coke Ovens.* Coke is made by heating coal in the absence of air. During this process certain compounds in the coal, some of which contain hydrogen, are decomposed, forming a mixture of gaseous products, and leaving a residue of carbon which is coke. Among these gases there is a considerable quantity of hydrogen, which can be recovered by liquefying the other gases. This separation is easily accomplished because hydrogen is not condensed under the conditions of temperature and pressure that cause the other gases to change to the liquid state.

(*d*) *Steam and Iron.* Because of the cheapness of the materials used and the relative purity of the hydrogen produced, this method (page 70) is frequently used to produce hydrogen for industrial purposes, and, sometimes, it is combined with the water gas method. Steam is passed over iron and liberates hydrogen, until the reaction ceases because of the formation of Fe_3O_4, which coats over and protects the iron from further action. A stream of

water gas is then passed over the mass, and the following reactions occur:

$$Fe_3O_4 + 4\,CO \longrightarrow 3\,Fe + 4\,CO_2,$$
$$Fe_3O_4 + 4\,H_2 \longrightarrow 3\,Fe + 4\,H_2O.$$

The oxide of iron is reduced by carbon monoxide and by hydrogen, and these substances are, at the same time, oxidized to carbon dioxide and water, respectively. Metallic iron is produced by these reactions and, therefore, it can be used once again to liberate more hydrogen from steam.

(*e*) *Other Methods.* A mixture of hydrogen and carbon monoxide is produced by the reaction of steam with methane and other hydrocarbons — compounds of carbon and hydrogen — at about 1000° in the presence of catalysts.

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

The carbon monoxide can be separated from hydrogen by the same methods as for water gas.

Hydrogen is also produced by decomposing, or *cracking*, hydrocarbons, such as methane, at a high temperature. It is also produced by cracking ammonia in a similar manner:

$$CH_4 \longrightarrow C + 2\,H_2$$
$$2\,NH_3 \longrightarrow N_2 + 3\,H_2.$$

9. The Reaction of Iron and Steam as a Reversible Reaction

From a theoretical point of view the reaction between iron and steam is interesting, because we find that it will take place, not only as indicated, but also in the opposite direction. Thus, if hydrogen is passed over hot magnetic oxide of iron (Fe_3O_4), it combines with oxygen to form water, and metallic iron is liberated. Since they may occur in either direction, reactions of this kind are said to be *reversible*. It will be noted, however, in the two reactions involving iron and steam — one changing iron to the oxide and the other changing the oxide back to iron — that only one reaction actually occurs under each set of conditions described. If steam is passed over iron, the latter is converted completely into magnetic iron oxide, provided the treatment with steam lasts long enough. The second reaction — between hydrogen and the oxide of iron — does not take place, because the hydrogen is removed as rapidly as it is produced. It is swept out of the reaction chamber by the constant flow of steam through the chamber. If hydrogen is passed over heated magnetic oxide of iron, the reverse reaction is complete, and the reaction of steam with iron does not have a chance to occur, because the steam is swept out of the chamber by the steady flow of hydrogen.

If iron and steam are placed in a closed tube and the mixture is heated, neither the steam nor the hydrogen has an opportunity to escape. When the tube is opened, all four substances will be present. We assume, therefore, that both reactions occur

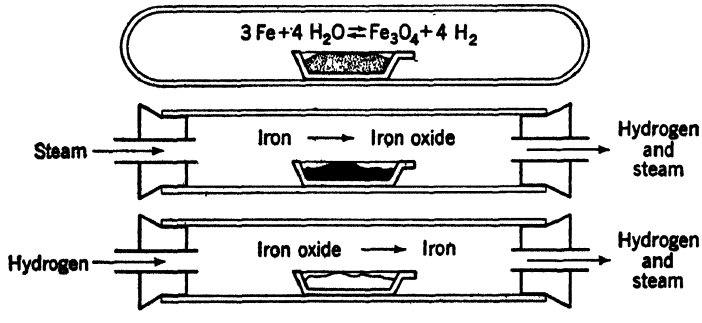


Figure 56. A Reversible Reaction

The reaction is shown (above) as it occurs in a closed tube, as it occurs in the presence of a constant flow of steam (middle), and a constant flow of hydrogen (bottom).

when none of the substances involved is removed or is allowed to escape. The two reactions reach a state of *equilibrium*, in which iron and steam react and are consumed at the same rate as they are formed by the reverse reaction. Equilibrium is attained only when none of the substances involved in the reactions is removed from the others.

PROPERTIES OF HYDROGEN

10. Physical Properties

Hydrogen is the lightest of the elements; one liter at 0° and the average pressure of the atmosphere at sea level weighs 0.08987 g. Because of its small density as compared with air, it can be poured upward from one vessel to another, since the lighter hydrogen tends to rise in the denser medium of the air. It has no color, taste, or odor. The gas can be liquefied at temperatures below − 240° C. by the application of the required pressure. Liquid hydrogen has the appearance of water. The liquid boils at − 253° C., and the melting point of the solid is − 259°. Hydrogen is only slightly soluble in water; at ordinary pressure and room temperature, approximately 2 ml. dissolves in 100 ml. of water. It is dissolved, or absorbed, very readily by certain finely divided metals. As much as 900 ml. of hydrogen may be adsorbed by 1 ml. of finely divided palladium. It is also adsorbed readily by finely divided platinum.

11. Chemical Properties

At ordinary temperatures, hydrogen shows little tendency to react with most of the other elements.

(1) *General Properties.* At higher temperatures hydrogen forms compounds with some metals and with many non-metals. In general, its compounds with the non-metals are of major importance. Its reactions with non-metals are usually very slow at ordinary temperatures, but many of them are very rapid at relatively high temperatures. Hydrogen and sulfur show no tendency to react at room temperature, for example, but at 250° C. hydrogen and sulfur vapor react very readily to form hydrogen sulfide, H_2S. With chlorine the reaction is negligible at low temperatures, but a lighted jet of hydrogen continues to burn in a vessel filled with chlorine. A mixture of the two is easily exploded by exposure to a very bright light. Hydrogen chloride (HCl) is formed. Nitrogen and hydrogen combine, under favorable conditions of temperature and pressure, to form ammonia, NH_3. All of these compounds are of the covalent type.

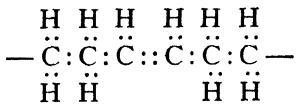
(2) *Reaction with Oxygen.* The reaction between oxygen and hydrogen is negligible at temperatures as high as 400° C. At 600° C., the speed of the reaction is rapid, and at 700° it occurs explosively. Because of the explosion that is certain to occur if a confined mixture of hydrogen and oxygen (or air) is ignited, great care must be taken in preparing hydrogen. The gas escaping from the outlet or delivery tube of a hydrogen generator should never be lighted, until tests show that the gas is pure. A sample should be collected in a test tube, removed to a distance of several feet from the source, and ignited. If the hydrogen burns quietly, it is pure. The safest procedure to follow consists of lighting the hydrogen from the generator only with a tube of burning hydrogen that has been collected from the same source. Catalysts, such as finely divided platinum or palladium, increase the speed of the reaction even at low temperatures, and, because of the heat that is liberated, the catalyst becomes red hot. It then heats the hydrogen-oxygen mixture around it to a temperature at which ignition results. This principle is used in lighters which ignite gas spontaneously.

(3) *Hydrogen and certain metals form* ionic compounds, such as ($Na^+ + H^-$) and ($Ca^{++} + 2\,H^-$), called *metallic hydrides*. These compounds react with water to liberate

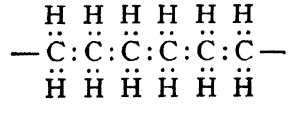
hydrogen and to form hydroxides of the metals:

$$CaH_2 + 2\,H_2O \longrightarrow (Ca^{++} + 2\,OH^-) + 2\,H_2.$$

(4) *Hydrogenation.* Hydrogen combines with certain compounds of carbon that are classified as *unsaturated,* because they contain some atoms of carbon that are not already combined with as many atoms of hydrogen, or other elements, as their full combining capacity allows. The reaction by which hydrogen is added to these compounds is called *hydrogenation.* Hydrogen reacts, for example, with unsaturated, liquid fats to form saturated, solid fats. The molecules of the liquid fats, such as coconut oil, contain two carbon atoms which, as the organic chemist usually writes the formula, share *two* pairs of electrons with each other:



(The formula shown above is not complete since there are other groups linked to the two carbon atoms at the ends of the chain.) When hydrogen reacts with a compound of this kind, its atoms become attached to the two carbon atoms that share two pairs of electrons, thus converting the compound into one in which the carbon atoms are all linked to as many atoms of hydrogen as possible.



Solid fats made by hydrogenating liquid fats are used as substitutes for butter, for cooking in place of lard, and to make hard soaps.

(5) *Hydrogen is a reducing agent.* As an example of the action of hydrogen as a reducing agent, we may recall the reaction of the element with magnetic iron oxide:

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

Hydrogen also acts as a reducing agent when it reacts with chlorine to form hydrogen chloride, with oxygen to form water, and with other non-metals. When it reacts with lithium, and with a few other very active metals, an atom of hydrogen appears to remove an electron from the atom of the metal and, therefore, acts as an oxidizing agent, a role that hydrogen rarely plays. Lithium hydride is an ionic compound, Li^+H^-, in which hydrogen appears as a negatively charged ion.

12. Atomic Hydrogen

In its normal, free state hydrogen is composed of molecules containing two atoms each. Under certain conditions, however, single atoms of the element — sometimes referred to as atomic hydrogen — do exist at least for brief periods of time. For example, the hydrogen that is liberated in the reaction of an acid and a metal is probably set free as single atoms, which then combine in pairs to form molecules. This reaction liberates a considerable quantity of energy:

$$H + H \longrightarrow H_2 + 102{,}600 \text{ calories.}$$

The *atomic hydrogen torch* is a device that makes use of the energy released by this reaction in producing a flame that attains a temperature of 4000–5000° C., and which is employed in the welding of certain metals. A stream of hydrogen is passed through an electric arc, by which molecules of H_2 are broken up into individual atoms, which then strike the metals that are to be welded. Almost immediately the atoms recombine to form molecules and, when they do, the heat that is liberated raises the temperature of the rods or sheets of metal to their melting points. The temperature of the metal is still further increased by the heat liberated when the hydrogen burns to form water. The surrounding of the heated portions of the metal by hydrogen excludes air and prevents the oxidation of the metal,

a condition which produces a smooth, welded surface that is free from pinholes and from flaws that otherwise would be produced by impurities such as oxides. The atomic hydrogen torch is used to produce temperatures that are seldom attained by other devices.

13. Deuterium

One of the isotopes (page 37) of hydrogen consists of atoms that contain one proton and one neutron in each nucleus. This isotope is called heavy hydrogen or in scientific circles *deuterium*. It can be separated from ordinary hydrogen by taking advantage of the fact that it is the last of the hydrogen to be set free from its combination with oxygen when water is electrolyzed. Hence, if a large quantity of water is almost completely decomposed by electrolysis, the last small portion can be electrolyzed separately to give hydrogen fairly rich in deuterium. This portion is then converted into the oxides (H_2O and D_2O), and the process is repeated. After several such separations almost pure deuterium is obtained. Water contains one atom of deuterium to about 5000 atoms of ordinary hydrogen.

The compound produced when deuterium burns is *deuterium oxide*, or *heavy water*. Its physical properties — density, boiling point, and freezing point, for example — are different from those of ordinary water. It also differs in its solvent action upon other substances, and in its reactions with other elements and compounds.

14. Uses of Hydrogen

Hydrogen is used extensively in the chemical industries. Some of its most important uses are discussed briefly below.

(1) The *oxygen-hydrogen torch* and the *atomic hydrogen torch* and their use in melting, welding, and cutting metals have been discussed previously (page 54 and page 74).

(2) Hydrogen is used *to reduce* the oxides

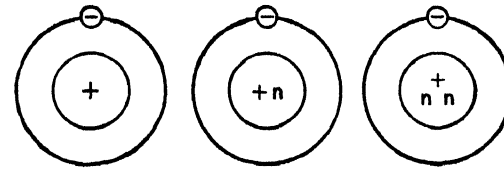


Figure 57. Hydrogen Atoms, Containing Different Numbers of Neutrons in Their Nuclei

The atomic weights are 1, 2, and 3 (approximate)

of certain metals by combining with the oxygen that they contain and setting the metals free. For example, the tungsten used to make the filaments in electric light bulbs is produced from the oxide in this manner. Hydrogen may be used, also, to provide a reducing atmosphere about metals that are heated to a high temperature, a treatment that is sometimes employed to give the metals certain properties. The metals would combine with oxygen if air were not excluded; and hence, hydrogen or some other reducing or inactive gas is used to replace the air. If any oxidation does occur, hydrogen reduces the oxides that are formed to the metals again.

(3) Hydrogen is used to fill balloons and dirigibles. The lifting power of hydrogen in air is greater than that of any other gas, under the same conditions of temperature and pressure, because no other gas has a smaller density, and also because the buoyancy in air of a container filled with a gas depends upon the difference between the weight of the container and the weight of the volume of air that it displaces. Because of the danger involved in its use, hydrogen is replaced by helium for such purposes whenever a supply of the latter is available. Helium, unlike hydrogen, will not burn.

(4) Hydrogen is used to *harden liquid fats* such as coconut and cotton-seed oils. Hydrogen under pressure is forced into the liquid fats at temperatures around 175° C. and in the presence of finely divided metal (usually nickel), which acts as a catalyst. The reaction that occurs involves the hydrogenation of "unsaturated" liquid fats to

form solid "saturated" fats (page 74). These solid fats are used as substitutes for lard and butter and in the production of candles and hard soaps.

(5) Hydrogen is used in the *synthesis of methyl (wood) alcohol* (CH_3OH), *ammonia* (NH_3) and other compounds. Until about twenty years ago, methyl alcohol was produced from wood. It is now produced by the reaction of hydrogen and carbon monoxide in the presence of a catalyst, which may be zinc oxide (ZnO) or finely divided copper.

$$CO + 2\ H_2 \longrightarrow CH_3OH.$$

The industrial importance of wood alcohol as a solvent in chemical manufacturing makes this use of hydrogen one of great importance. The production of ammonia depends upon the direct combination of nitrogen and hydrogen:

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3.$$

This reaction is one of the most important of the reactions used commercially. It provides a means of producing ammonia from the nitrogen of the air and, therefore, makes available unlimited potential supplies of this important compound. The ammonia produced by this method can be converted readily into nitric acid, which is required in the manufacture of many explosives, dyes, drugs, fertilizers, plastics, and many other products.

15. Hydrogenation of Coal

Coal is composed of carbon and compounds of carbon, hydrogen, nitrogen, and other elements. Gasoline consists of several liquid compounds of carbon and hydrogen called *hydrocarbons*; for example, *octane*, C_8H_{18}, is present in gasoline. If hydrogen could be made to combine with the carbon in coal, or if the compounds containing carbon and hydrogen could be changed to produce molecules in which the ratio of carbon to hydrogen atoms is somewhat similar, or the same, as in octane, liquid hydrocarbons, such as those contained in gasoline, should be produced. This reaction — which is nothing more or less than the hydrogenation of certain substances in coal — can be accomplished by treating powdered coal, usually mixed with oils, with hydrogen at moderately high temperatures and under high pressures. The product is a mixture greatly resembling petroleum. From it can be recovered gasoline, kerosene, lubricating oil, and other products normally obtained from petroleum. This process, which was first developed on a large scale in Germany about 1925, is sometimes called the *Bergius Process* for the liquefaction of coal. During World War II, Germany depended upon this process for a very important part of her supply of petroleum products. The process has thus far not attracted much attention in the United States because of our large available supplies of natural petroleum.

REVIEW EXERCISES

1. Compare and contrast oxygen and hydrogen as to physical and chemical properties.
2. How could the hydrogen that escapes from the earth in the gases from some volcanoes have been produced from water? Why should such gases be more likely to contain hydrogen than oxygen?
3. What reactions discussed in this chapter involve water as an oxidizing agent? Name one reaction in which hydrogen acts as a reducing agent.
4. Name four reactions by which hydrogen can be produced from water.
5. Why are laboratory samples of hydrogen not often produced by the electrolysis of water? Why is industrial hydrogen not produced by the reaction between acids and metals?
6. Why cannot sodium hydroxide be regarded as a catalyst in the production of hydrogen by means of the reaction involving silicon?
7. Name four uses of hydrogen and describe the chemical changes upon which these four uses depend.

8. Why does an oxygen-hydrogen blowpipe give a hotter flame than one in which a mixture of hydrogen and air is burned?
9. Could a balloon filled with hydrogen rise to an unlimited altitude?
10. Which of the following metals displace tin from a solution containing stannous chloride, $SnCl_2$? Copper, gold, magnesium, iron, lead, aluminum, platinum, and silver. Which of these metals would tin displace?
11. How could you prove that one of the elements of which a sheet of paper is composed is hydrogen?
12. Why would oxygen have been a better name for the element now called hydrogen than it is for the element to which it is applied?
13. How would you expect calcium to react with (1) water, (2) hydrochloric acid, and (3) a solution of cupric sulfate?
14. Why does hydrogen combine more readily with non-metals than with metals?
15. Under what condition will a reversible reaction occur only in one direction?
16. Account for the displacement of one metal from its compounds by another metal, or by hydrogen, in terms of changes involving electrons.
17. When iron displaces copper from cupric chloride, $CuCl_2$, which element is the oxidizing agent and which is the reducing agent?
18. Why was the production of gasoline by the hydrogenation of coal more widely used in Germany than in the United States even prior to 1939?
19. Arrange the following metals in the order of their chemical activity: iron, copper, aluminum, lead, calcium, silver. Which of these metals will liberate hydrogen from acids? Which will liberate copper from solutions containing a compound of copper, such as $CuCl_2$? Which metal will liberate hydrogen most rapidly from the solution of an acid such as HCl?
20. In the water gas reaction (page 70) which element is oxidized and which one is reduced? What changes in oxidation numbers occur?
21. Under what conditions would it be unsafe to ignite the gas escaping from the outlet tube of the hydrogen generator pictured on page 68?
22. Refer to the apparatus (page 46) used in the electrolysis of water in the laboratory. How could you determine which of the two tubes contains hydrogen if you did not know which of the electrodes is the negative one?
23. Connect a rubber tube to the outlet tube of a hydrogen generator (page 68) and place the other end of the rubber tube in a bottle open at the top and standing upright. Would this be a practical method of collecting a sample of hydrogen? Give a reason for your answer.
24. Hydrogen explodes when ignited. Correct this statement.

REFERENCES FOR FURTHER READING

Riegel, E. R., *Industrial Chemistry.* New York: Reinhold Publishing Corporation, 1942.

Weeks, M. E., *The Discovery of the Elements*, p. 29.

Atomic Hydrogen: *J. Chem. Ed.*, **4,** 39 (1927).

Isotopes: *J. Am. Chem. Soc.*, **55,** 4335 (1933); **57,** 780 (1935); **61,** 1594 (1939); *Ind. and Eng. Chem.*, **26,** 803 (1934); **30,** 1139 (1938).

Production: *Chem. and Met. Eng.*, **27,** 1263 (1922); **28,** 764, 939, 1072 (1923); **37,** 751 (1930); **43,** 122 (1936); *Ind. and Eng. Chem.*, **14,** 1118 (1922); **17,** 183 (1925); **30,** 1139 (1938); *J. Chem. Ed.*, **8,** 490 (1931); **9,** 916 (1932).

Uses: *Chem. and Met. Eng.*, **28,** 931 (1923); *Chem. and Eng. News*, **21,** 1238 (1944).

7

THE BEHAVIOR OF GASES AND THE KINETIC MOLECULAR THEORY

1. Introduction: A Comparison of Gases, Liquids, and Solids

A solid retains its form and occupies the same space regardless of the shape or size of the container. A liquid fills its container to a certain height, which is determined by the quantity of liquid and the shape and size of the vessel. A liquid differs from a solid in its ability to flow and to fill its container uniformly in all directions except vertically. A solid in a fine, granular state, such as sugar, salt, or sand, can be poured and tends to flatten out when placed in a heap, because the grains are free to move in response to forces, such as gravitation. This condition of a solid approaches somewhat the condition of a liquid, in which molecules are free to move about more or less freely, because there is no strong attraction that holds them in fixed positions relative to one another. The difference is in the size of the particles of the solid as compared with the molecules of the liquid. Gases are still less restricted in movement than liquids. They expand rapidly and, in a short time, are uniformly distributed throughout the entire volume of their containers, although the containers may be occupied already by other gases. If the container is not closed, they continue to expand indefinitely in the surrounding space.

Gases also differ from solids and liquids in the ease with which they are compressed. The volume that a gas occupies is reduced one half, when the pressure upon the gas is doubled, and to approximately one tenth, when the pressure is increased ten fold. To produce the same effect upon the volume of a liquid or a solid, the pressure would have to be increased many thousand fold.

Finally, the densities of gases (density equals mass divided by volume) are small in comparison with the densities of liquids and solids. One gram of liquid water occupies 1 ml. at 4° C., and at other temperatures the volume is only slightly different. When this same weight of water is changed into water vapor at 100° C., its volume is increased about 1500 times. The density of (liquid) water, therefore, is about 1500 times as great as the density of water vapor.

2. The Pressure Exerted by a Gas

Gases also differ from liquids and solids in the manner in which they exert pressure. The pressure of a gas is sometimes said to be caused by the weight of the gas, but if this were the only factor involved, the pressure of the atmosphere or of any other gaseous material would be exerted only downward — toward the center of the earth. However, in a closed vessel containing a gas there is just as much pressure, for an equal surface, on the top of the vessel as there is on the bottom, regardless of the quantity of gas in the container. If we

force more air into the vessel, the increased pressure is distributed equally over all the walls. The pressure exerted by a gas is, therefore, another problem that we must explain in building a theory concerning the nature of gases.

3. The Barometer

The pressure of the atmosphere is measured by a barometer (Figure 58). A simple form of barometer can be prepared by filling a tube, closed at one end and about 80–85 cms. in length, with mercury. When the tube is inverted and placed with its open end beneath the surface of mercury in an open vessel, the mercury column falls slightly, leaving a vacuum at the top. There is, then, no pressure, or only the negligible pressure of a little mercury vapor, above the surface of the mercury in the closed tube. Since mercury is a liquid, it will continue to fall until the level is the same in the vessel and in the tube, if there is no downward pressure upon the surface of the mercury in the open vessel to hold the column above this level. The pressure that holds the mercury up in the tube is produced by the atmosphere. It varies from place to place on the earth's surface and from day to day, or even from hour to hour, at any one place. The pressure under a definite set of conditions — temperature, place, and time — is recorded as the height of the column of mercury that the atmosphere's pressure will support. The height of the mercury column is the distance between the two levels of mercury, one in the open vessel and the other inside the barometer tube. The average pressure at sea level will support a column of mercury 760 mm. in height. This amounts to a pressure of about 14.7 pounds per square inch.

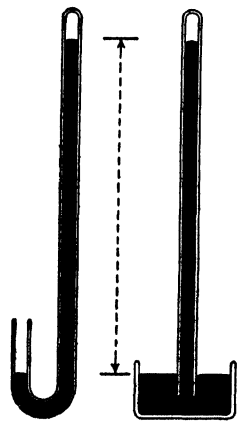


Figure 58. Two Forms of the Barometer

4. How the Pressure of a Gas is Measured and Expressed

The pressures exerted by all gases can be measured in the same manner as the pressure of the atmosphere. We speak, therefore, of the pressure exerted by a gas in terms of the height of the column of mercury that the pressure of the gas will support against gravity — the earth's attraction. The pressure measured by a column 760 mm. in height is called *one atmosphere.* When we state that the pressure of a gas is 200 atmospheres, for example, we mean that the pressure is approximately 200 times the average pressure exerted by the atmosphere at sea level.

5. Boyle's Law: The Relation of Pressure and Volume

The relation between the volume of a definite weight of a gas and its pressure was first recognized and expressed by Boyle in 1660. The statement of this relation is called Boyle's Law: *Provided that the temperature does not change, the volume of a definite weight of a gas varies inversely with the pressure.* This law can also be stated in the form of the following equation:

$$p_1v_1 = p_2v_2,$$

in which p_1 and p_2 represent two pressures and v_1 and v_2 represent the corresponding volumes. This equation is nothing more or less than a concise statement to the effect

that *the product of the pressure and the volume of a definite quantity of a gas (at constant temperature) is a constant.* If either changes, then the other must change in the opposite direction and to the same extent. This is what we mean when we say that the volume varies *inversely* with the pressure. This law can be verified by means of the simple apparatus shown in Figure 59. If 64 liters of a gas at 1 atmosphere is subjected, at constant temperature, to increasing pressure, the relation between pressure and volume at different pressures will be found to be as follows:

Pressure	Volume	Product, pv.
1 atmosphere	64 liters	64
2 "	32 "	64
4 "	16 "	64
8 "	8 "	64
16 "	4 "	64
32 "	2 "	64
64 "	1 "	64

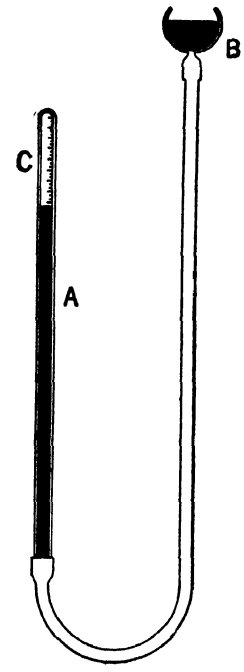


Figure 59. Apparatus Used in Verifying Boyle's Law

6. Calculations Based upon Boyle's Law

It is often necessary to calculate the volume of a definite quantity of a gas at some pressure that is different from the pressure under which the volume is actually measured. As an illustration, let us say that we measure 100 ml. of a gas at a pressure of 720 mm., although we wish to determine the volume of the same quantity of the gas at 760 mm. of pressure. It is evident that the volume at 760 mm. will be less than 100 ml., because the pressure increases and, therefore, the volume must decrease. To calculate the volume at 760 mm. we must multiply the observed volume by a fraction, in which we write the smaller pressure as the numerator and the larger pressure as the denominator:

$$\frac{p_1 v_1}{p_2} = v_2$$

or, $100 \times \frac{720}{760} = 100 \times 0.947 = 94.7$ ml. The pressure increases in the ratio of $\frac{760}{720}$ and the volume decreases in the inverse ratio; and hence, the new volume is $\frac{720}{760}$ of the first volume in accordance with Boyle's law.

If the second pressure is lower than that at which the volume is measured, the calculation is made in the same manner, with the exception that the fraction by which the observed volume is multiplied must contain the larger pressure in the numerator. If 100 ml. of the gas is measured at 760 mm., the volume at 720 mm. is calculated as follows:

$$100 \times \frac{760}{720} = 100 \times 1.055 = 105.5 \text{ ml.}$$

7. Effect of Temperature Changes on Volume and Pressure

It is a well-known fact that a gas tends to expand as its temperature rises. If the expansion is prevented by the walls of a container, there will be, of course, no change in volume, and the increased temperature will produce an increase in pressure. But if the gas is allowed to expand, with increasing

temperature against a constant pressure, one observes a very definite relation between the rise in temperature and the increase in volume, or between the fall in temperature and the decrease in volume. A temperature change of one degree causes a change in volume of *one-two hundred seventy-third* ($\frac{1}{273}$) *of the volume that the gas occupies at 0° C.*, provided that there is no change in pressure. At constant volume, the change in pressure is $\frac{1}{273}$ of the pressure at 0° C. for each temperature change of 1° C.

8. Absolute Zero and the Absolute Temperature Scale

Let us assume that a certain weight of a gas occupies 273 ml. when the volume is measured at 0° C. Since the volume decreases $\frac{1}{273}$ of the volume at 0° for each drop of one degree, the volume at − 273° C., at constant pressure, should be zero. Likewise, at constant volume, the pressure at − 273° C. should be zero. The temperature − 273° C. is called, therefore, the *absolute zero* because a lower temperature is inconceivable. All gases are liquefied above − 273° C., and, hence, we must define the absolute zero as the temperature at which the volume of a gas, at constant pressure (and likewise the pressure at constant volume) would be zero if the volume (or pressure) continued to change in the same manner down to − 273° as it does under conditions that permit observation.

The scale of Absolute (or Kelvin) temperature is based upon this zero. The relation between this scale and the Centigrade scale is shown below:

	Centigrade	Absolute
Water boils	100°	373°
Water freezes	0°	273°
Absolute zero	−273°	0°

9. Charles's Law

What volumes will a sample of gas occupy at − 100° and at 100° if the volume at 0° C. is 273 ml.?

Volume at − 100° = Volume at 0° − $\frac{100}{273}$ × Volume at 0° = 273 − ($\frac{100}{273}$ × 273) = 173 ml.

Similarly, the volume at 100° C. = 273 + ($\frac{100}{273}$ × 273) = 373 ml.

The Absolute temperatures corresponding to 0° C., − 100° C., and 100° C., are 273°, 173°, and 373°, respectively. Now

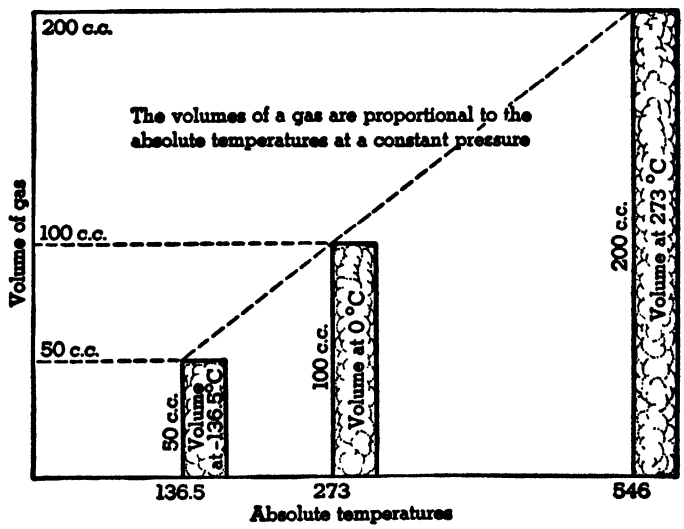


Figure 60. Relation of Volume to Absolute Temperature at Constant Pressure

the volumes of the same gas sample at these temperatures and at constant pressure are:

Absolute Temperature	Volume
173° (T_1)	173 ml. (v_1)
273° (T_2)	372 ml. (v_2)
373° (T_3)	373 ml. (v_3)

When the Absolute temperature changes from 173° to 273°, the volume increases from 173 ml. to 273 ml.

From these data we may formulate the following general principle: *If the pressure does not change, the volume of a definite weight of a gas varies directly with the Absolute temperature.*

$$\frac{T_1}{T_2} = \frac{v_1}{v_2}, \quad \text{or} \quad v_2 = \frac{v_1 T_2}{T_1}.$$

These equations show that the volume changes (increases or decreases) in the same direction as the Absolute temperature and to the same extent; if the Absolute temperature is doubled, the volume is doubled, and so on.

10. Calculation of Gaseous Volumes and Pressures by Charles's Law

Let us calculate, at constant pressure, the volume at 10° C. of a definite weight of a gas which occupies 100 ml. at 45° C. The two Absolute temperatures are 283° and 318°, respectively, and the volumes are v_2 and 100 ml. To find the new volume, v_2, the old volume, v_1, must be multiplied by a fraction of which the smaller of the two Absolute temperatures is the numerator, since it is evident that the new volume will be smaller than the old because the volume, at constant pressure, becomes smaller as the temperature is lowered. Accordingly,

$$v_2 = 100 \text{ ml.} \times \frac{283}{318},$$

which can be written in the form of the general equation above:

$$v_2 = \frac{v_1 T_2}{T_1}.$$

11. Change of Pressure with Temperature at Constant Volume

If the volume of a definite weight of any gas remains unchanged, the pressure is also directly proportional to the Absolute temperature:

$$\frac{T_1}{T_2} = \frac{p_1}{p_2},$$

where p_1 is the pressure exerted by the gas at the Absolute temperature T_1, and p_2 is the pressure when the Absolute temperature is T_2.

12. Standard Conditions

In order that there may be a common basis for the comparison of the weights of equal volumes of all gases, it is necessary that we select a standard temperature and a standard pressure. The standards in use are 0° C., or 273° Absolute, and 760 mm. It is not necessary, of course, that the volumes to be compared should be *measured* under these conditions in an experiment. It is seldom, if ever, convenient to carry out an experiment under these exact conditions. The volume of a definite weight of any gas at 0° C. and 760 mm. can be calculated from the volume measured at any other temperature and pressure by applying Boyle's and Charles's laws.

13. Change in Volume when Both Pressure and Temperature Change

Frequently, it is necessary to *calculate* the volume of a gas at a temperature and at a pressure both of which are different from the conditions under which the volume is *actually measured.* Let us consider the case of a gas of which a definite weight occupies 200 ml. when the temperature is 20° C., and the pressure of the gas is 720 mm. To reduce this volume to the volume occupied under standard conditions we must calculate the volume at 0° C. and 760 mm.

Let us first calculate the change in volume caused by the change in pressure at constant temperature. Since the pressure is increased, when we change to 760 mm., the volume will be diminished to $\frac{720}{760}$ of 200 ml. Now with a constant pressure of 760 mm., let us calculate the change

in volume caused by the change in temperature at constant pressure. Since the temperature is reduced, the volume of $\left(\frac{720}{760} \times 200\right)$ ml. will be further reduced in the ratio of $\frac{273}{293}$, and the final volume under standard conditions will be

$$\frac{273}{293} \times \left(\frac{720}{760} \times 200\right) \text{ml.}$$

14. Dalton's Law: Partial Pressures of Gases in a Mixture

If two or more gases are contained in the same vessel, the total pressure upon the walls is the sum of the pressures that the different gases of the mixture would exert, at the same temperature, if each gas occupied the vessel alone. Frequently, situations arise in the laboratory in which it is necessary to collect a gas in the presence of other gases, although we must be able to calculate the volume one gas would occupy at the same temperature and pressure, if the others were not present. To do so we make use of Dalton's Law of Partial Pressures: *The partial pressure of each gas in a mixture is the same fractional part of the total pressure of the mixture as the volume which that gas would occupy — when measured at the total pressure — is of the volume of the mixture, temperature remaining constant.*

Let us consider a mixture of oxygen and nitrogen that occupies 2 liters and has a pressure of 2 atmospheres. Let us assume that the partial pressure of oxygen is 1 atmosphere, i.e., the oxygen if it alone occupied the 2 liters of the container would exert a pressure of 1 atmosphere, or one-half of the total pressure. Therefore, according to Dalton's Law, the volume occupied by the oxygen alone *at a pressure of 2 atmospheres* is also one-half of the total volume, or 1 liter. We assume, of course, that the temperature remains unchanged.

15. Collection of Gases over Water

Many gases are collected over water as shown in Figure 61. In such cases, the containing vessel is filled with a mixture of the gas collected and water vapor. At any one temperature, a definite quantity of water evaporates into the vessel — enough to saturate the space — and hence, for that temperature, the water vapor exerts a definite pressure upon the vessel's walls. At any other temperature, the pressure exerted by the vapor will be greater or smaller, as the case may be, because the quantity of water vapor required to saturate the space depends upon the temperature. When the volume of a gas is measured in the presence of water vapor, a correction must be made for the presence of the water vapor, because the volume that the gas would occupy, if it were dry, is less, at the same temperature and pressure, than the volume of the mixture containing water vapor.

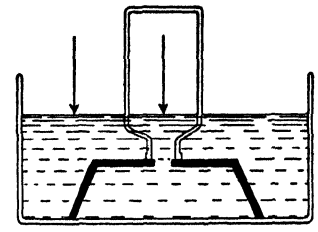


Figure 61. The Collection of a Sample of Oxygen over Water

The gaseous pressure inside the bottle is made up of the partial pressure of oxygen and the partial pressure of water vapor. Together they are equal to the atmospheric pressure.

Let us consider a volume of 200 ml. of oxygen collected over water at 20° C. and 770 mm. To find the volume of dry oxygen we can make use of Dalton's Law, but to do so we must know the partial pressure of the oxygen in the mixture. The pressure of 770 mm. is the *total pressure of water vapor and oxygen.* To find the partial pressure of oxygen, the pressure of the water vapor must be subtracted from the total pressure. The pressures of water vapor at different temperatures have been determined by experiment and are given in Table 1 of the Appendix. We find in this table that the partial pressure of water vapor at 20° C. is 17.5 mm. Hence, the partial pressure of oxygen (Figure 61) is 770 − 17.5 = 752.5 mm.

This is the pressure that would be exerted by the dry oxygen if the whole volume of 200 ml. were occupied by that substance. This pressure is $\frac{759.5}{770}$ of the mixture's pressure and, by Dalton's Law, the volume of oxygen at a pressure of 770 mm. is $\frac{759.5}{770}$ of 200 ml., or 195.5 ml.

16. Diffusion of Gases: Graham's Law

A gas that is liberated in one part of a closed vessel distributes itself uniformly throughout the vessel, in which one or more gases may be present already. We say that the gas *diffuses* into every part of the container. Graham, in 1832, measured the rates of diffusion of different gases and, from his results, formulated the following law: *The rates of diffusion of gases are inversely proportional to the square roots of the densities of the gases.* The density of a gas can be defined as the weight of one liter, measured under standard pressure and at some specified temperature, usually 0° C.

Differences in the rates of diffusion of hydrogen, which is the lightest of all gases, and the oxygen and the nitrogen in the air can be demonstrated by the experiment shown in Figure 62. A vessel containing hydrogen is lowered over a porous cylinder filled with air and connected, by means of a glass tube, with a flask partially filled with water. Hydrogen diffuses through the porous walls of the cylinder more rapidly than oxygen and nitrogen diffuse outward, with the result that the pressure inside the cylinder and the vessel with which it is connected is increased. Because of the increase in pressure, water is forced through the outlet tube of the flask.

The average density (weight per liter) of air is 1.293 and that of hydrogen is 0.08987, at 0° C. and 760 mm. According to Graham's law, therefore, the rates of diffusion (R) of hydrogen and the air are related as follows:

$$\frac{R_H}{R_{Air}} = \frac{\sqrt{1.293}}{\sqrt{0.08987}} = \frac{1.138}{0.3} = \frac{4}{1} \text{ (approximately).}$$

This ratio means that hydrogen diffuses almost four times as rapidly as air. The square roots of the densities of the two gases are in the ratio of 1 to 4, but the rates of diffusion are in a ratio that is the inverse of this, i.e., 4 to 1.

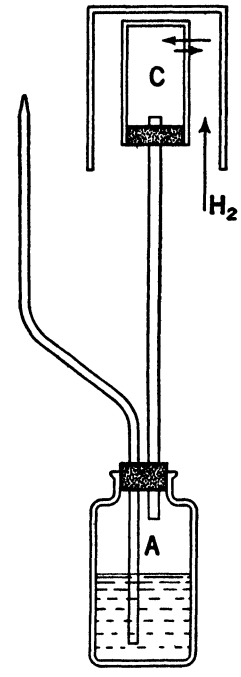


Figure 62. Apparatus Used to Show the Different Rates of Diffusion of Hydrogen and Air

THE KINETIC MOLECULAR THEORY

17. Introduction

We are now ready to consider a theory dealing with the structure of gases. This theory must be based upon the general properties of gases and upon the laws that concern their behavior. How does a gas exert pressure in all directions against the walls of its container? Why are gases much more compressible, and why do they diffuse more rapidly, than liquids and solids? Why do they not settle? Why are their densities so very small when compared to the densities of the liquid and solid states of the same substances? How can two gases occupy the same container? How can one gas diffuse into the space that another already

occupies? How can we explain the effects of changes in volume and temperature upon the pressure that a gas exerts? The theory that most satisfactorily answers these and similar questions is built around the central idea that gases are composed of *moving molecules*, and it is called, therefore, the *Kinetic Molecular Theory*.

18. A Summary of the Theory

The principal concepts of the Kinetic Molecular Theory are summarized as follows:

(1) Gases are composed of molecules, which are widely separated by empty space.

(2) The molecules of a gas are in rapid motion. They collide with one another and strike the walls of the containing vessel, thus producing pressure against the walls, This pressure depends upon the frequency of the molecular impacts with the walls and for each impact it depends upon the momentum (product of the mass m and the velocity v) of each molecule.

(3) In collisions with one another and with the walls of the container, the molecules are perfectly elastic and, therefore, have the same average velocities, at constant temperature, even after many collisions.

(4) The velocities of the molecules are so great — oxygen molecules at ordinary temperature are said to travel at a speed of about 15 miles per minute — and the molecules are so far apart, except for occasional collisions, that attractive forces of one molecule for another have little effect in holding them together.

(5) The average kinetic energy of different kinds of (gas) molecules at the same temperature is the same, regardless of differences in mass. Since the kinetic energy of a molecule depends upon the mass and the square of the velocity of the particle, the light molecules of hydrogen, for example, must travel faster than the heavier molecules of oxygen.

HOW THE KINETIC THEORY EXPLAINS THE BEHAVIOR OF GASES

19. Boyle's Law

The fact that all gases are compressible can be explained best by the assumption that gases are composed of molecules that are relatively far apart and are separated by empty space. Added pressure crowds the molecules closer together, thereby decreasing the volume by "crowding out" some of the space between the molecules. The kinetic theory assumes that the molecules of a gas actually occupy only a very small part of the volume occupied by the gas as a whole under ordinary pressure conditions. As long as the volume actually occupied by the molecules themselves is not compressed, all gases should respond in the same manner to changes in pressures. This does not mean that individual molecules of two different gases are of the same size and would occupy the same space if we could consider them as single particles. It means that the space occupied by the molecules of any gas is always about the same fraction of the entire volume, regardless of the character of the gas. This condition is possible, of course, because the fraction is small.

The pressure of a gas is explained by the assumption that the molecules are in rapid motion. Hence, the pressure against the walls of the container is caused by the bombardment of the walls by molecules and is directly proportional to the number of molecules confined within a given volume. Let us consider a definite weight of a gas that occupies *two* liters at a temperature that is not changed. If the same number of molecules is crowded into *one* liter, Boyle's law predicts that the pressure will be twice as great as when the volume is two liters. The kinetic theory explains the increase in pressure as follows. When the molecules are crowded into one half of the volume that they first occupied, there are twice as many impacts upon the same area of wall

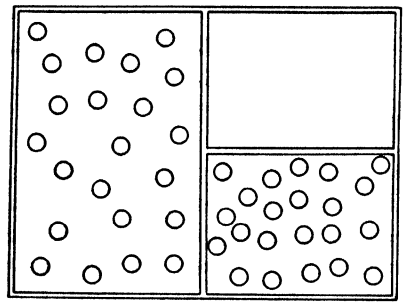


Figure 63. An Explanation of Boyle's Law

The same number of molecules will exert twice as much pressure per unit of surface when they are crowded into one half of the original volume.

surface as before. The increased number of impacts results in twice as much pressure.

20. The Kinetic Energy of Molecules

The pressure of all the molecules of a gas in a container of definite volume and at constant temperature depends upon the same factors as the total kinetic energy of these molecules (page 85), namely the number of molecules, the mass of one molecule, and the average velocity of the molecules. Since they depend upon the same factors, it can easily be shown that the pressure of a gas is proportional to the kinetic energy of the molecules of the gas. By Charles's Law, pressure (at constant volume) is proportional to the Absolute temperature of the gas. Hence, it follows that the kinetic energy of the molecules of a gas is proportional to the Absolute temperature.

The statement just made above defines clearly the conditions that should prevail at Absolute zero. Since the kinetic energy of the molecules is proportional to Absolute temperature, the kinetic energy of the molecules at Absolute zero must be zero. At this temperature, the molecules would not move, and, therefore, they could not exert any pressure, because their pressure is also proportional to their kinetic energy.

21. The Kinetic Energy of Molecules of Different Gases

We have stated (page 85) that the average kinetic energy of the molecules of all gases is the same at the same temperature. What evidence is there to support this statement?

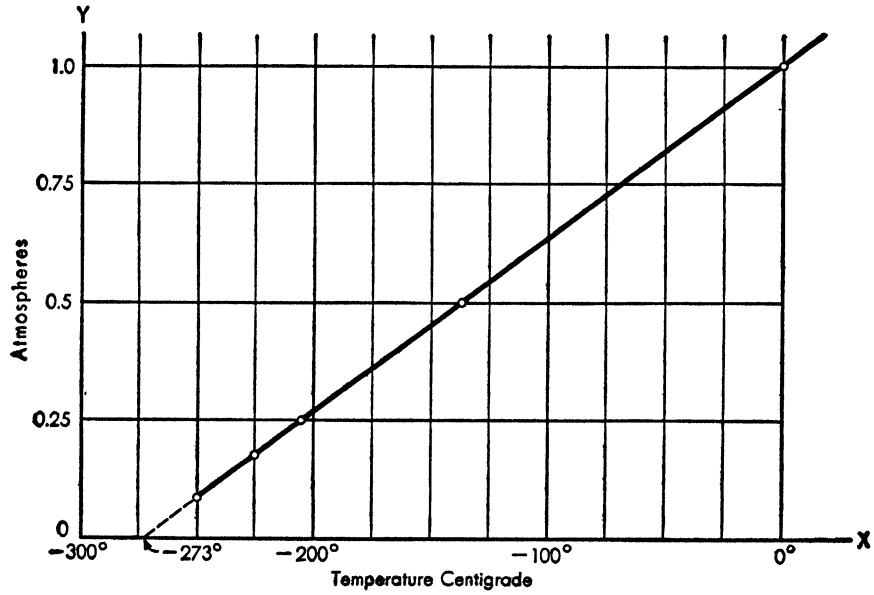


Figure 64. A Decrease in Temperature Lowers the Kinetic Energy of Molecules

When two gases, at the same temperature, are mixed, the pressure of the mixture is the sum of the pressures that the two gases would exert if each gas occupied the volume of the mixture by itself. Now the pressure that a gas exerts is proportional to the average kinetic energy of its molecules. Therefore, we must conclude that the average kinetic energy of the molecules of two gases are not changed when the gases are mixed, because their pressures are not changed — each gas exerts the same pressure as it would if the other were not present. If there is no change when the molecules are mixed, then the two kinds of molecules must have had the same average kinetic energy before they were mixed. Otherwise, as a result of collisions, the faster moving molecules would have lost, and the slower ones would have gained, and, therefore, the average kinetic energy of each would have been altered.

22. Charles's Law

Since the mass of a molecule does not vary with the temperature, the increase in pressure produced by an increase in temperature at constant volume must be caused by an increase in the average velocity of the molecules. Now if the molecules move more rapidly at a higher temperature, not only will more of them strike a definite area at a given instant, but each impact, because of the greater momentum of the molecule, will exert a greater pressure. An increase in temperature, therefore, produces an increase in pressure at constant volume or an increase in volume, if the pressure does not change. A decrease in temperature reduces the velocity of the molecules, thus resulting in decreased pressure.

23. Gases do not Settle

A gas does not settle to the bottom of a closed container. We cannot fill a room with a gas and return later, expecting to find all the gas collected near the floor. This must mean that the moving molecules of a gas suffer no loss of average kinetic energy when they collide with one another or strike against the walls of their container, a condition called *perfect elasticity*.

If they lost energy ($\frac{1}{2}\ mv^2$), this would mean that they would also lose in velocity, since mass (m) does not change. If they suffered a loss of energy when they collided, the molecules would soon cease to move, and the gas would settle.

Why do the molecules of gases suffer no loss in average kinetic energy as a result of collisions? We have seen (Section 20) that the Absolute temperature is a measure of the kinetic energy of the molecules that compose the gas. Therefore, when molecules collide there can be no conversion of the kinetic energy of the molecules into heat, which would raise the Absolute temperature because this temperature is proportional to the kinetic energy; and, hence, we cannot expect that one of these quantities can be increased at the expense of the other. We can look at this problem in another way. Heat energy is regarded as the kinetic energy of molecules. The faster the molecules move the more heat energy they possess and the higher their temperature, which is a measure of the intensity of heat or molecular motion. It is, therefore not possible to think of the collisions of molecules as resulting in a conversion of kinetic energy into heat because these terms refer to one and the same thing, and it would be absurd to say that either kinetic energy or heat could change into itself. Molecules of gases are, therefore, perfectly elastic in collisions.

If molecules of a gas did not move with high velocities and in all directions, they would settle under the influence of gravity. As a matter of fact there is some settling when one considers a large mass of gas, as the atmosphere, which extends many miles above the earth. At an altitude of thirty to forty miles there are many fewer mole-

cules per unit of volume than at the earth's surface, and most of the molecules at this altitude are those of the lighter components of the atmosphere. Gravity does, therefore, have some effect upon the molecules of gases. If it did not, the molecules composing the atmosphere would leave the earth and move out into interstellar space.

24. Dalton's Law

Dalton's Law of Partial Pressures states that the partial pressure of each gas in a mixture, at constant temperature, depends only upon the relative amount by volume, or the relative number of molecules, *of that gas* in the mixture. The different kinds of molecules in the mixture have no effect upon one another; a liter of nitrogen and a liter of oxygen, for example, when placed together in one liter, exert a pressure equal to the sum of their original pressures, and therefore, each gas in the mixture exerts the same pressure as when it alone occupies the whole space. If each gas is composed of particles widely separated by empty space, then in a mixture the particles of one gas may find room to spare in the space between and around the molecules of the other. Each kind of molecule strikes the walls as often and exerts as much pressure as if the other were not there.

As might be expected, Dalton's law does not hold for gases under high pressures, which cause the molecules to be crowded closely together, thus leaving little free space that molecules of other gases can occupy. The law also fails to hold accurately for mixtures of gases if the different kinds of molecules react or have strong attractions for one another.

25. Diffusion

One of the most significant properties of gases is their tendency to diffuse into space already occupied by other gases. If gases are composed of molecules in rapid motion and separated by relatively great distances

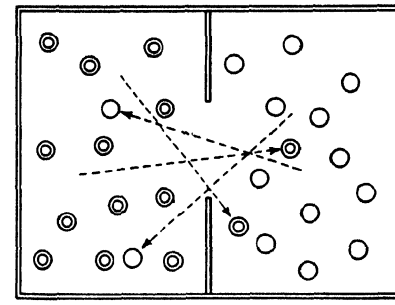


Figure 65. An Explanation of How One Gas can Diffuse into the Space Occupied by Another

as compared to their diameters, it is possible that the space occupied by one gas can be penetrated by the molecules of another.

We believe that molecules of gases, regardless of their masses, possess the same average kinetic energy at the same temperature and pressure. Since the kinetic energy of the molecule is defined as $\frac{1}{2} mv^2$, the molecules of a gas of low density must move with a greater velocity than the molecules of heavier gas. The rates of diffusion of gas molecules depend upon how rapidly these molecules are moving. Hence, it follows that the rate of diffusion is slower, the greater the mass of the molecules.

26. Deviations from the Gas Laws: Perfect Gas

The gas laws discussed in this chapter hold only for what we may call a *perfect*, or *ideal*, *gas*. Actually, the behavior of any gas deviates at least to a slight extent from the behavior predicted by the laws.

When gases already subjected to great pressure are further compressed, their volumes are not diminished as much as Boyle's law would lead one to predict. Since the decrease in the volume of a gas under increased pressure results from a reduction in the extent of the empty space between the molecules, it is evident that the reduction in volume is limited. When the pressure becomes very great, the molecules are crowded so closely together that the volume

that they occupy is, relatively, a large part of the whole volume. Under these conditions, the effect of increased pressure upon volume cannot be the same effect as it would be if there were still empty space between and around the molecules.

27. Van der Waals Forces

For all three states of matter there must be certain forces that cause the molecules or other particles that compose a substance to attract one another. If there were no attraction, the molecules would not stay in the same place, and energy would not be required to separate them as, for example, when a liquid evaporates. This attraction is the result of forces largely of an electrical nature and called *Van der Waals forces.* For gases these forces are weak because the greater velocities of gas molecules allow them to overcome more nearly completely than liquid-molecules the forces that tend to hold them together. As a result of their greater velocities and because of the relatively weak attraction for one another, the gas-molecules, unless they are confined in a closed vessel, diffuse indefinitely, and even when confined under ordinary pressure, they are separated by relatively great distances in comparison with their own dimensions.

Van der Waals forces, however, do result to some extent in pulling the molecules closer together. When the molecules of a gas are subjected to increased pressure, the volume is decreased inversely in proportion to the change in pressure in accordance with Boyle's law *and slightly more* because of the compression resulting from the increase in the strength of the Van der Waals forces when the molecules are crowded closer together. This effect, therefore, shows one more cause for deviation in the behavior of gases from the behavior of a perfect gas.

28. The Liquefaction of Gases

If we convert a gas into a liquid, we must increase the attraction between the molecules, and we must reduce their velocities so that they will no longer possess sufficient energy to overcome the forces that tend to hold them together. The first of these conditions is fulfilled by crowding the molecules together, i.e., by increasing the pressure. The second may be accomplished by cooling, since the velocity of the molecules decreases as the temperature falls.

For some gases, cooling without an increase of pressure results in liquefaction. This is true, for example, in the condensation of water vapor, which at a pressure of 760 mm. is converted to liquid water at 100° C. But if the boiling point of the liquid is very low, the gas must be cooled to an extremely low temperature (−183° in the case of oxygen and −252.7° in the case of hydrogen) before it can be liquefied at one atmosphere of pressure. These gases are more easily liquefied when increased pressure as well as cooling is used. Thus, oxygen can be liquefied at −118.8° if a pressure of 49.7 atmospheres is applied. Carbon dioxide can be liquefied at 0°, when a pressure of 38 atmospheres is applied; at 30°, 71 atmospheres must be used; and above 31.35°, it cannot be liquefied at any pressure.

29. Critical Temperature and Critical Pressure

The temperature above which a gas cannot be liquefied by any pressure is called the *critical temperature* of that gas.

TABLE 1

CRITICAL TEMPERATURES OF GASES

Gas	Boiling Point, °C. (1 atmosphere)	Critical Temperature °C.
Hydrogen	− 252.7	− 239.9
Nitrogen	− 196	− 147.1
Oxygen	− 183	− 118.8
Carbon dioxide	Sublimes	31.35
Ammonia	− 33.3	132.4
Sulfur dioxide	− 10	157.2
Water	100	374

Since the velocity and, therefore, the kinetic energy of the molecules of a gas increases with the temperature, liquefaction of a gas requires higher pressure as the temperature increases. At some definite temperature for each gas, therefore, the kinetic energy of the molecules is sufficiently great to overcome the Van der Waals forces completely and no pressure, however great, will cause the gas to be liquefied. At this temperature the molecules cannot be crowded closely enough together so that they are held by their Van der Waals forces. For example, oxygen at ordinary temperatures cannot be liquefied by any pressure. In fact, oxygen cannot be liquefied by any pressure if its temperature is above − 118.8°. At and below this temperature oxygen molecules are moving slowly enough so that they can be held together if they are subjected to sufficient pressure. The pressure required to liquefy a gas at the critical temperature is the *critical pressure*. For oxygen this pressure is 49.7 atmospheres.

REVIEW EXERCISES

1. The volume of a sample of gas at 20° C. and 770 mm. is 280 ml. What will be its volume if the temperature is reduced to − 250° C.?
2. A sample of gas measured at 22° C. and 740 mm. occupies 200 ml., and weighs 0.21 g. What is the weight of a liter of the same gas measured under standard conditions?
3. A mixture of two gases, *A* and *B*, exerts a pressure of 700 mm. and occupies 500 ml. If the pressure of gas *A*, alone, is 200 mm., under the same conditions of temperature and volume, what volume would each gas alone occupy at a pressure of 770 mm.?
4. One liter of a gas measured at 0° C. weighs 2.42 g. What will one liter of the same gas weigh if measured at 273° C., the pressure remaining unchanged?
5. The volume of a sample of oxygen, measured over water at 30° C. and 738 mm., is 468 ml. What would be the volume of the sample if it were dry and were measured under standard conditions?
6. Ten liters of air at 0° C. are brought into a room, where the temperature is raised to 25° C. What pressure would have to be exerted on the air to prevent a change in volume if the original pressure was 760 mm.?
7. To what (Centigrade) temperature would a sample of gas have to be heated to change its volume of 150 ml. at 30° C. to a volume of 300 ml.? Assume a constant pressure.
8. Sulfur dioxide is approximately 32 times and carbon dioxide is approximately 22 times as heavy as hydrogen, liter for liter. Compare the rates of diffusion of sulfur dioxide and carbon dioxide.
9. In terms of the kinetic theory account for the following features of the behavior of gases: (1) diffusion; (2) compressibility; (3) effect of temperature upon pressure at constant volume and upon volume at constant pressure.
10. How do cooling and increase of pressure aid in the liquefaction of gases?
11. Enumerate the differences in behavior of gases and liquids. How are these differences explained?
12. What evidence indicates that the molecules of gas are perfectly elastic?
13. Why do gases not obey Boyle's law exactly under very high pressures?
14. What are some of the indications that molecules of a gas are (1) moving, (2) far apart, and (3) have relatively slight attraction for one another?
15. What conditions of atmospheric pressure prevail in a region indicated on a weather map as a cyclone? What is the general direction of movement of cyclones in the United States? What kind of weather usually accompanies a cyclone? What is the difference between a cyclone and a hurricane or tornado? (Consult some reference on meteorology or an encyclopedia.)
16. What conditions cause the atmospheric pressure to vary from day to day at one place on the earth's surface?
17. Describe the measurements and calculations that would be necessary in order that the weights of equal volumes of two gases can be compared.

18. The density of a gas is 1.5. What further information must be given, or understood, about this statement before it can be regarded as having much meaning or value?
19. The pressure of a mixture of gases A and B is 400 mm., when the volume is 400 ml. If the partial pressure of A is 100 mm., what volume would the quantity of A that is present in the mixture occupy if its pressure were 400 mm. and B were not present? If its pressure, when alone, were 100 mm.?
20. If all of the air in a room 15 by 9 by 20 feet and at a pressure of 760 mm. were compressed until the volume became 1 cu. ft., what pressure would it exert, temperature remaining constant?
21. A liter of dry oxygen under standard conditions weighs 1.429 g. The volume of a sample of oxygen collected over water at 25° and 740 mm. is 754 ml. What is the weight of the dry oxygen in the sample?
22. What is the weight of a liter of dry oxygen measured at 22° C. and 732 mm.?
23. What evidence indicates that the velocities of molecules increase as the temperature rises?
24. Would two gases that reacted with each other form a mixture that would behave in accordance with Dalton's Law? Justify your answer.
25. What conclusions (if any) would you be justified in making if you knew:
    (*a*) That the volumes and pressures of samples of two gases at 0° are the same; that they contain the same number of molecules; and that the two volumes weigh 1 and 2 g., respectively?
    (*b*) That the volumes of the two gases described in (*a*) remain unchanged when the temperature is increased to 20° C., but the pressures increase, each by the same amount, from 720 mm. to 773.5 mm.?
    (*c*) That samples of two gases at 0° C. have the same volume and the same pressure?
    (*d*) That samples of two gases at 0° C. have the same volume and contain the same number of molecules?
26. Show that the average kinetic energy of gas molecules is proportional to their Absolute temperature.
27. Show that the average kinetic energy of the molecules of all gases at the same temperature must be the same.
28. Why should one not expect Dalton's law of partial pressures to hold true for mixtures of gases under very high pressures?
29. Why do gases escaping from a container in which they have been compressed undergo a decrease in temperature?
30. A flask containing water is heated until the water boils. It is then removed from the flame, stoppered, and cooled. The water begins to boil again. Is this possible? Explain.

REFERENCES FOR FURTHER READING

Bragg, Sir W., *Concerning the Nature of Things*, New York: Harper Bros., 1925.

Dampier-Whetham, W. C., *A History of Science.*

Faraday, M., *Liquefaction of Gases*, Alembic Club Reprint, No. 12. Edinburgh: E. and S. Livingstone, 1823.

Leonard, W., *Crusaders of Chemistry.*

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry.*

Moore, F. J., *The History of Chemistry.*

The Kinetic Theory: *J. Chem. Ed.*, **4,** 327 (1927); **6,** 1797 (1929); **12,** 31 (1935); **24,** 186 (1946); *Science Leaflet*, **11,** 457.

8

MOLECULAR AND ATOMIC WEIGHTS

MOLECULAR WEIGHTS

1. Introduction

In this chapter our first problem deals with the methods used to calculate the relative weights of the molecules of different substances. However, several other important questions will be considered: (1) Why are we certain that molecules of some elements contain two or more atoms? (2) What method can be used to determine the relative numbers of atoms of two or more elements in a compound? For example, how many atoms of hydrogen and oxygen does a molecule of water contain?

Clues to the answers of these questions were first found in studies involving the behavior and reactions of gases and, especially, in the ratios of the volumes of gases that react or are produced by reactions. For example, it was found that two volumes of hydrogen always react with one volume of oxygen to form two volumes of water vapor, if all volumes are measured under the same conditions. Thus, 10 cc. of hydrogen react with 5 cc. of oxygen to form 10 cc. of water vapor.

2. Gay Lussac's Law of Combining Volumes of Gases

Gay Lussac, in 1808, pointed out that: *The volumes of all gases that take part in a reaction, or are produced by the reaction, are in the proportion of small, whole numbers to one another.* The combining volumes of hydrogen and oxygen are in the ratio of 2 to 1. The ratio of the volume of water vapor and the volume [1] of oxygen is 2 to 1; and the volumes of hydrogen and water vapor are in the ratio of 1 to 1.

3. An Explanation of the Reaction of Hydrogen and Oxygen

Let us consider the reaction of *two* volumes of hydrogen with *one* volume of oxygen to form *two* volumes of water vapor. How is this possible? If we did not know the facts, we might assume that two volumes of one gas and one volume of another would form *three* volumes of the product. The following explanation is suggested as a possible answer to the question.

Let us assume that equal volumes of hydrogen, oxygen, and water vapor — all measured at the same temperature and pressure — contain the same number of molecules. As our unit of volume, and solely for simplicity and convenience, let us select the volume occupied by one molecule of oxygen (Figure 66), and greatly magnify it for the purpose of illustration. Now the volume of hydrogen that reacts with this volume of oxygen is twice as large and contains — since we have assumed that equal volumes contain

[1] We use volume here in the sense of a unit of volume, which might be a liter, a cubic centimeter, a cubic foot, etc.

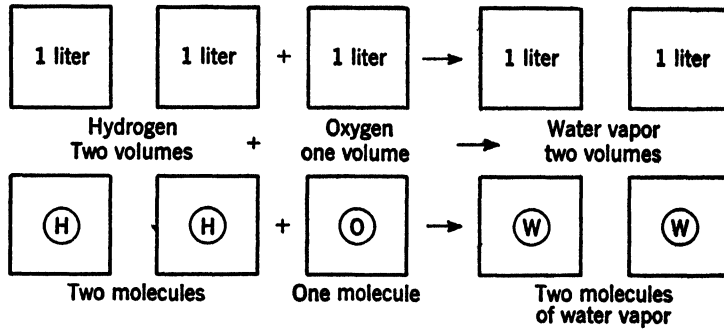


Figure 66. The Reaction of Hydrogen and Oxygen

If equal volumes of different gases contain the same number of molecules, it is obvious that the molecules that react and are produced are in the same proportion as the volumes of the different gases involved in the reaction.

the same number — twice as many, or two, molecules. For every molecule of oxygen there are, then, two of hydrogen. Next, consider the product of the reaction. There are also two volumes of water vapor and, hence, two molecules of this substance. We may conclude, therefore, that two molecules of hydrogen react with one of oxygen to form two of water vapor.

4. Explanations of Other Reactions

Let us consider the reaction of hydrogen and chlorine. In this reaction (Figure 67) one volume of hydrogen reacts with an equal volume of chlorine. If equal volumes of all gases, under the same conditions, contain the same number of molecules, it is evident that one molecule of hydrogen reacts with one of chlorine. The volume of hydrogen chloride is twice that of the hydrogen, or chlorine, and, if our assumption is valid, there must be produced two molecules of hydrogen chloride from one molecule each of hydrogen and chlorine.

We have now provided a reasonable explanation of the fact that the volumes of hydrogen, oxygen, and water vapor are in the proportion of 2 to 1 to 2, while the volumes of hydrogen, chlorine, and hydrogen chloride are in the proportion of 1 to 1 to 2.

The reaction of one volume of nitrogen with three volumes of hydrogen to form two volumes of ammonia is explained, upon a similar basis, in Figure 68. In this reaction we must conclude that one particle of nitrogen reacts with three of hydrogen to form two of ammonia.

5. Avogadro's Principle

The assumption stated in Section 3 was first made by Avogadro in 1811, and it has since become so firmly established that it is

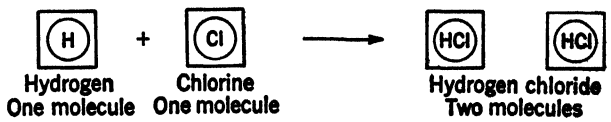


Figure 67. One molecule each of hydrogen and chlorine form two molecules of hydrogen chloride

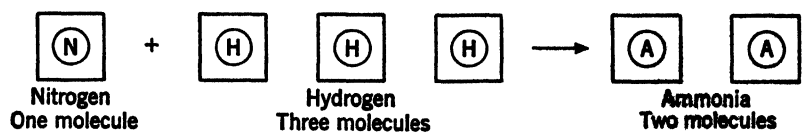


Figure 68. One molecule of nitrogen and three of hydrogen form two molecules of ammonia

now called Avogadro's Principle: *Equal volumes of all gases, at the same pressure and temperature, contain the same number of molecules.*

What evidence of the truth of Avogadro's principle do we have? Let us consider two vessels of equal volume containing two different gases at the same temperature and such quantities as are required to make their pressures also the same. Now the pressure of a gas, at constant temperature, depends upon the average kinetic energy of the molecules, the number of molecules, and the volume occupied by them. The average kinetic energy of the molecules of the two gases under consideration is the same because (page 86) the temperatures are the same. The volume and pressure are also the same for each gas. What about the number of molecules of each? This must also be the same, otherwise the two gases would not exert the same pressure.

6. Method of Comparing the Weights of Molecules

Avogadro's law provides a means of determining the relative weights of molecules of different substances in the gaseous state. Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules. Hence, to compare the weights of the molecules of two gases, all that we need to do is to find the weights of equal volumes of the two under the same conditions. If we select a definite weight of some gas as a standard, then the volume occupied by this weight of the standard and an equal volume of any other gas will contain the same number of molecules. If we find the weights of this volume of several different gases, we obtain a group of values that represent the relative weights of the different molecules. These are called the *molecular weights* of the different substances.

7. Determination of the Molecular Weights of Gases

Oxygen has been selected as the substance to be used as the basis of a scale of molecular weights. Since the number 16 has been selected to represent the weight of an atom of oxygen (page 28), and since there are two atoms of oxygen in a molecule, 32 is obviously the number to be used as the molecular weight of oxygen. This gives us just one scale for the comparison of the weights of all atoms and molecules.

Under standard conditions, 32 g. of oxygen occupies a volume of 22.4 liters. To compare the weight of a molecule of carbon dioxide, for example, with the weight of a molecule of oxygen, we must obtain, in some way, the weight of the *same number of molecules* of carbon dioxide as we have in 32 g. of oxygen. This number (page 29) is 6.023×10^{23}. The weight of this number of molecules of carbon dioxide can be determined by finding the weight of 22.4 liters of carbon dioxide, also under standard conditions. By experiment and calculation we find that this volume weighs 44 g. Now we know that

6.023×10^{23} molecules of oxygen weigh 32 g.
6.023×10^{23} molecules of carbon dioxide weight 44 g.

Therefore, the weights of *single* oxygen and carbon dioxide molecules are in the ratio of 32 to 44.

8. Gram-Molecular Weights and Gram-Molecular Volumes

In much of the work that he does, the chemist must know how many molecules of a substance he is using, or must use to obtain a certain result; at least he must know the weight of one substance that he must use to obtain the number of molecules

Nitrogen	Oxygen
28 grams	32 grams
1 g. mol. wt.	1 g. mol. wt.
6.023×10^{23} molecules	6.023×10^{23} molecules
0° 0	0° C
760 mm. pressure	760 mm. pressure

Figure 69. A Comparison of 22.4 Liters Each of Nitrogen and Oxygen

required to react with a definite number of another substance. Let us say, for example, that he wishes to obtain the same number of molecules of carbon dioxide and oxygen. How can he do this? As shown above, 32 g. of oxygen and 44 g. of carbon dioxide contain the same number of molecules. Therefore, if he uses 44 g. of carbon dioxide for every 32 g. of oxygen, or if the weights of the two substances are kept in the ratio of 44 to 32 (for example, 22 g. and 16 g., 11 g. and 8 g., 4.4 and 3.2 g., etc.) he may be certain that he is dealing with equal numbers of molecules of the two substances.

When molecular weights are expressed in grams, they are called *gram-molecular weights*. We may also define the gram-molecular weight of a substance as the weight in grams of 6.023×10^{23} molecules of that substance. Instead of gram-molecular weight the shorter term *mole* is sometimes used.

Since 22.4 liters is the volume occupied by the *gram-molecular* weight (or 6.023×10^{23} molecules) of any pure gas, under standard conditions, this is called the *gram-molecular volume*, or mole-volume.

9. A Sample Calculation of the Molecular Weight

In finding the molecular weight of a gas it is not necessary, of course, that we should weigh 22.4 liters of the gas. If the volume of 1 g. of a gas at 20° C. and under a pressure of 720 mm. is 200 ml., the volume, at standard conditions, is Volume (standard) $= 200 \times \frac{273}{293} \times \frac{720}{760} = 176.5$ ml. We can now calculate the gram-molecular weight of the gas as follows:

Weight of 176.5 ml. = 1 g.

22.4 liters = 22,400 ml.

$$\text{Weight of 22.4 liters} = \frac{22{,}400}{176.5} \times 1 = 126.9 \text{ g.}$$

The gram-molecular weight, or the weight of one mole, of the gas is, therefore, 126.9 g.

10. Molecular Weights of Liquids and Solids

The method that we have outlined for the determination of the molecular weights of gases cannot be applied to substances in their liquid or solid states. If a solid or a liquid can be converted readily into the gaseous state, however, the weight of any definite volume, measured at any temperature and pressure, can be employed to calculate the weight of 22.4 liters of the vapor under standard conditions. Since the weight does not change upon converting the vapor into the liquid and solid states, or *vice versa*, and if the number of molecules of the substance remains the same during the transition, the molecular weight of the substance in the vapor state may be taken, also, as the molecular weight of the substance in its liquid or solid states. This is not always true. There are substances which are composed of one kind of molecule in the vapor state and of another kind in the liquid or solid state. Sulfur vapor, for example, appears to be composed of molecules containing eight atoms, S_8, but in the liquid the molecules appear to consist of S_8 units tied together to form long chains, each chain constituting a molecule.

Many substances cannot be obtained conveniently in the gaseous state, and some cannot be obtained in this state at all, because they decompose when heated. To determine the relative weights of the molecules of these substances other methods must be employed. These are discussed in a later chapter.

11. Molecular Weights from the Formulas of Compounds

If we know the formula of a compound, we can calculate its molecular weight as the sum of the atomic weights of its elements. Each atomic weight must be considered, in finding the sum, as many times as the atom of the element is represented in the formula. Thus, the formula for sucrose (cane sugar) is $C_{12}H_{22}O_{11}$ and the molecular weight is:

$$(12 \times 12) + (22 \times 1.008) + (11 \times 16) = 342.18.$$

12. Molecules and Atoms of Hydrogen and Chlorine

In the reaction between hydrogen and chlorine (page 93), one molecule of hydrogen reacts with one molecule of chlorine to form two molecules of hydrogen chloride. Now each of the molecules of hydrogen chloride must contain some hydrogen, and since all hydrogen chloride molecules are identical, each molecule should contain the same weight of hydrogen. *But this must mean that the molecule of hydrogen is composed of two equal parts, and that one of these goes into one molecule of hydrogen chloride and the other goes into another.* Similarly, the chlorine molecule also consists of two parts. These parts, or fractions, of molecules of hydrogen and chlorine are atoms. Here, then, is one reason why we find it necessary to distinguish between two kinds of particles of the elements, atoms and molecules. The atom of an element is not, as Dalton thought, the smallest particle of the element that can exist alone. Such a particle is a molecule of the element.

13. Does a Molecule of Hydrogen Contain More than Two Atoms?

This question naturally arises as one follows the reasoning of the preceding paragraph. The molecule might contain two atoms, each of which forms a molecule of hydrogen chloride. The molecule cannot contain three, or any odd number of atoms, because this would mean that one and one-half, or some other number involving the half of an atom, would be used to form each molecule of hydrogen chloride. However, the molecule might possibly contain four, six, or some other even number of atoms. If the molecule of hydrogen contained four atoms, each molecule of hydrogen chloride would contain two atoms of hydrogen.

However, the gram-molecular weight of hydrogen — the weight of 22.4 standard liters — is 2.016 g., and the gram-atomic weight is 1.008 g. Furthermore, if the molecule contained more than two atoms, there should be reactions in which one molecule of hydrogen produces more than two molecules of some other substance. No such reactions have ever been found. Hence, there can be only two atoms in a molecule of this element. Likewise, the chlorine molecule can contain but two atoms.

14. The Reaction of Hydrogen and Oxygen

The reaction between oxygen and hydrogen to form water indicates that the oxygen molecule is composed of two atoms:

2 Volumes of Hydrogen + 1 Volume of Oxygen ⟶ 2 Volumes of Water vapor.

Hence, in accordance with Avogadro's principle, we conclude that

2 Molecules of Hydrogen + 1 Molecule of Oxygen ⟶ 2 Molecules of Water vapor.

We must conclude that one-half of the oxygen molecule goes into each of the water molecules, and that the molecule of oxygen contains two atoms. Since a molecule of oxygen never produces more than two molecules of any substance, the molecule must not contain more than two atoms. Since each hydrogen molecule also contains two atoms, we may say that four atoms of hydrogen react with two atoms of oxygen. Two molecules of water are produced by this reaction, and each of these is composed of two atoms of hydrogen and one atom of oxygen.

15. The Composition of Molecules of Other Elements

The molecules of some elements, such as the inert gases of the atmosphere, are *monatomic*, i.e., their molecules are single atoms. Many other gaseous elements, including nitrogen, oxygen, chlorine, and hy-

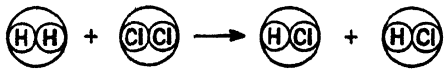


Figure 70

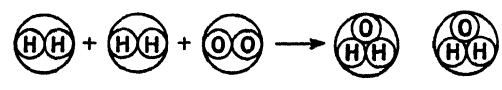


Figure 71

drogen, are *diatomic*, i.e., their molecules contain two atoms each. Elements that are solids under ordinary conditions often consist of complex molecules in which the number of atoms cannot always be determined. For some elements an entire crystal of the substance may be regarded as one "giant" molecule (page 20). In the absence of definite information concerning their molecular composition, they are usually regarded as monatomic in the solid state. Molecules of phosphorus (vapor) contain four atoms (P_4), and molecules of sulfur contain different numbers of atoms, S_2, S_6, S_8, depending upon the temperature. In writing equations for reactions involving the solid states of these elements we usually employ the simple symbols of the elements, P and S.

ATOMIC WEIGHTS

16. Introduction

Now that we have learned how the molecular weights of certain elements and compounds are determined, we shall turn our attention to methods used in determining the relative weights of different atoms. We shall discuss, first, two approximate methods, one of which was mentioned briefly on page 29, and later we shall describe the method generally used to calculate more nearly exact values. As we study this chapter, we should keep in mind our definition of an atom as the smallest particle of an element that takes part in a chemical change. *This means, then, that the smallest weight of the element found in the molecular weight of any of the compounds of the element should be the atomic weight.*

In a later chapter we shall study other methods that are used to compare the weights of atoms. These methods are physical rather than chemical in character. They have been used, for example, to determine the number of isotopes of an element and the relative weights of the atoms of the isotopes. The methods used by the chemist, however, were in use long before anything was known about electrons and atomic nuclei. They are based, for the most part, upon the weights of different elements that react to form compounds. They provide, of course, not the relative weights of the different isotopes of an element, but the mean atomic weight of all the isotopes, because in a chemical reaction all the isotopes of an element are present and participate in the same proportion as they occur in the free element. The mean atomic weight depends, of course, upon the relative numbers of atoms of the different isotopes as well as upon the relative weights of the atoms.

17. Atomic Weights Determined by the Method of Dulong and Petit

One of the earliest methods used to calculate the atomic weights of the elements was suggested by Dulong and Petit in 1818. They pointed out that the product of the atomic weight of an element multiplied by the specific heat of the substance is approximately the same for all elements in the solid state. The numerical value of this product is usually between 6 and 7, and the average is about 6.3.

Element	Atomic Weight	Specific Heat	Product Atomic Weight × Specific Heat
Sodium	23	0.29	6.7
Magnesium	24.3	0.245	6.0
Phosphorus	31	0.20	6.2
Iron	55.8	0.112	6.3
Copper	63.6	0.095	6.0
Gold	197.2	0.032	6.3
Mercury (solid)	200.6	0.0335	6.7

The *specific heat* of a substance is defined as the quantity of heat (in calories) required to raise the temperature of one gram of the substance one degree (C.).

$$\text{Atomic weight} \times \text{specific heat} = 6.3.$$

$$\text{Atomic weight} = \frac{6.3}{\text{specific heat}}.$$

If the specific heat of a solid element is known, the approximate atomic weight can be calculated by means of this equation. The values thus obtained are not accurate, because the product of the atomic weight by the specific heat varies slightly for different elements.

The general principle upon which this procedure is based indicates that the heat required to raise the temperature of the same number of atoms of any solid element is approximately the same, namely 6.3 calories for 6.023×10^{23} atoms.

18. Method Involving the Analysis of Gram-Molecular Weights of Compounds of the Element

This method was first discussed on page 29. We have defined an atom as the smallest portion of an element that participates in a chemical reaction, and we have found evidence to indicate that a molecule of a compound contains one or more atoms of each of its constituent elements. *Therefore, it is evident that a gram-molecular weight of any compound of an element contains one, two, three, or some whole number of gram-atomic weights of that element.*

This method involves, therefore, the analysis of as many compounds of an element as possible with the view of determining the weight of the element in a gram-molecular weight of each. The different weights of the element found in these analyses will be approximate multiples of some relatively small weight, which is the gram-atomic weight. The results thus obtained are approximate only, largely because of errors in the measurement of gram-molecular weights.

Let us apply this method to the determination of the atomic weight of chlorine. First, we must determine the molecular weight of each of several compounds that contain this element. Then we must analyze each compound to determine the weight of chlorine in a gram-molecular weight of each. An inspection of these results will show that the weight of chlorine in the gram-molecular weight of any compound of the element is, approximately, 35 g. or a multiple of 35 g. This number, therefore, may be regarded as the approximate atomic weight of the element.

Some elements do not form many compounds. In such cases it is possible that the element forms no available compound whose molecular weight contains *one* atomic weight of the element. If we should find, for example, that the molecular weights of compounds of element x contain 14, 42, 63 and 84 parts of x and if no other data were available, we could not conclude that the atomic weight of x is the smallest weight (14), since 63 is not a multiple of 14. All of these weights are multiples, however, of 7, which would, therefore, be regarded as the atomic weight.

19. Equivalent Weights

A more accurate method of determining atomic weights involves the *equivalent weights* of the elements. *The gram equivalent weight of an element is the weight of the element that combines with 1.008 g. of hydrogen or the weight of the element that is equivalent in combining capacity to one gram-atomic weight of hydrogen.* Thus, the gram-equivalent weight of oxygen in water is the weight — 8 g. — that combines with 1.008 g. of hydrogen. Likewise, for chlorine in hydrogen chloride it is 35.46 g. The equivalent weight of any other element can be calculated as the weight of it that combines with 8 g. of oxygen to form an oxide or with 35.46 g. of chlorine to form a chloride of this element. That weight of the element is equivalent to 1.008 g. of hydro-

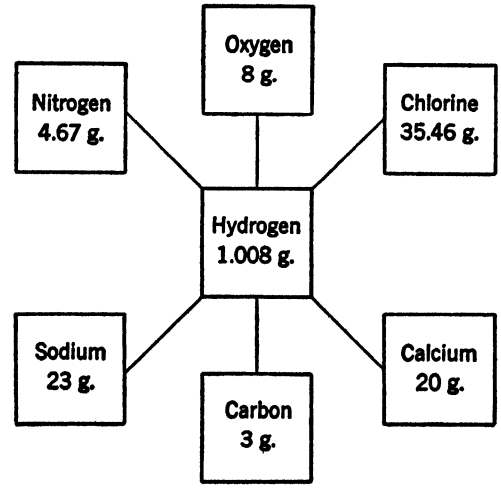


Figure 72. Equivalent weights of oxygen in water, chlorine in hydrogen chloride, calcium in calcium oxide, sodium in sodium oxide, and nitrogen in ammonia

gen in its combining capacity — it combines with the same weight of oxygen as 1.008 g. of hydrogen does. Many of the elements have different equivalent weights in different compounds. Thus, carbon in CO and CO_2 has equivalent weights of 6 and 3, respectively.

20. Atomic Weights from Equivalent Weights

Let us remember, first, that the gram-equivalent weight of an element combines with, or takes the place of, one gram-atomic weight of hydrogen. Now one atom of hydrogen never combines with more than one atom of another element, but one atom of some elements combines with one of hydrogen; for other elements, one atom combines with two of hydrogen; and for others, three or four atoms of hydrogen are required. These differences are illustrated in such compounds as HCl, H_2O, NH_3, and CH_4. Therefore, for chlorine (in HCl), the equivalent weight is the same as the atomic weight; a whole atomic weight of chlorine is required to combine with an atomic weight of hydrogen. For oxygen, the equivalent weight is one-half the atomic weight. For nitrogen in ammonia, NH_3, the equivalent weight is one-third of the atomic weight, and for carbon in methane, CH_4, it is one-fourth. We note, therefore, that the atomic weight is equal to the equivalent weight, *or* it is two, three, four, or some whole number times as great. These numbers for different elements are the same as those previously referred to (page 43) as the valence numbers of the elements. Hence,

$$\frac{\text{Atomic weight}}{\text{Equivalent weight}} = \text{a small, whole number.}$$

If the equivalent weight and the number indicated in this equation are known, the exact atomic weight can be calculated by multiplying these two quantities, one by the other. The number can be determined by dividing the *approximate* atomic weight, as determined by one of the methods first described, by the equivalent weight and selecting the *whole* number that is nearest the number thus obtained.

21. An Example of the Calculation of Atomic Weight

The calculation of the atomic weight of an element from its equivalent weight is illustrated by the following example. We know that the atomic weight of sulfur is somewhere near 32 from the fact that the weights of sulfur in the gram-molecular weights of its compounds are (approximately) multiples of 32 g. The equivalent weight of sulfur can be determined from its combination with any one of a number of elements. We find, for example, that the combining ratio of sulfur and silver is one part of sulfur to 6.73 parts of silver. Now the equivalent weight of silver is 107.88, since this weight (in grams) combines with 8 g. of oxygen to form silver oxide and with 35.46 g. of chlorine to form silver chloride. The weight of sulfur, therefore, which combines with an equivalent weight of silver is:

$\frac{107.88}{6.73} = 16.03 =$ The equivalent weight of sulfur.

Since the equivalent weight is evidently one-half of the atomic weight (the approximate atomic weight is already known to be 32), the accurate value for the atomic weight is $2 \times 16.03 = 32.06$.

REVIEW EXERCISES

1. State Gay-Lussac's law of combining volumes and explain the statement by means of appropriate illustrations.
2. What are the proportions of the volumes of gases involved in the following reactions?
   $S + O_2 \rightarrow SO_2$; all except S are gases.
   $C_7H_{16} + 11\ O_2 \rightarrow 7\ CO_2 + 8\ H_2O$; all substances in the gaseous state.
   $3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2$; Fe and Fe_3O_4 are solids.
3. What explanation is offered for the reaction of *two* volumes of hydrogen with *one* volume of oxygen to form only *two* volumes of water vapor?
4. What important assumption was originally made in arriving at this explanation?
5. Using this assumption, account for the vol-

ume relations in the reaction of (1) hydrogen and chlorine and (2) hydrogen and nitrogen.

6. Show how Avogadro's law makes possible a method of determining the molecular weights of gases.
7. By what line of reasoning do we conclude that a molecule of hydrogen contains two atoms? What evidence indicates that it does not contain one? four? three?
8. How can we show that a molecule of oxygen contains two atoms, and that two atoms of hydrogen react with one atom of oxygen to form water?
9. What is the meaning of the terms *molecular weight* and *gram-molecular weight* as applied to an element or a compound? Why is 22.4 liters, rather than some other volume, used in determining the gram-molecular weights of gases?
10. Starting with the weight of any volume of a pure gas at any pressure and temperature, show how you would calculate the molecular weight.
11. How can the molecular weights of some liquids and solids be determined?
12. Define Avogadro's number.
13. A liter (under standard conditions) of each of three gases weighs 0.178, 2.85, and 6.87 grams, respectively. Calculate the molecular weights of the three gases.
14. The density of a gas as compared to air (under standard conditions) is 2.45. Calculate the molecular weight of the gas, if one (standard) liter of air weighs 1.293 g.
15. A sample of hydrogen sulfide, H_2S, occupies 643 ml. at a certain temperature and pressure and weighs 0.952 g. What is the molecular weight of another gas if 2.105 g. of it occupies 1422 ml., at the same temperature and pressure?
16. What evidence indicates the validity of Avogadro's Principle?
17. What are the molecular weights of the following compounds? CH_4, methane; H_2SO_4, sulfuric acid; $C_3H_5(OH)_3$, glycerine; C_2H_5OH, ethyl alcohol; and CS_2, carbon disulfide.
18. Criticize the following statement: The gram-molecular weight of any substance is the weight of 22.4 liters of it.
19. Criticize the following statement: The molecular weight of a compound is the sum of the atomic weights of the elements that compose the compound.
20. What would the gram-molecular volume of a gaseous substance be if the molecular weight of oxygen were arbitrarily fixed as 50 instead of 32?
21. What is the weight of 22.4 liters (standard conditions) of ammonia, NH_3? Of 10 liters?
22. What (standard) volume would 20 g. of ammonia occupy?
23. Which of the following statements are correct?
    (*a*) Under standard conditions 22.4 liters of oxygen contain the same number of molecules as there are atoms in 16 g. of oxygen.
    (*b*) One gram-molecular weight of oxygen contains twice as many atoms of oxygen as one gram-atomic weight.
    (*c*) Under the same conditions of temperature and pressure equal volumes of two different gaseous elements contain the same number of atoms.
    (*d*) The atomic weight of oxygen is one-half of the molecular weight of that element.
    (*e*) Under the same conditions of temperature and pressure one gram-molecular weight of oxygen occupies a volume twice as great as that occupied by one gram-atomic weight of that element.
    (*f*) Equal volumes of hydrogen and oxygen under the same conditions of pressure and temperature contain the same number of atoms.
24. The simplest formula of a compound is CH but 22.4 liters of the compound in the vapor state (reduced to standard conditions) weighs 78 g. What is the true formula?
25. The specific heat of a solid element is 0.032. Calculate the approximate atomic weight of the element.
26. Define *equivalent weight* of an element and show how the equivalent weight can be used in calculating the atomic weight of an element.
27. The approximate atomic weight of the element x appears to be 58. Experiment shows that 1 gram of x combines with 1.2084 grams of chlorine. What is the actual atomic weight of x?
28. A compound containing phosphorus and

chlorine is composed of 22.5 per cent of phosphorus. The molecular weight of the compound is 137.5 g. Calculate the formula.

29. The percentage compositions of two oxides of chromium (approximate at. wt., 50) are:

(1)		(2)	
Cr	52%	Cr	68.4%
O	48%	O	31.6%

(*a*) Calculate the equivalent weight of chromium in each compound.

(*b*) The equivalent weight of chromium in No. 2 is found by a more accurate determination than that indicated to be 17.34. Calculate the atomic weight of the element.

30. Calculate from the formulas, the weight of 1 liter of each of the following gases: hexane, C_6H_{14}; acetylene, C_2H_2; ammonia, NH_3; hydrogen sulfide, H_2S; and sulfur dioxide, SO_2.

31. By reacting with hydrochloric acid, 0.327 g. of a metal displaces 112.0 ml. of hydrogen (under standard conditions). What is the valence number of the metal? The atomic weight of the metal is 65 4.

32. With what weight of oxygen will the same weight of the metal mentioned above combine?

33. If the valence number of aluminum is 3 and its atomic weight is 26.97, what (standard) volume of hydrogen will be liberated when 10 g. of aluminum react with hydrochloric acid?

34. One gram-molecular weight of a compound of element x and hydrogen contains one gram-atomic weight of x and one and one-half times as much hydrogen as is contained in a gram-molecular weight of water. What is the valence number of x?

35. Gram-molecular weights of compounds of the hypothetical element E contain 21, 49, and 70 grams, respectively, of E. What is the largest number that might be the atomic weight of E on the basis of these data? How would your answer be changed if analyses of other compounds showed 7, 10.5, and 3.5 grams of E in gram-molecular weights of three compounds?

36. Describe an experiment by which you could determine the equivalent weight of aluminum.

37. How many electrons are contained in the valence shell of an atom of a metal the atomic weight of which is three times the equivalent weight?

38. What weight of magnesium is required to liberate one liter of hydrogen (standard conditions) from hydrochloric acid if the equivalent weight of magnesium is 12.16?

39. How are valence numbers of one for sodium, two for magnesium, and three for aluminum explained in terms of the structures of the three kinds of atoms?

40. If the equivalent weight of a metal is one third of the metal's atomic weight, what (standard) volume of hydrogen will be liberated when one-fourth of the gram-atomic weight of the metal reacts with hydrochloric acid?

41. The number of atoms of hydrogen with which one atom of an element will combine, or the number of hydrogen atoms that one atom of an element can replace, can be calculated by dividing the element's atomic weight by its equivalent weight. Why is this true?

REFERENCES FOR FURTHER READING

Cannizzaro, S., *Sketch of a Course in Natural Philosophy*, Alembic Club Reprint, No. 18. Edinburgh: E. and S. Livingstone, 1858.

Dalton, J., J. Gay-Lussac, and A. Avogadro, *Foundations of the Molecular Theory*, Alembic Club Reprint, No. 4.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry.*

Moore, F. J., *History of Chemistry.*

Tilden, Sir W. A., *Famous Chemists*, New York: E. P. Dutton and Company, 1921. (Gay-Lussac, Avogadro, and Cannizzaro.)

Atomic Weights: *J. Chem. Ed.*, **9,** 453 (1932); **11,** 441 (1934); **24,** 528 (1949).

Avogadro's Number: *J. Chem. Ed.*, **6,** 299 (1929).

Cannizzaro's Work: *J. Chem. Ed.*, **3,** 1361 (1926); **4,** 7, 836 (1927).

9

SYMBOLS, FORMULAS, AND EQUATIONS

1. Introduction

This chapter explains the chemist's language — the symbols, formulas, and equations that he uses in place of words to express certain facts concerning substances and the chemical changes in which they engage. He uses them, not to conceal his information in strange and mystical forms as the alchemist did, but because they are simple and convenient forms of expression.

2. Symbols of the Elements

The symbols of the elements are the initials or abbreviations of their names; usually, the English name is abbreviated, but sometimes the Latin, and in one or two instances the German, name is used. Thus, H, O, Cl, N, Br, P, S, Al, Mg, and Ca are the symbols respectively of hydrogen, oxygen, chlorine, nitrogen, bromine, phosphorus, sulfur, aluminum, magnesium, and calcium. The symbol of iron is Fe, which is taken from the Latin word, *ferrum*. The following symbols also have Latin origins: Na, from *natrium*, for sodium; Au, from *aurum*, for gold; Ag, from *argentum*, for silver; Pb, from *plumbum*, for lead; Sn, from *stannum*, for tin; W, from the German *wolfram*; and so on. Symbols of this kind were first used by Berzelius in the first half of the nineteenth century.

Not only does the symbol represent the element in general, but it indicates a very definite weight of the element. When we write H_2, for example, we refer to a molecular weight of hydrogen or, more specifically, to a gram-molecular weight (2.016 g).

FORMULAS OF COMPOUNDS

3. Formulas

The composition of a compound composed of molecules — and formed, therefore, by atoms sharing electrons — is expressed by placing together the symbols of the elements that compose the compound. A statement of this kind is called a *formula*. The symbol of each element must occur as many times in the formula as there are atomic weights of the element in a molecular weight of the compound — as many times as there are atoms of the element in a molecule of the compound. The number of atoms (unless that number is one) of each element is indicated by a figure written below and to the right of the symbol of the element. Thus, the formula for carbon dioxide, CO_2, indicates that a molecule contains one atom of carbon and two atoms of oxygen.

The formula of a compound composed of molecules states the following facts concerning the compound:

(1) The elements of which it is composed.

(2) The number of atoms of each element in a molecule of the compound.

(3) The combining proportion (by

weight) of the elements of the compound. The formula CO_2, for example, shows that 1 gram-atomic weight (12 g.) of carbon combines with 2 gram-atomic weights (32 g.) of oxygen.

(4) The molecular weight of the compound. This is numerically equal to the sum of the atomic weights of the constituent elements, each atomic weight being taken as many times as there are atoms of that element in a molecule of the compound.

The formula of a compound composed of ions, as $(Na^+ + Cl^-)$ or $(2\ Na^+ + SO_4^=)$, represents the simplest set of ions in the compound and states the relative numbers of the two ions. Thus, NaCl, or $(Na^+ + Cl^-)$ indicates that in sodium chloride there is one sodium ion for each chloride ion. The formula Na_2SO_4, or $(2\ Na^+ + SO_4^=)$ indicates that there are two sodium ions for each sulfate, $SO_4^=$, ion in sodium sulfate. Since there are no molecules of these substances, we can scarcely speak of their molecular weights. We sometimes, however, use the term *formula* weight in much the same sense to refer to the sum of the atomic weights of the elements composing both ions. Thus, the formula weight of sodium chloride is 23 + 35.46, or 58.46, and for sodium sulfate it is $(2 \times 23) + 32 + (4 \times 16)$, or 142.

4. The Determination of the Simplest Formula of Water

When a compound is analyzed the results are usually stated as the percentages of the different elements in the compound. Percentage means parts per hundred. Since the percentage of hydrogen in water is 11.19, for example, this means that 11.19 g. of every 100 g. of water consist of hydrogen.

The formula of a compound must express the combining proportions *in terms of the number of atoms of each element* — not in terms of the number of grams of each element. To determine the numbers of atoms of each element that combine, we may divide the weight representing the percentage of each element by the atomic weight of the element. Thus, we divide 11.19 by 1.008 and 88.81 by 16:

$\frac{11.19\text{ g.}}{1.008\text{ g.}} = 11.10$ gram-atomic weights of hydrogen in 100 g. of water.

$\frac{88.81\text{ g.}}{16\text{ g.}} = 5.55$ gram-atomic weights of oxygen in 100 g. of water.

Thus, we learn that hydrogen and oxygen combine to form water in the ratio of 11.10 to 5.55 gram-atomic weights. The gram-atomic weights of all elements contain the same number (6.023×10^{23}) of atoms; and hence, 11.10 atoms of hydrogen combine with 5.55 atoms of oxygen, or $\frac{11.10}{5.55} = 2$ atoms of hydrogen combine with one atom of oxygen. The *simplest* formula that agrees with this requirement is H_2O.

5. The Actual Molecular Formula of Water

The formula of water might be H_2O, H_4O_2, H_6O_3, etc., because all that we proved above was that there are two atoms of hydrogen for each atom of oxygen. We did not decide how many atoms of oxygen there are in a molecule of water. Now we can calculate the gram-molecular weight of water vapor by finding the weight of 22.4 liters, under standard conditions. If the weight of this volume of water vapor is 18 g., we conclude that the formula of water is H_2O, since 18 is approximately the sum of one atomic weight of oxygen and two atomic weights of hydrogen. But if the molecular weight were found to be 36 g., we would have to decide that the formula is $(H_2O)_2$, or H_4O_2, and so on. It is needless, perhaps, to add that we know now that the molecular weight of water (vapor) is 18, and that the correct formula, therefore, is H_2O.

6. The Formula of Sodium Sulfate

Let us determine, next, the formula of a substance composed of ions instead of molecules. A certain compound is found by

analysis to have the following composition: sodium, 32.38 per cent; sulfur, 22.57 per cent; and oxygen, 45.05 per cent. These figures mean that 100 g. of the compound contain 32.38 g. of sodium, 22.57 g. of sulfur, and 45.05 g. of oxygen. The atomic weights of sodium, sulfur, and oxygen are 23, 32, and 16, respectively. Therefore, 100 g. of the compound contain

$$\frac{32.38 \text{ g.}}{23 \text{ g.}} = 1.408 \text{ gram-atomic weights of sodium.}$$

$$\frac{22.57 \text{ g.}}{32 \text{ g.}} = 0.704 \text{ gram-atomic weight of sulfur.}$$

$$\frac{45.05 \text{ g.}}{16 \text{ g.}} = 2.816 \text{ gram-atomic weights of oxygen.}$$

These results show that 1.408 atoms of sodium, 0.704 atom of sulfur, and 2.816 atoms of oxygen combine, but the formula must show *whole numbers* of sodium, sulfur, and oxygen atoms. To determine what these whole numbers are, let us calculate the numbers of sodium and oxygen atoms for each atom of sulfur, since it is evident that the atoms of sulfur are present in the compound in the smallest number.

$1.408 \div 0.704 = 2$, the number of atoms of sodium.

$2.816 \div 0.704 = 4$, the number of atoms of oxygen.

Hence, the formula for this compound is Na_2SO_4. We cannot say, however, that this represents a molecule of sodium sulfate, because there are no molecules of this substance. The crystals are composed of regularly spaced sodium and sulfate ions, $2\ Na^+ + SO_4^=$.

COMBINING CAPACITY OR VALENCE

7. Introduction

In Chapter 3 we discussed the combining capacities and the valence numbers of different kinds of atoms in relation to their structures. The valence numbers of the elements were calculated from chemical data, however, long before anything was known about the structures of atoms. Indeed, information concerning valence contributed no small part to the working out of theories concerning the arrangement of electrons in the different shells of the atom. Chemical methods of calculating valence numbers are, therefore, worthy of our attention. The structure of an atom may be useful in helping us to predict the chemical behavior of that atom, but it alone cannot always be used to find the number of electrons that a chlorine atom shares with oxygen in a particular compound, or whether the oxidation number of iron in a compound in a test tube is + 2 or + 3.

In discussing the equivalent weights of the elements, we have pointed out that atomic weights of different elements may combine with one, two, three, or four atomic weights of hydrogen; in other compounds, one atomic weight of an element may combine with as much oxygen, chlorine, or some other element as one, two, three, four, or some other whole number (up to eight) atomic weights of hydrogen. The atoms of different elements, therefore, may possess different *combining capacities*, or *valence numbers*.

The valence of an element is expressed by a small, whole number. The valence number of hydrogen, arbitrarily, is fixed as 1. Since one atomic weight of chlorine, in hydrogen chloride, combines with an atomic weight of hydrogen, and since the atomic weights of all elements contain the same number of atoms, it is evident that *one atom* of chlorine combines with *one atom* of hydrogen. The chlorine atom in this compound has, therefore, the same combining capacity as the atom of hydrogen, and the valence number of chlorine is one — the same as the valence of hydrogen.

8. The Valence Numbers of Carbon in Carbon Dioxide and of Nitrogen in Ammonia

In carbon dioxide 12 g. of carbon is

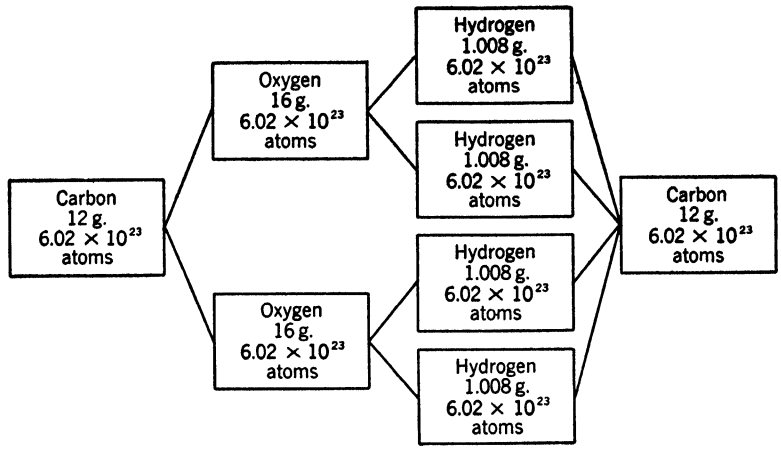


Figure 73. Valence

One atomic weight of carbon combines with two atomic weights of oxygen or four atomic weights of hydrogen. One atomic weight of oxygen combines with two atomic weights of hydrogen. Refer now to Figure 74.

combined with 32 g. of oxygen — one gram-atomic weight of carbon and two gram-atomic weights of oxygen. Since the gram-equivalent weight of oxygen is 8 g., that of carbon must be 3 g., or one-fourth of the atomic weight. In this particular compound with oxygen, a whole atomic weight of carbon has the same combining capacity as four atomic weights of hydrogen; a single carbon atom, therefore, combines with as much oxygen as four atoms of hydrogen. As compared with 1 for hydrogen, the valence number of carbon in carbon dioxide is 4.

In ammonia, NH_3, one atomic weight of nitrogen is combined with three atomic weights of hydrogen; hence one atom of nitrogen has the same combining capacity as three atoms of hydrogen, and the valence number of nitrogen in this compound is 3.

9. The Valence Numbers of Other Elements

The valence numbers of other elements can be calculated in a manner similar to that used for carbon, oxygen, nitrogen, and chlorine. The general equation upon which these calculations are based is

$$\text{Valence Number} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}.$$

As explained for carbon, for example, the use of this equation depends upon the fact that it allows us to calculate the number of atomic weights of hydrogen that one atomic weight of an element combines with *or* the number of atomic weights of hydrogen to which one atomic weight of the element is equivalent in combining with other elements. By its use, therefore, we are able to make a direct comparison of the combining capacities of different kinds of elements.

10. Two or More Valence Numbers of the Same Element

If two elements combine to form two or more compounds, the valence number of one of the elements must be different in the different compounds. The valence number

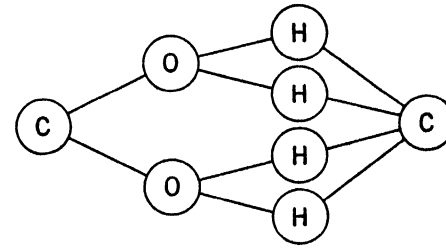


Figure 74. Valence

One atom of carbon must combine with two atoms of oxygen or with four atoms of hydrogen. One atom of oxygen combines with two atoms of hydrogen.

of carbon in methane (CH_4) and carbon dioxide (CO_2) is 4, but in carbon monoxide (CO) its valence number is only 2. Nitrogen forms five oxides, and must therefore possess five different valence numbers in its compounds with oxygen. The different valence numbers of an element represent different states of oxidation of that element and, therefore, are usually called the *oxidation numbers* (page 61) of the element.)

Oxide	No. of H atoms equivalent to each N atom	Equivalent Wt. of N	Oxidation Number of N
N_2O	1	14	1
NO	2	7	2
N_2O_3	3	$4\frac{2}{3}$	3
NO_2	4	$3\frac{1}{2}$	4
N_2O_5	5	$2\frac{4}{5}$	5

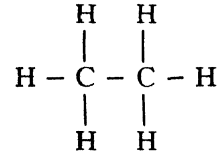
11. The Use of Valence Numbers in Writing the Formulas of Compounds

Fortunately, it is not necessary to determine the formula of every compound with which we may be concerned by taking a sample of it into the laboratory and analyzing it to determine the percentages of the different elements that it contains. Each element has only a few possible valence numbers, and some have but one. If we know the valence number of each element in the compound, it is possible to write the formula without recourse to laboratory determinations, provided the compound is a relatively simple one composed of the atoms of two elements or of two ions. Even for more complicated compounds the same procedure is possible if something is known about the class of substances to which the compound belongs and the manner in which its different atoms are grouped. One simple rule must be observed: The total valence numbers of the two parts of the compound must be the same. Thus, in H_2O the two hydrogen atoms have a total valence number of 2, which is the same as the valence number of one atom of oxygen.

If the valence numbers of the elements that combine with oxygen to form oxides are known, it is an easy matter to write the formulas. Sodium has the same combining capacity as hydrogen; and hence, the formula of sodium oxide is Na_2O. Calcium has a valence number of two. One atom of calcium combines, therefore, with one atom of oxygen. The formula for the oxide is CaO. Iron displays a valence number of three. This means that one atom of iron combines with as much oxygen as three atoms of hydrogen. This is one and one-half atoms of oxygen. Hence, in this compound there must be two atoms of iron for every three atoms of oxygen, and the formula, therefore, is Fe_2O_3.

12. Formulas of Compounds that Indicate Abnormal Valence Numbers

The valence number of an atom or ion is always represented by a *whole* number. There are some compounds, however, for which this rule does not appear to hold. Thus, the valence number of iron in magnetic iron oxide, Fe_3O_4, appears to be $2\frac{2}{3}$. This oxide probably contains iron in two oxidation states + 2 and + 3, and is composed of two oxides, FeO and Fe_2O_3. Sodium peroxide, Na_2O_2 is best represented by the formula ($2\ Na^+ + O_2^=$) which shows that the two oxygen atoms act as a negative ion. Hence, the valence number of sodium is one and not two, as one might conclude from the formula Na_2O_2. Many carbon compounds are also abnormal in a similar sense. The formula of ethane, for example, is C_2H_6. This formula indicates that the valence number of carbon is three, but it is really four.



One of the valence bonds of carbon serves

to unite the two carbon atoms. The other three unite carbon and hydrogen. Formulas of this kind, which show how atoms are arranged within the molecule, as well as the number of atoms of each element, are called *structural* formulas.

13. Derivation of Percentage Composition from the Formula

Since the formula of a compound expresses the proportion by weight in which the elements combine, the percentage of each element in the compound can be determined from the formula. To find the percentages of sodium, sulfur, and oxygen in sodium sulfate (Na_2SO_4), for example, we must first calculate the weight of the compound corresponding to this formula. This is found by adding together the atomic weights of the elements, taking the atomic weight of each element as many times as there are atoms of that element in the formula of the compound.

$$(2 \times 23) + 32 + (4 \times 16) = 142.$$

Of 142 g. of the compound, 46 g. are sodium, 32 g. are sulfur, and 64 g. are oxygen. Therefore, in 100 g. of the compound there are, for example, $\frac{46}{142} \times 100 = 32.38$ g. of sodium. Since percentage means parts per hundred, the percentages of sodium, sulfur, and oxygen are 32.28, 22.57, and 45.05, respectively.

EQUATIONS

14. The Chemical Equation

We can, of course, state all the facts about a reaction by writing out several sentences. Such a statement becomes tedious and complicated to the writer and to the reader. The equation that the chemist uses to express all these facts is concise and simple. It consists of symbols, formulas, and numbers in place of words.

To write a completely balanced equation one must know several facts concerning the reaction and the substances involved in it. Iron dissolves in a solution of hydrogen chloride (hydrochloric acid) to form hydrogen, which escapes as a gas, and a chloride of iron, which remains in the solution but forms crystals when the water is removed by evaporation. These facts alone are not sufficient information to permit us to write the equation for this reaction. We must know that hydrogen chloride is represented correctly by the formula HCl and that iron exists as Fe, not Fe_2, Fe_3, or Fe_4. We must know, too, that of the two chlorides of iron, $FeCl_2$ and $FeCl_3$, the former (ferrous chloride) is produced in this reaction. When all these facts are known, we can write the equation in tentative form as follows:

$$Fe + (H^+ + Cl^-) \longrightarrow (Fe^{++} + 2\ Cl^-) + H_2.$$

To balance this equation, twice as much hydrochloric acid, HCl, as shown is required to supply the two hydrogen atoms and the two chlorine atoms needed to form the products. Hence,

$$Fe + 2\ (H^+ + Cl^-) \longrightarrow (Fe^{++} + 2\ Cl^-) + H_2.$$

It is evident that the chloride ions undergo no change in this reaction; only iron and hydrogen are involved. For this reason, the equation is sometimes written to show the change that these elements undergo, and the chlorine is omitted:

$$Fe + 2\ H^+ \longrightarrow Fe^{++} + H_2.$$

This equation shows that each atom of iron gives two electrons to hydrogen, one to each of two atoms. This is the whole story.

In writing the equation for a reaction that occurs in an aqueous solution, the water in which the reacting substances are mixed is not indicated. It takes, usually, no direct part in the reaction and, therefore, need not be shown.

15. The Use of Valence Numbers in Writing Equations

Let us illustrate the balancing of an equation involving ions by means of the following example, in which we shall use the ions of barium hydroxide and aluminum

sulfate. Let us assume that the formulas of the original substances are known, and that the products are known to be aluminum hydroxide and barium sulfate, although we do not as yet know their formulas. The original substances, $Ba(OH)_2$ and $Al_2(SO_4)_3$, are dissolved together in water. Since both are substances composed of ions the solution contains $(Ba^{++} + 2\ OH^-) + (2\ Al^{+++} + 3\ SO_4^=)$. Both products are insoluble (or slightly soluble), and, therefore, each precipitates. We, therefore, write a first draft of the equation:

$$(Ba^{++} + 2\ OH^-) + (2\ Al^{+++} + 3\ SO_4^=) \longrightarrow AlOH\downarrow + BaSO_4\downarrow .$$

The downward pointing arrow ($\downarrow$) indicates the formation of a slightly soluble substance (a precipitate).

As written, the formulas of aluminum hydroxide and barium sulfate are not necessarily correct. The valence numbers of Al^{+++}, OH^-, Ba^{++}, and $SO_4^=$, are three, one, two, and two respectively, as shown by their electrical charges and also by the formulas of their original compounds. To complete these formulas, we must use a sufficient number of Al^{+++} ions and OH^- ions so that the total valence numbers, or charges, of the two parts of the compound, are the same, because in any complete set of ions the units of negative charge balance the number of units of positive charge; likewise, the barium ion must be shown as combining with a sufficient number of sulfate ions to satisfy the same requirement. To equalize the valence numbers of Al^{+++} and OH^-, we must use one ion of aluminum and three hydroxyl (OH^-) ions. This gives a total valence number of three for each part of the compound. The formula of aluminum hydroxide, therefore, is $Al(OH)_3$. For barium sulfate just one ion of barium is needed to balance one sulfate ion, since the valence number of barium is two, and that of sulfate is also two. The formula for barium sulfate is $BaSO_4$. We now write the equation:

$$(Ba^{++} + 2\ OH^-) + (2\ Al^{+++} + 3\ SO_4^=) \longrightarrow Al(OH)_3\downarrow + BaSO_4\downarrow .$$

There are two aluminum ions on the left, and both of these must appear on the right in aluminum hydroxide; hence, the formula of aluminum hydroxide must be doubled, i.e., $2\ Al(OH)_3$. To do this we must provide $6\ OH^-$ ions, and, therefore, the formula for barium hydroxide must appear three times on the left, i.e., $3\ (Ba^{++} + 2\ OH^-)$. We now note that we have $3\ Ba^{++}$ and $3\ SO_4^=$ ions. The complete equation, therefore, is:

$$3\ (Ba^{++} + 2\ OH^-) + (2\ Al^{+++} + 3\ SO_4^=) \longrightarrow 2\ Al(OH)_3\downarrow + 3\ BaSO_4\downarrow .$$

This method of balancing equations will apply to all reactions except those in which changes in the valence of certain elements occur during the reaction and which, therefore, involve oxidation and reduction.

16. What an Equation States Concerning a Reaction

The equation, $2\ H_2 + O_2 \longrightarrow 2\ H_2O$, states that two gram-molecular weights of hydrogen react with one gram-molecular weight of oxygen to form two gram-molecular weights of water. Hence, it states the proportions, by weight, of the reacting substances to one another and, also, to the product of the reaction. It also states the composition of each substance in terms of the kinds of elements and the number of atoms of each in a molecule, and the number of gram-atomic weights of each element in a gram-molecular weight of each substance.

We use an equation, therefore, when we wish to determine the weight of one substance that will react with, or that can be produced from, a definite weight of another. If, for example, we must find the weight of water, that can be produced from 40 g. of oxygen, we first write the equation for the reaction:

$$\underset{\text{2 gm. mol. wts.}}{2\,H_2} + \underset{\text{1 gm. mol. wt.}}{O_2} \longrightarrow \underset{\text{2 gm. mol. wts.}}{2\,H_2O}.$$

4.032 g. 32 g. 36.032 g.

The equation states that 32 g. of oxygen produce 36.032 g. of water. To determine the weight of water that can be formed from 40 g. of oxygen, we may proceed as follows:

32 g. of oxygen produce 36.032 grams of water

1 g. of oxygen produces $\frac{36.032}{32}$ g. of water

40 g. of oxygen produce $40 \times \frac{36.032}{32}$ g. of water.

Not only does the equation express the relative weights of all substances that react or are produced, but it also expresses the relative volumes of all gaseous substances involved in the reaction. Since gram-molecular weights of gases occupy 22.4 liters under standard conditions, the equation for the reaction between hydrogen and oxygen states that 44.8 liters of water vapor are produced from 44.8 liters of hydrogen and 22.4 liters of oxygen. The volumes of all three substances are those *calculated* for 0° and 760 mm., from the volumes actually involved in a reaction occurring at much higher temperature and probably at a different pressure.

CHANGES IN ENERGY DURING REACTIONS

17. Introduction

Sometimes our chief concern in a reaction is, not what products it forms, but the kind and quantity of energy which it liberates. In burning coal and wood as fuels, we are concerned primarily with the quantity of energy that may be released when a definite weight of the fuel is burned. Likewise, we are interested not in the products of the chemical changes that occur in a storage battery, or other types of electrochemical cells, but in the electrical energy output of these cells. For other reactions, it is important that we know, or be able to determine, the quantities of energy which must be absorbed before the reactions can occur. Energy is expensive, as expensive as some forms of matter, and the amount of energy required to carry out a process must be as seriously considered as the cost of the raw materials used in the process. The study of the energy changes accompanying a chemical reaction often provides valuable clues as to the exact nature of the changes occurring in the reacting system and, in addition, provides information that is useful in selecting the most favorable conditions under which the reaction can be employed.

18. Endothermic and Exothermic Reactions

A reaction that is accompanied by a liberation of energy is said to be *exothermic*. One accompanied by an absorption of energy is *endothermic*. Since the energy that is liberated or absorbed is usually in the form of heat, the energy change during a reaction is usually expressed in calories and is called the *heat of the reaction;* the weights of the substances involved are those represented by the balanced equation for the reaction.

19. Measurement of the Heats of Reactions

A *calorimeter* is used to measure the heat absorbed or liberated in chemical reactions. This instrument consists essentially of a vessel in which the reaction occurs, and which is carefully insulated to prevent heat exchanges with the surroundings. The cover is made of some substance that also acts as an insulator. It is perforated to take an accurate thermometer, a tube

through which the reactants can be added, and a stirrer. A simple calorimeter for elementary experiments can be constructed by placing a beaker upon corks within a larger beaker and providing an insulating cover.

To determine the heat of the reaction between a solution of sodium hydroxide and hydrochloric acid, for example, measured volumes of the two solutions, which must contain known quantities of the two substances per unit of volume of solution, i.e., per cubic centimeter or per liter, are poured through the tube into the inside vessel of the calorimeter. The temperatures of the two solutions should be known and, for convenience, they should be the same, before they are mixed in the calorimeter. The stirrer is started and the maximum temperature reached by the reacting mixture is noted. The heat liberated is used to raise the temperature of the solution and the calorimeter. Therefore, if we multiply the number of calories required to raise their temperature 1° C. by the rise in temperature, expressed in degrees, we have the total number of calories liberated by the reaction. The heat absorbed by the water is equal, of course, to the weight of water in grams times the rise in temperature. The heat absorbed by the different parts of the calorimeter is measured, or calculated, from their weights and specific heats, or we can calculate the heat absorbed by the calorimeter during a reaction from information concerning the rise in temperature produced by reactions for which the quantities of heat released are known.

20. The Bomb Calorimeter

In the calorimeter that is used in determining the calorific value of coal, a bomb made of strong steel is the inside vessel. The bomb is lined with an alloy that is resistant to chemical action, and it is fitted with a tight screwcap cover. The sample whose calorific value is to be determined is placed in a small platinum cup (Figure 75), and a small iron wire is embedded in the charge. The wire is connected to the terminals of the electrical circuit on the cover of the bomb. Oxygen, under pressure, is forced into the bomb through a valve at the top, and the bomb is then completely immersed in a definite quantity of water in a well-insulated outer vessel. A thermometer for the measurement of temperature changes and a stirrer are suspended in the outer vessel. The electrical circuit is then closed, whereupon the iron wire becomes hot enough to ignite the sample. Combustion proceeds rapidly in the presence of the compressed oxygen, and the heat is absorbed largely by the water, which consequently undergoes a rise in temperature. Some of the heat is also used to raise the temperature of the bomb, the stirrer, the walls of the outside vessel, and other parts of the apparatus to the same temperature that the water attains. The quantity of heat liberated by the combustion is calculated upon the basis that one calorie raises the temperature of one gram of water one degree Centigrade. From the specific heats and weights of the materials in the apparatus, a correction is made for the heat which they absorb. This is added to the heat absorbed by the water in finding the total heat of the reaction.

In expressing the calorific value of fuels, the British thermal unit (B.T.U.) is gener-

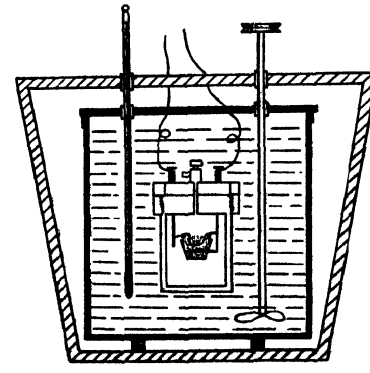


Figure 75. A Calorimeter

ally used as the unit of heat, instead of the calorie. This unit represents the quantity of heat which is required to raise the temperature of one pound of water one degree Fahrenheit. This quantity of heat is equal to 252 calories.

21. Thermochemical Equations

For some reactions, the energy involved may be of as much importance as the weights of the reacting substances, and for such reactions *thermochemical* equations are written. If there can be any doubt concerning the physical states of the reacting substances and the products, these states are indicated in the equation, because the different states of a substance contain different amounts of energy. More energy is required to decompose a definite weight of liquid water, for example, than the same weight of water vapor, because the vapor already contains more energy than the liquid. The decomposition of liquid water is shown by the following equation:

$$2\,H_2O\,(liq.) \longrightarrow 2\,H_2 + O_2 - 136{,}800 \text{ calories.}$$

Thermochemical equations may be added and subtracted to calculate the heats of reactions that have not been studied, or to find the heats of formations (from their elements) of compounds that are not formed by the direct combination of the elements. Let us take as an illustration the determination of the heat of formation of hydrogen peroxide from hydrogen and oxygen. The direct synthesis of this compound from the two elements is not possible, but we may calculate the heat of this reaction as follows. We know the quantity of heat that is liberated when 2 gram-molecular weights of hydrogen peroxide decompose:

$$(1)\ 2\,H_2O_2 \longrightarrow 2\,H_2O\,(liq.) + O_2 + 47{,}800 \text{ calories.}$$

We also know the heat of formation of water, when this substance is produced from the elements:

$$(2)\ 2\,H_2 + O_2 \longrightarrow 2\,H_2O\,(liq.) + 136{,}800 \text{ calories.}$$

We may now write the following equation in which the water is eliminated by subtracting (1) from (2).

$$(3)\ 2\,H_2 + O_2 - 2\,H_2O_2 \longrightarrow - O_2 + 89{,}000 \text{ calories.}$$

This equation may also be written in the following form:

$$(4)\ 2\,H_2 + 2\,O_2 \longrightarrow 2\,H_2O_2 + 89{,}000 \text{ calories.}$$

The heat of formation of hydrogen peroxide is shown to be 44,500 calories per gram-molecular weight.

22. Heats of Combustion and Formation

The *heat of combustion* is usually expressed as the number of calories liberated when the gram-molecular weight of the substance burns, although it is sometimes used in speaking of the heat released when one gram of the substance undergoes combustion. The *heat of formation* of a compound is usually expressed as the number of calories liberated or absorbed when one gram-molecular weight of the compound is formed from the constituent elements. Thus, the heat of formation of carbon dioxide, as the term is ordinarily used, refers to the heat liberated when 44 g. of carbon dioxide are formed by the combination of carbon and oxygen.

23. Equations Showing the Heats of Reactions

The following examples of endothermic and exothermic reactions will serve to illustrate the differences between the two types of change. The data are for gaseous states of all products except NaCl and CaO, and represent the quantities of heat liberated or absorbed when the number of gram-molecular weights shown in the equations are formed.

			Calories
$2C$	$+ O_2 \longrightarrow$	$2CO$	$+ 52{,}860$
$2CO$	$+ O_2 \longrightarrow$	$2CO_2$	$+ 135{,}910$
C	$+ O_2 \longrightarrow$	CO_2	$+ 94{,}385$
$2H_2$	$+ O_2 \longrightarrow$	$2H_2O$	$+ 115{,}660$
$2Na$	$+ Cl_2 \longrightarrow$	$2NaCl$	$+ 196{,}720$
C	$+ 2S \longrightarrow$	CS_2	$- 25{,}400$
H_2	$+ S \longrightarrow$	H_2S	$+ 5{,}260$
N_2	$+ 3H_2 \longrightarrow$	$2NH_3$	$+ 22{,}000$
N_2	$+ O_2 \longrightarrow$	$2NO$	$- 43{,}200$
H_2	$+ Cl_2 \longrightarrow$	$2HCl$	$+ 4{,}400$
H_2	$+ I_2 \longrightarrow$	$2HI$	$- 12{,}800$
$2Ca$	$+ O_2 \longrightarrow$	$2CaO$	$+ 302{,}600$
S	$+ O_2 \longrightarrow$	SO_2	$+ 70{,}900$

In a way, the heat of formation of a substance is a measure of the stability of the substance, since it is also the energy that must be supplied to decompose the compound into its constituent elements. We should expect, therefore, that hydrogen sulfide is more easily decomposed than water. In general, we may say that endothermic compounds are less stable than exothermic compounds.

REVIEW EXERCISES

1. What weights of hydrogen are represented by H and H_2, respectively?
2. A mixture of substances in their gaseous states contains 3 g. of argon, 27 g. of water vapor, 7 g. of nitrogen, and 4 g. of oxygen. How many gram-atomic weights of all elements, free or combined, does the mixture contain? How many gram-molecular weights?
3. What does a chemical equation state concerning the reaction which it represents?
4. State all the facts which are expressed by the following equation:

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

5. What information must be available for the determination of the actual formula of a compound? How is this information obtained for gaseous substances?
6. What facts concerning the compounds which they represent are shown by the following formulas? Calcium phosphate (solid) $Ca_3^{++}(PO_4^{\equiv})_2$; ethane (gas), C_2H_6; ammonia (gas) NH_3; calcium oxide (solid) $Ca^{++}O^{=}$; and sugar (solid); $C_{12}H_{22}O_{11}$; calcium chloride (solid), $Ca^{++}2\,Cl^{-}$.
7. The weight of 1335 ml. of a pure gaseous substance measured at 100° C. and 740 mm. is 2.589 g. Analysis shows that it consists of 62.07 per cent of carbon, 27.59 per cent of oxygen, and 10.34 per cent hydrogen. What is the formula of the compound?
8. What is the simplest formula of a solid substance which has the following percentage composition? Sodium 32.39 per cent; phosphorus 21.85 per cent; oxygen 45.06 per cent; hydrogen 0.70 per cent.
9. Calculate the percentage composition of each of the following substances: NH_3, CO_2, C_2H_6O, H_2O, Fe_2O_3.
10. What volume of oxygen (standard conditions) can be produced by the decomposition of 25 grams of water? What volume of hydrogen is produced at the same time?
11. What weight of tin will react with chlorine to form 110 g. of stannic chloride, $SnCl_4$?
12. What volume of carbon dioxide measured at 20° and 760 mm. can be produced from 1 kg. of $CaCO_3$ by the following reaction?

$$CaCO_3 \rightarrow CaO + CO_2.$$

13. Propane has the formula C_3H_8. Write the equation to show the reaction when this substance burns completely. What volume of oxygen (standard conditions) would be required to burn 132 g. of propane?
14. The formula for silver oxide is Ag_2O. What weight of carbon will be required to produce 20 g. of metallic silver from silver oxide by the following reaction?

$$Ag_2O + C \rightarrow CO + 2\,Ag.$$

15. Define: Exothermic and endothermic reactions. Give examples of each.
16. How many grams of water could be heated from 0° C. to 100° C. by the complete utilization of the heat which is liberated when 10 g. of carbon are converted into carbon dioxide?
17. What weight of ten per cent sulfuric acid solution must be used to produce ten standard liters of hydrogen by action upon an

excess of zinc? If the density (weight per ml.) of this solution is 1.072, what volume of sulfuric acid would be required?

18. What are the valence numbers of the elements combined with oxygen in the following oxides? Bi_2O_3, PbO, PbO_2, B_2O_3, P_2O_5, SiO_2, Ag_2O. Write the formulas for the corresponding chlorides.

19. A compound contains 1.8 g. of carbon, 0.4 g. of hydrogen, and 2.4 g. of oxygen in a sample weighing 4.6 g. If one liter of this compound in its gaseous state weighs 4.108 g. (volume measured under standard conditions), what is the molecular formula of the compound?

20. How is the heat of a reaction measured? What is the unit that is used in expressing the heats of reactions?

21. Calculate the heat of formation of carbon monoxide from the following data:

$$C + O_2 \rightarrow CO_2 + 94{,}385 \text{ cal.}$$
$$2\,CO + O_2 \rightarrow 2\,CO_2 + 135{,}910 \text{ cal.}$$

22. Complete and balance the following equations:

(*a*) $Al + Cl_2 \rightarrow AlCl_3$

(*b*) $Al + (H^+ + Cl^-) \rightarrow AlCl_3 + H_2$

(*c*) $Cl_2 + H_2S \rightarrow (H^+ + Cl^-) + S$

(*d*) $(Ag^+ + NO_3^-) + (Ca^{++} + 2\,Cl^-) \rightarrow AgCl\downarrow + (Ca^{++} + 2\,NO_3^-)$

(*e*) $CS_2 + O_2 \rightarrow CO_2 + SO_2$

(*f*) $(3\,Ba^{++} + 2\,PO_4^{\equiv}) + (2\,H^+ + SO_4^{=}) \rightarrow BaSO_4\downarrow + (3\,H^+ + PO_4^{\equiv})$

23. What quantity of heat will be liberated in the combustion of 1 ton (2000 lbs.) of coke if we assume that the coke is pure carbon and that the carbon is converted completely into carbon dioxide? What (standard) volume of carbon dioxide will be produced?

24. What are the simplest formulas of the oxides and chlorides of the following elements which have the valence numbers indicated?

Mn (7); Sn (4); Cr (6); Be (2); Os (8); Al (3); Hg (1); P (5).

25. Which of the following reactions would liberate the greater quantity of heat, assuming that the same weight of water is formed in the two reactions?

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \text{ (liquid)}$$
$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \text{ (water vapor)}$$

Why?

REFERENCES FOR FURTHER READING

Chapin, W. H., and L. E. Steiner, *Second Year College Chemistry*, 5th ed. New York: John Wiley and Sons, 1943.

Berzelius: *J. Chem. Ed.*, **9**, 477 (1932).

10

THE GENERAL CLASSIFICATION OF ELEMENTS AND COMPOUNDS

Instead of attempting to learn the characteristic behavior of each and every substance with which we have to deal, it is often sufficient to associate different substances with the classes to which they belong. All the substances belonging to one class have certain properties in common. Hydrochloric acid, for example, possesses very few properties which are peculiar to itself. In general, its properties are those of all acids. Before considering other elements and their compounds, let us turn our attention, therefore, to *substances in general*, with the purpose of determining the classes into which they can be divided and the characteristic properties of each class. In this chapter we shall concern ourselves first, with the classification of the elements and, later, with the classification of compounds.

CLASSIFICATION OF THE ELEMENTS; MENDELEEFF'S PERIODIC TABLE

1. Introduction

The study of the elements has been greatly simplified by classifying them into a few families, or groups, the members of which are very closely related in chemical, and often in physical, properties. Among the works of man there is no more beautiful example of our definition of science as classified and organized knowledge than this classification of the elements. Mendeleeff, in 1869, laid the foundation for the present scheme of classification, when he arranged the elements in the order of *increasing atomic weights*. In Chapter 12 we shall extend our study to include a scheme of classification based upon the atomic numbers of the elements.

2. The Periodic Table

To show the different classes, or groups, of related elements, the symbols or names of the elements are arranged in tabular form. This table is known in chemistry as the *Periodic Table* because it is divided into definite periods, or groups, of elements.

Let us now describe the manner in which this table is constructed, remembering that the elements are arranged in it in the order of their atomic weights, and that as a system of classification the table must be so constructed that elements possessing similar properties will be classified together, e.g., in the same column.

Mendeleeff's table, as we now know it, is divided horizontally into *periods* — rows across the table from left to right. Of these, hydrogen occupies the first by itself; each of the next two periods contains eight elements, which make a single row, called a *short period*, across the table. The others are *long periods*; each of these consists of two rows of elements. It will be noted, however, that all periods — short and long

— begin with similar elements and end with similar elements, except of course the first period, which contains only hydrogen.

Prior to about 1898, the table consisted of eight (vertical) *groups* of elements. The eighth group consisted of the so-called transition elements, which lie midway in the long periods. The discovery of the inert gases of the atmosphere made necessary an additional vertical column, which came to be called the zero group. This group is sometimes placed just after group eight and sometimes just before group one. The position is of no importance, since the groups are continuous. We are to think of the table as arranged on a cylinder instead of a sheet. Hence, the zero group lies between groups eight and one, and its position on a flat table depends upon where we cut the cylinder when it is flattened out.

3. The Short Rows or Periods

In explaining the construction of the Periodic Table we shall locate hydrogen at the top of the table in the horizontal row all by itself. Next, we place helium, the element with the second smallest atomic weight, as the first member of the second horizontal row. In the same row, or period, we now place the next seven elements (lithium to fluorine) in the order of their atomic weights and with lithium occupying a position directly below hydrogen:

H
He Li Be B C N O F

Hydrogen is placed above lithium, which it resembles at least in having the same valence number and to some extent in having a tendency to lose its valence electron, rather than above helium, an inert gas, or any other element in this list, none of which it resembles at all in a chemical sense.

Beginning with lithium, which is a typical *metal*, there is a gradual change in the properties of the elements up to fluorine as the atomic weight increases. In general, the elements become more non-metallic in character, a condition which means in terms of atomic structure that their atoms exert stronger attraction for electrons. As we pass along the row from lithium to beryllium, boron, carbon, nitrogen, oxygen, and fluorine, the atoms of the elements show an increasing tendency to pull electrons off of other atoms and to form compounds in which they act as negative ions. Fluorine is the most active of all the non-metallic elements, and lithium is an active metal.

The next element, neon, is entirely unlike fluorine, and, therefore, at this point the first real break in the properties of the elements occurs. Neon is one of the inert gases and resembles helium in every respect. In agreement, therefore, with the idea that the table should group together elements of similar properties, neon is made the first element in a new row, or period, and is placed directly beneath helium. It appears, therefore, that we are about to start on a new portion of the table, a new period.

When the seven elements next succeeding in the order of atomic weights are placed beneath the corresponding elements of the first horizontal row, it is found that very closely related elements are brought together in each of the columns. Thus, sodium is like lithium, magnesium like beryllium, aluminum like boron, silicon like carbon, phosphorus like nitrogen, sulfur like oxygen, and chlorine like fluorine. The similarities are best illustrated by the valence numbers of the elements and by the formulas of their compounds. This similarity must indicate a corresponding similarity in chemical behavior and in the structures of the atoms of the elements.

He LiOH BeO B_2O_3 CO_2 N_2O_5 H_2O HF
Ne NaOH MgO Al_2O_3 SiO_2 P_2O_5 H_2S HCl

4. The Double Rows or Long Periods

After chlorine, the next element in the

Group ⟶	0	1	2	3
Hydrides		RH	RH_2	RH_3
Oxides		R_2O	RO	R_2O_3
Period 1		1 H 1.008		
2	2 He 4.003	3 Li 6.94	4 Be 9.02	5 B 10.82
3	10 Ne 20.183	11 Na 22.997	12 Mg 24.32	13 Al 26.97
4A	18 A 39.944	19 K 39.096	20 Ca 40.08	21 Sc 45.10
4B		29 Cu 63.57	30 Zn 65.38	31 Ga 69.72
5A	36 Kr 83.7	37 Rb 85.48	38 Sr 87.63	39 Y 88.92
5B		47 Ag 107.88	48 Cd 112.41	49 In 114.76
6A	54 Xe 131.3	55 Cs 132.91	56 Ba 137.36	57 * La 138.92
6B		79 Au 197.2	80 Hg 200.61	81 Tl 204.39
	86 Rn 222	87 Fr 223 (?)	88 Ra 226.05	89 ** Ac 227.05

*Rare Earths Lanthanum (58-71) Series	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il 147	62 Sm 150.43	63 Eu 152.0
**Rare Earths Actinium (90-98) Series	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu 239	95 Am 241

Figure 76. The Periodic Table (Based upon Mendeleeff s Classification)

Atomic numbers above symbols of elements; atomic weights below.

4	5	6	7	8
RH_4	RH_3	RH_2	RH	
RO_2	R_2O_5	RO_3	R_2O_7	
6 C 12.01	7 N 14.008	8 O 16.00	9 F 19.00	
14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	
22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 27 28 Fe Co Ni 55.85 58.94 58.69
32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	
40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Tc 99 (?)	44 45 46 Ru Rh Pd 101.7 102.91 106.7
50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	
72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 77 78 Os Ir Pt 190.2 193.1 195.23
82 Pb 207.21	83 Bi 209.00	84 Po 210	85 At 211 (?)	

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	
96 Cm 242	97 Bk ?	98 Cf ?						

Figure 76 (continued).

order of atomic weights is potassium. Here is one of the few exceptions in which Mendeleeff's classification fails to place an element in the position where it clearly belongs. The next element after chlorine in the order of atomic weights is potassium which, therefore, should be placed just below neon, but it is argon rather than potassium that resembles neon, and it is potassium rather than argon that resembles lithium and sodium. Hence, disregarding the atomic weights, we place the two elements in the order that will cause them to fall in the groups that contain elements similar to them. Therefore, we place argon under neon.

Argon represents the beginning of a fourth period. The next two elements resemble those in the corresponding positions in the second and third, or short periods. Thus, potassium resembles sodium, and calcium has many properties in common with magnesium. The next five elements, however, display many differences when compared with aluminum, silicon, phosphorus, sulfur, and chlorine, respectively. These differences are especially pronounced in chromium and manganese, which are metals, and, therefore, entirely unlike sulfur and chlorine. Because of these differences the seven elements following argon in the fourth period are set, sometimes, to the *left* instead of directly below the elements of the first and second rows. (See the table below.)

After manganese, the next three elements (iron, cobalt, and nickel) certainly cannot be placed in a fifth and new period, since their properties are entirely unlike those of argon, potassium, and calcium, which would lie directly above them. They are placed, therefore, in an additional, or *transitional*, group. It is not necessary that *three* such transitional groups should be provided for these elements since they are very much alike. They are placed, therefore, in one group. Because it more closely resembles iron than nickel, cobalt is placed between these elements, although strict adherence to the order of atomic weights would place nickel second. The elements following next after iron, cobalt, and nickel are placed in another row in the fourth period, beginning with the second column. The elements of this row are not placed directly below the elements of the second and third periods, but a little to the *right*.

We see, therefore, that it takes two rows in the fourth period to complete what we may call a "complete trip" across the table; i.e., from one inert gas (argon), to another (krypton). The row including the elements from potassium to manganese is called *series A* of period 4, and the row from copper to bromine is *series B*.

After bromine, the next element is krypton, which is another inert element and belongs, therefore, directly under argon. The remainder of the table represents repetitions of the same general arrangement of elements as we find in period four, i.e., the periods are long ones, containing series *A* and series *B* elements with a transitional group corresponding to iron, cobalt, and nickel between the two series. In period 6, however, there are more elements than in

Period 1		H							
Period 2	He	Li	Be	B	C	N	O	F	
Period 3	Ne	Na	Mg	Al	Si	P	S	Cl	
Period 4 Series A	Ar	K	Ca	Sc	Ti	V	Cr	Mn	(Fe, Co, Ni)
Series B		Cu	Zn	Ga	Ge	As	Se	Br	

periods 4 and 5; from xenon to radon there are 32 elements, and we may assume that, if a sufficient number of elements were known, there would also be 32 in the seventh period. For the sake of convenience certain elements in these two last periods are omitted from their proper positions in the table and placed in groups at the bottom (Figure 76).

5. Families of Elements

Each of the groups (except the zero and eighth groups) is divided into two *families*, one containing *A* and the other *B* elements. Thus in group one there are two families of elements: (1) lithium, sodium, potassium, rubidium, and cesium; (2) copper, silver, and gold. The first of these families is called the alkali metals, and the second may be called the silver family. Here the elements of the short periods belong to the same family as the members of the *A* sub-group, In group seven, however, the elements of the short periods belong to the same family as the members of the *B* sub-group. This family consists of fluorine, chlorine, bromine, and iodine — the so-called *halogens*, or "salt-formers."

Other important families are:

(1) The alkaline earths, Group II, *A*.

(2) The nitrogen family, Group V, *B*.

(3) The oxygen-sulfur family, Group VI, *B*.

(4) The inert gases, Group 0.

6. The Periodic Law

Because the arrangement of the elements in the order of their atomic weights causes them to fall into rows or "periods," Mendeleeff stated that *the properties of the elements are periodic functions of their atomic weights*. This statement is called the *Periodic Law*. It calls attention to the recurrence of the same or very similar properties in different elements when the elements are arranged in the order of increasing atomic weight. Thus, the properties of a very active metal occur in lithium, and the same general properties occur again in sodium, potassium, rubidium, and cesium. The chemical inertness of helium occurs again in neon, argon, krypton, and zenon. The periodicity of properties, as revealed by the periodic classification, concerns physical as well as chemical properties. The elements display a definite periodicity, for example, in such properties as color, melting point, boiling point, hardness, conductivity of heat and electricity, magnetic susceptibility, specific gravity, compressibility, atomic volume, coefficient of expansion, malleability, ductility, and even places and forms of their occurrence in nature.

7. Uses of the Periodic Table

The periodic table brings together in the same group elements that possess similar properties. It also displays the gradual changes in properties that occur from group to group within a period (across) and from top to bottom within a group. Such a classification is of inestimable value to the student. It allows the different elements to be studied as a few well-defined groups, or families, instead of ninety individual substances. For example, an acquaintance with the periodic table allows one to predict many of the properties of an element, although that element may not have been studied previously. We should expect that cesium, for example, since it is in group one and an *A* element, would form a chloride having a similar formula (CsCl) and similar properties to sodium chloride, NaCl.

Secondly, the system, as suggested by Mendeleeff, led to more accurate determinations of the atomic weights of the elements than were available previously. The atomic weights of some of the elements were not accurately known in 1870. If some element, when placed in the table in the order of its atomic weight, fell in a group or family where it was associated

with elements with which it had no common properties, the value assigned as its atomic weight naturally became the subject of suspicion.

Lastly, the periodic system encouraged the search for elements previously undiscovered. Blanks in the table indicated definitely that certain other elements existed. Not only was the prediction of the existence of these elements successful, but even their properties were foretold. Slowly the search has narrowed until at the present time it can be stated, without serious doubt, that no positions remain unfilled between hydrogen and californium (number 98). It is possible, even likely, that elements beyond number 98 may sometime be added. It should be noted, however, that a few of the ninety-eight elements are not known to occur in nature. These few, or at least one or more of their isotopes, have been and can be produced in the laboratory from other elements by reactions involving atomic nuclei.

CLASSIFICATION OF COMPOUNDS

There are many thousand compounds and they can be classified in many different ways. We shall be content in this chapter to describe several important groups and to mention a few of the more important differences in properties that are used as bases of classification.

8. Electrolytes and Non-Electrolytes

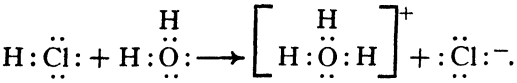
Some compounds when dissolved in water, or in certain other liquids, form solutions that conduct the current of electricity. Such substances are called *electrolytes*, When solutions of these substances form a part of a circuit in which there is an electric lamp, for example, the lamp will "light" just as if the circuit were completed with a copper wire. Of course, solutions, like wires, vary greatly in their resistance to the flow of current. Hydrochloric acid, HCl, sodium hydroxide, NaOH, and sodium chloride, NaCl, are examples of substances that form solutions which are excellent conductors, and these substances are classified, therefore, as *strong electrolytes*. Acetic acid (the acid in vinegar), a solution of ammonia in water (ammonium hydroxide), and mercuric chloride conduct the current only feebly and are called, therefore, *weak electrolytes*. Glycerine, sugar, and naphthalene (moth balls) are examples of nonconductors or *non-electrolytes*. The extent to which a solution conducts electricity depends upon the number of *ions* in a definite volume of the solution and upon the velocities with which the ions move. Strong electrolytes produce many more ions than weak electrolytes for the same number of gram-molecular, or formula, weights of the substance dissolved in a definite quantity of water. Non-electrolytes produce no ions, or at most a negligible number in comparison with the number produced by electrolytes.

9. How Ions are Produced in Solutions of Electrolytes

Many of the substances that produce ions in solutions are ionic compounds, like sodium chloride, that have been produced by the transfer of electrons from one element to another, e.g., from sodium to chlorine. Sodium hydroxide is also a substance of this kind. The crystals of these substances are composed of ions, and when the crystals are dissolved, the ions are set free.

Many compounds of hydrogen with nonmetals (HCl, HBr) or with groups of atoms containing two, and sometimes more, nonmetals (H_2SO_4, HNO_3) also form conducting solutions, which, therefore, must contain ions, although the substances before they are dissolved do not appear to contain any ions. For example, pure hydrogen chloride, HCl, even when it is in the liquid state does not conduct the electric current as fused salt or sodium hydroxide do. How-

ever, the aqueous solution of hydrogen chloride — called hydrochloric acid — is an excellent conductor. The ions must be formed, therefore, when these compounds dissolve in water. The oxygen atom of water has eight electrons, four of which it shares with hydrogen. Now when HCl, in which hydrogen and chlorine share two electrons between them, is dissolved in water, the following reaction may occur:



The hydrogen, in leaving chlorine, leaves its electron with that atom, which, therefore, becomes a negatively charged ion. When the positively charged atom of hydrogen — or proton — attaches itself to the water molecule, it forms a positive ion, H_3O^+. This is called the *hydronium* ion. For the present we shall represent this ion simply by the symbol H^+. We are justified in doing so, since the water molecule is a more or less inert partner of H^+ in H_3O^+. In a reaction, for example, it is the H^+ of the H_3O^+ ion that reacts with another ion, such as OH^- from the hydroxide of a metal, and the H_2O molecule is again set free.

10. The Reactions of Electrolytes

The three classes of substances that produce ions in aqueous solutions are acids, bases, and salts. If the ions of two or more electrolytes are placed together in the same solution, the positive ions of one may combine with the negative ions of the other if by so doing molecules of a *non-electrolyte* or of a *very slightly ionized electrolyte* are produced. Thus H^+, or H_3O^+, ions react with OH^- to form molecules of water, which is very little ionized:

$$H_3O^+ + OH^- \longrightarrow 2\ H_2O$$

Or representing H_3O^+ by H^+, as we have agreed to do:

$$H^+ + OH^- \longrightarrow H_2O.$$

If the two ions of a *slightly soluble compound* are placed in the same solution, the compound precipitates. Thus, the chloride ion from sodium chloride and the silver ion from silver nitrate, when these compounds are dissolved in the same solution, will form a precipitate of silver chloride, AgCl. The sodium and nitrate ions remain in the solution, because sodium nitrate is very soluble:

$$(Ag^+ + NO_3^-) + (Na^+ + Cl^-) \longrightarrow AgCl\downarrow + (Na^+ + NO_3^-).$$

CLASSES OF ELECTROLYTES

11. Acids

At one time, acids were defined as substances that liberate hydrogen ions when they are dissolved in water. For aqueous solutions this definition is still satisfactory in most cases, if by the hydrogen ion we understand that it is the hydronium ion, H_3O^+, that is produced. The following is a more satisfactory general definition, because it is not limited to aqueous solutions: *An acid is a substance that supplies protons, or hydrogen ions, for reactions with other substances.* In aqueous solutions acids form ions if they react with molecules of water to form hydronium ions, H_3O^+, Section 9. When the acid reacts in the same solution with another substance that can combine with protons, it is this hydronium ion that supplies the H^+ for the reaction. The water molecule with which the H^+ is combined in H_3O^+ is then set free. For example,

$$H_3O^+ + NH_3 \longrightarrow NH_4^+ + H_2O.$$

In an aqueous solution of an acid such as HCl the real acid is, therefore, H_3O^+, the hydronium ion.

Hydrogen chloride can also react with ammonia when the substances are not dissolved in water. In such reactions it is the HCl molecule itself which supplies the pro-

ton and which, therefore, acts directly as an acid:

$$HCl + NH_3 \longrightarrow NH_4^+ + Cl^-.$$

12. Properties of Acids

Lemons, oranges, and grape fruit contain *citric acid*; sour milk contains *lactic acid*; and vinegar is a solution of *acetic acid*. As our acquaintance with these substances indicates, substances commonly recognized as acids are characterized by a sour taste. They produce definite changes in the color of substances called *indicators*. They turn blue *litmus* red, and render a red solution of phenolphthalein colorless, if added in sufficient quantity to neutralize any base that may be present. They react with hydroxides, such as NaOH, to form salts, such as NaCl, and water. The characteristics that we have just mentioned apply to aqueous solutions of the substances most often used as acids. They are actually, therefore, properties of hydronium ion. They are not to be regarded as properties that can always be relied upon to identify an acid. For example, water sometimes acts as an acid, as in the reaction

$$NH_3 + HOH \longrightarrow NH_4^+ + OH^-,$$

but water is not sour and it does not affect litmus. All acids can supply protons, or hydrogen ions, and their common properties depend upon this characteristic behavior. For example, a substance that can and does supply H^+ to react with OH^- to form H_2O is an acid. The acids most commonly used in the laboratory are hydrochloric, HCl; nitric, HNO_3; sulfuric, H_2SO_4; and acetic, $HC_2H_3O_2$.

13. The Names of Acids

Acids which contain only two elements are called binary acids and are named by attaching the prefix *hydro* and the suffix *ic* to the name of the element combined with hydrogen. The name is sometimes shortened, as in *hydro*chlor*ic* acid. Other binary acids are hydrosulfuric, H_2S, hydrobromic, HBr, and hydriodic, HI.

Some scheme of distinguishing by name two or more acids containing the same elements, such as H_2SO_3 and H_2SO_4, is necessary. If there are only two such acids, the endings *-ous* and *-ic* are used. The former is used in naming the acid that contains the smaller amount of oxygen for a definite quantity of the other non-metallic element. Thus, H_2SO_3 is *sulfurous*, and H_2SO_4 is *sulfuric* acid. The *-ous* ending indicates the compound in which sulfur has the lower oxidation number. This number is 4 in H_2SO_3 and 6 in H_2SO_4.

If there are more than two oxygen-acids of the same element the different compounds cannot, of course, be distinguished by the use of the two suffixes. Thus, there are four oxygen-containing acids of chlorine: HClO, $HClO_2$, $HClO_3$, and $HClO_4$. Since hydrogen has an oxidation number of + 1 and oxygen − 2, it is evident that in these four compounds the oxidation numbers of chlorine are + 1, + 3, + 5, and + 7, respectively. The names *chlorous* and *chloric* are assigned to the second and third acids, $HClO_2$ and $HClO_3$. The first, HClO, shows a smaller oxidation number of chlorine than chlorous acid, $HClO_2$. It is also named chlorous acid, but the prefix *hypo* is added to distinguish it from $HClO_2$. For the fourth acid, $HClO_4$, the prefix *per* is added to distinguish it from chloric acid, $HClO_3$.

The names and formulas of the five acids of chlorine are listed below:

		Oxidation no. of chlorine
HCl	*Hydro*chlor*ic* acid	− 1
HClO	*Hypo*chlorous acid	+ 1
$HClO_2$	Chlor*ous* acid	+ 3
$HClO_3$	Chlor*ic* acid	+ 5
$HClO_4$	*Per*chlor*ic* acid.	+ 7

14. Bases

Bases are substances that remove H^+ ions, or protons, from acids and combine with

them to form ions or neutral molecules. The most familiar base is the hydroxyl ion, OH^-, which is present in an aqueous solution of sodium hydroxide, for example, and in solutions of ammonium hydroxide. Because it supplies the hydroxyl ion, sodium hydroxide — or any similar hydroxide — is sometimes called a base, although it is only the hydroxyl ion of such a compound that acts as a base. When the hydroxyl ion acts as a base, it removes a proton from an acid and forms a molecule of water. *For a long time, and until fairly recently in fact, a base was defined as a substance — like NaOH — that produces OH^- ions in an aqueous solution.* Most of the bases with which we shall be concerned in this course are the hydroxides of metals and are, therefore, in agreement with this definition, but since this ion, OH^-, is not the only particle that will combine with the protons from an acid, let us refer to it, or to the substance that produces it, as a *hydroxide-base.* There are many other ions and even molecules that combine with the protons from acids, and all of these must be classified as bases. For example, water itself acts as a base when it combines with protons from acids (page 120) to form hydronium ions. Ammonia, likewise, acts as a base when it combines with protons from an acid to form ammonium ion, HN_4^+.

$$NH_3 + H^+ \longrightarrow NH_4^+.$$

15. Properties of Hydroxide-Bases

Solutions of the hydroxide-bases — such as sodium hydroxide and calcium hydroxide — are bitter in taste; they supply hydroxyl ions to react with the hydrogen ions, or protons, of acids; and they produce characteristic color changes of indicators. For example, a base, such as sodium hydroxide, turns red litmus blue and changes a colorless solution of phenolphthalein to red. The hydroxide-bases most commonly used in the laboratory are sodium hydroxide, NaOH; potassium hydroxide, KOH; calcium hydroxide, $Ca(OH)_2$; and ammonia, NH_3, which in water forms a solution containing NH_4^+ and OH^- ions:

$$NH_3 + HOH \longrightarrow NH_4^+ + OH^-.$$

These hydroxides react with acids, such as HCl and H_2SO_4, to produce salts and water.

If a metal forms two hydroxides, the suffixes *-ous* and *-ic* are added to a shortened form of the name of the element. Thus, $Fe(OH)_2$ and $Fe(OH)_3$ are called ferrous and ferric hydroxide, respectively.

16. Hydroxides that Do Not Act as Bases

We may also speak of the hydroxides of non-metallic elements, but this practice is not in keeping with the usual terminology. Instead of referring to a certain compound of chlorine, hydrogen, and oxygen as chlorine hydroxide, ClOH, we call it *hypochlorous acid* and write its formula as HClO. This formula emphasizes the fact that, when this substance reacts with others which can accept protons, it gives up its hydrogen ion, or proton, leaving the hypochlorite ion, ClO^-; it does not produce Cl^+ and OH^- ions.

Some hydroxides and the corresponding oxides react with both acids and bases. For example, aluminum hydroxide, $Al(OH)_3$, reacts with hydrochloric acid to form aluminum chloride and it also reacts with sodium hydroxide to form sodium aluminate (page 70). Hydroxides that react in this manner — i.e., as both acids and bases — are classified as *amphoteric*, or *amphiprotic*, hydroxides.

17. Salts

Salts are composed of positive — usually metallic — ions and the negative ions of an acid, e.g., Cl^-, NO_3^-, or $SO_4^=$. Some salts have for their positive ions, not those of a metal, but ions composed of a group of atoms, e.g., the ammonium ion, NH_4^+. When a solution containing HCl is mixed with one containing NaOH, sodium and chloride ions remain in the solution, after

the hydroxyl and hydrogen ions are converted into molecules of water. If the water is evaporated, these ions form crystals of the salt. The simplest salts are composed of metallic ions and the negative ions of a single non-metal, e.g., Na^+Cl^-. Others are composed of metallic ions and negative ions containing two or more non-metallic elements, e.g., $Na^+NO_3^-$.

18. The Names of Salts

The names of *binary salts* (containing two elements) consist of two parts: (1) The name of the metal from whose hydroxide the salt is prepared; and (2) the name of a non-metallic element (the name is usually shortened) to which the suffix *-ide* is attached. If the negative ion of the salt contains two elements (as in $MgSO_4$), the second word is the name of this ion. The names of many of these ions usually end in *-ate*. Thus, $CaCO_3$ is calcium carbon*ate*, $MgSO_4$ is magnesium sulfate, $KClO_3$ is potassium chlorate, and so on. But if there are two or more ions showing different combining capacities of the same non-metal with oxygen, different endings and prefixes must be employed as in the naming of acids. The salts corresponding to the *-ous* acids are given names ending in *-ite*. Those that correspond to the *-ic* acids are distinguished by the use of the suffix *-ate*. For the "hypo——ous" acids the corresponding salts are the "hypo——ites." The "per——ic" acids form salts which are named the "per——ates." Thus the four sodium salts of the oxygen-acids of chlorine are:

NaClO, sodium hypochlorite
$NaClO_2$, sodium chlorite
$NaClO_3$, sodium chlorate
$NaClO_4$, sodium perchlorate.

The sodium salts of sulfurous and sulfuric acids are:

Na_2SO_3, sodium sulfite
Na_2SO_4, sodium sulfate.

Most metals form only one or two binary salts with chlorine, bromine, iodine, sulfur, and other non-metals. Hence, the endings *-ous* and *-ic* suffice to distinguish between two binary salts of the same elements. Thus, CuCl and $CuCl_2$ are cuprous and cupric chlorides; Hg_2Cl_2 and $HgCl_2$ are mercurous and mercuric chlorides; and $FeCl_2$ and $FeCl_3$ are ferrous and ferric chlorides, respectively.

19. Classes of Salts

Salts constitute one of the largest classes of substances. They may be further divided upon the basis of the metals from which they are formed. They may be subdivided, also, into groups, each of which consists of salts containing the same negative ion. Thus, we may have a group of sodium salts, or calcium, or iron salts; or we may classify them as chlorides, nitrates, and sulfates of different metals. Each group shows certain properties common to all its members. Thus, sodium salts impart a yellow color to a flame, and they react in other ways that are characteristic of the sodium rather than of the entire salt. Similarly all nitrates have certain common properties; they are all soluble in water, for example.

Acid salts are produced when only a part of the hydrogen in a molecule of the acid is replaced by a metal or by a positive radical, such as NH_4^+. If all the hydrogen is replaced, a *normal salt* is formed. Thus, Na_2SO_4 is the normal salt, sodium sulfate, and $NaHSO_4$, is the acid salt, sodium bisulfate, or sodium hydrogen sulfate. Likewise for phosphoric acid, H_3PO_4, we may have NaH_2PO_4, sodium dihydrogen phosphate; Na_2HPO_4, sodium monohydrogen phosphate; and Na_3PO_4, normal, or trisodium phosphate.

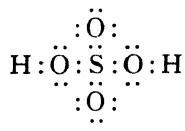
THE RADICALS AND IONS OF ACIDS AND SALTS

20. Radicals and Ions

There are many groups of atoms that occur in many different compounds, and

which are transferred from one compound to another in certain kinds of reactions without any change in their own composition. Such groups are sometimes called *radicals*, and, of course, if they are electrically charged they are also called ions. There are many uncharged radicals in organic compounds; for example, the hydroxyl radical, OH, is found in sugar, starch, cellulose, and all the different alcohols. In sodium hydroxide and in similar compounds the same group occurs as an ion, OH^-.

Most of the radicals with which we are concerned at this time are ions or can act as ions under certain conditions. They are found in ionic compounds, such as sodium sulfate, Na_2SO_4, and in aqueous solutions of such substances. Many of them are also found in acids. In the pure acids the radicals do not exist as ions; in sulfuric acid, for example, the two hydrogen atoms share electrons with two of the oxygen atoms of the sulfate radical, SO_4, and the whole structure, H_2SO_4, is a molecule rather than a group of ions:



When acids like sulfuric are dissolved in water, the molecule gives up the two protons to molecules of water; hydronium ions, H_3O^+, are formed, and the sulfate group is released as an ion, $SO_4^{=}$.

In most of the reactions that involve sulfuric acid (hydrogen sulfate) or any other sulfate, such as sodium sulfate, the sulfate ion, or radical, is not changed; it is only transferred from one compound to another. For example, when a solution of sulfuric acid is mixed with a solution of barium hydroxide, the following reaction occurs:

$$(2\ H^+ + SO_4^{=}) + (Ba^{++} + 2\ OH^-) \rightarrow BaSO_4\downarrow + 2\ H_2O.$$

Barium sulfate, $BaSO_4$, is only very slightly soluble and, therefore, precipitates. The same substance is formed when any soluble sulfate and any soluble barium salt (barium chloride, $BaCl_2$, for example) are mixed.

21. The Valence Numbers of Radicals and Ions

Since one nitrate radical is combined with one atom of hydrogen in nitric acid, it is evident that its valence number is one. Similarly, the sulfate radical (SO_4) in sulfuric acid (H_2SO_4) has a valence number of two. The phosphate radical (PO_4) in phosphoric acid (H_3PO_4) has a valence number of three. The following list contains the formulas and names of several acids and salts that contain radicals. The student is advised to inspect these with the view of determining (from the formula) the valence number of each radical.

H_3AsO_3	Arsenious acid or hydrogen arsenite
Na_3AsO_3	Sodium arsenite
H_3AsO_4	Arsenic acid or hydrogen arsenate
Na_3AsO_4	Sodium arsenate
$HClO$	Hypochlorous acid or hydrogen hypochlorite
$Ca(ClO)_2$	Calcium hypochlorite
$HClO_2$	Chlorous acid or hydrogen chlorite
$KClO_2$	Potassium chlorite
$HClO_3$	Chloric acid or hydrogen chlorate
$Ba(ClO_3)_2$	Barium chlorate
$HClO_4$	Perchloric acid or hydrogen perchlorate
$KClO_4$	Potassium perchlorate
H_3PO_4	Phosphoric acid or hydrogen phosphate
$AlPO_4$	Aluminum phosphate
$KMnO_4$	Potassium permanganate
Na_2CrO_4	Sodium chromate
Na_2CO_3	Sodium carbonate
$Ca(C_2H_3O_2)_2$	Calcium acetate
$Mg_3(PO_4)_2$	Magnesium phosphate

Some radicals do not contain oxygen, and some act as positive ions, e.g., the ammonium ion, NH_4^+, and the thioarsenite ion, $AsS_3^{=}$, in which sulfur takes the place of oxygen.

The valence number of the hydroxyl radical, OH, can be explained as follows. Its structure is  , and hence, it contains eight electrons in the valence shells of the oxygen and hydrogen atoms, or one more than these atoms normally have — oxygen

has six and hydrogen has one. Therefore, the OH group has a valence number of 1. In the sulfate radical the total number of valence electrons is 32, whereas each of these atoms normally possesses six valence electrons, or all of them (one sulfur and four oxygen atoms) normally have 30. The valence number of the sulfate group, therefore, is 2. The two additional electrons required to form the SO_4 group are left by the two hydrogen atoms when these atoms are removed from a molecule of sulfuric acid by a base. The valence numbers of other radicals and ions can be explained in a similar manner.

OXIDES

22. Oxides of Non-Metals; Acid Anhydrides

The oxides of the non-metallic elements if they react with water form acids:

$$CO_2 + H_2O \longrightarrow H_2CO_3.$$

This is not a general method of producing all acids, because there are several acids (HCl, HBr, HI, etc.) that contain no oxygen. The composition of each of the inorganic acids that contain oxygen, however, can be represented in terms of the combining proportions of water and the oxide of some non-metal. Thus, nitric acid, HNO_3, may be regarded as produced from one molecule of water for each molecule of the oxide, N_2O_5:

$$N_2O_5 + H_2O \longrightarrow 2\ HNO_3.$$

Oxides which react with water to form acids, or which may be formed by the removal of water from acids, are called *acid anhydrides*. They are also called *acidic oxides*. The student is advised to determine the anhydrides of the following acids: Nitric, HNO_3; nitrous, HNO_2; sulfurous, H_2SO_3; sulfuric, H_2SO_4; phosphorous, H_3PO_3; phosphoric, H_3PO_4; hypochlorous, HClO; arsenic, H_3AsO_4; carbonic, H_2CO_3; boric, H_3BO_3; iodic, HIO_3; and silicic, H_2SiO_3.

23. Oxides of the Metals

The oxides of certain metallic elements react with water to produce hydroxides, which if soluble in water form solutions containing the hydroxyl ion and are, therefore, said to act as bases. The oxides of sodium, potassium, calcium, strontium, and barium react readily with water. The reaction of calcium oxide (CaO), which we call quicklime, with water produces "slaked" lime or calcium hydroxide,

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$

Some of the oxides react very slowly with water. This is true, for example, of the oxide of magnesium. Others do not appear to react at all. Hence, as in the case of oxygen-acids, this is not a general method for the preparation of all hydroxides. An indirect method of preparation is often used. If we wish to prepare bismuth hydroxide, for example, the following reaction is easier to employ and produces a much more definite product:

$$(Bi^{+++} + 3\ Cl^-) + 3\ (Na^+ + OH^-) \longrightarrow Bi(OH)_3\downarrow + 3\ (Na^+ + Cl^-).$$

Since bismuth hydroxide is only slightly soluble, it is easily separated by filtration from the sodium chloride, which remains in solution.

The oxides of the metals are sometimes called *basic anhydrides*. Thus, Na_2O is the anhydride of sodium hydroxide, NaOH.

24. Hydrous Oxides

The oxides of several elements are found combined with water in compounds corresponding to hydroxides but differing from hydroxides in containing varying quantities of water. Such compounds are called *hydrous oxides*. Thus, the compound frequently referred to as ferric hydroxide, $Fe(OH)_3$, is probably more accurately represented by the formula $Fe_2O_3.xH_2O$. If x is 3 the formula is $Fe_2O_3.3H_2O$ or

$2\,Fe(OH)_3$, but x may vary even in the same sample of material. For convenience, however, the formula $Fe(OH)_3$ is used very frequently in writing equations. Zinc, silicon, lead, chromium, aluminum and a few others form hydrous oxides.

25. The Names of Oxides

The naming of an oxide of an element that combines with oxygen in a single proportion is a simple matter. Thus, we speak of calcium oxide, magnesium oxide, and aluminum oxide; these elements each have just one valence number. But some elements form two, three, four, or even five oxides and these, evidently, cannot all be called by the same name. In different oxides the metal displays, of course, different oxidation numbers. If an element forms only two oxides, the names assigned to the two compounds may differ only in the ending affixed to the name of the element. The ending *-ous* is used frequently to denote the lower state of oxidation and the ending *-ic* to denote the higher. Thus, we have two oxides of mercury, copper, iron, and tin:

Hg_2O, Mercurous oxide
HgO, Mercuric oxide
Cu_2O, Cuprous oxide
CuO, Cupric oxide
FeO, Ferrous oxide
Fe_2O_3, Ferric oxide
SnO, Stannous oxide
SnO_2, Stannic oxide

Most of the oxides of the non-metals and those of all elements that form several oxides are named in a different manner. Very often the name indicates the number of oxygen atoms in a molecule:

CO, Carbon monoxide
CO_2, Carbon dioxide
SO_3, Sulfur trioxide
V_2O_5, Vanadium pentoxide
N_2O_3, Nitrogen trioxide
PbO_2, Lead dioxide

26. Inorganic and Organic Compounds

All the salts, all the bases, and all the acids except acetic that have been mentioned in this chapter are classified as inorganic compounds. This classification refers to the fact that they are associated with inanimate materials; many of them are produced from ores, rocks, and minerals, such as salt, sulfur, limestone, quartz, and the ores of iron, copper, and other metals; the oxygen and nitrogen of the air and, sometimes, water enter into the formation of some of them. Many organic compounds, on the other hand are obtained directly from plant and animal sources — sugar from beets and cane; quinine from the bark of one tree, and rubber from the sap of another; fats from animals and from corn, coconut, and olives; and musk from the musk ox. Some are produced by the destructive distillation (heating in the absence of air) of coal, wood, and other like materials. Others are obtained directly from petroleum which, like coal, is a product of changes in the remains of once living matter.

Many of the compounds now known to organic chemistry, however, are synthesized, sometimes by many consecutive reactions, from the relatively simple materials obtained from coal, petroleum, and similar sources, and from still simpler substances, such as water, hydrogen, oxygen, chlorine, nitrogen, and sulfur. Many of the compounds thus produced do not exist in plants or animals, and they are not found among the products of their decay.

REVIEW EXERCISES

1. State the meaning of the following terms as they are used in describing parts of the periodic table: Period, *A* and *B* series, group, family.
2. State the Periodic Law. Show that it is not entirely valid as Mendeleeff formulated it.
3. What are some of the weaknesses of Mendeleeff's classification?

4. What does the periodic system suggest concerning the structures of atoms?
5. How has the periodic classification aided in the development of chemistry?
6. From their positions in the periodic table, predict the formulas of oxides of the following elements: Mo, W, Si, Sn, Sb, Te, and Ra.
7. Would you expect the chloride of silicon to resemble NaCl more closely than it does CCl_4? Explain.
8. Define *electrolyte*. What classes of compounds act as electrolytes?
9. Name three compounds that are not electrolytes.
10. What is an ion? How are ions produced in solutions of NaCl and NaOH?
11. How are ions produced in aqueous solutions of substances such as HCl?
12. What change occurs when aqueous solutions containing NaOH and HCl are mixed?
13. What properties do acids have in common?
14. What properties do bases have in common?
15. How are salts produced from acids and bases?
16. Define, according to the information now before us, the following: acid, base, salt.
17. Into what two classes are oxides divided upon the basis of their reactions with water?
18. Define acid and basic anhydrides.
19. What are the anhydrides of H_3BO_3, H_3AsO_4, NaOH, HPO_3, H_2CO_3, and $Mn(OH)_2$?
20. How are acids which contain two elements named? Illustrate.
21. How are acids which contain three elements (one of which is oxygen and one hydrogen) named? Illustrate.
22. Name: $Mn(OH)_2$ and $Mn(OH)_3$; $FeSO_4$, and $Fe_2(SO_4)_3$.
23. Name: Na_2CO_3, $NaNO_3$, $NaClO_3$, $MgSO_4$, Na_3PO_4, Na_2S, NaBr, Na_2SO_3, and Na_2SO_4.
24. Name the four sodium salts of the four acids composed of hydrogen, chlorine, and oxygen.
25. What are some of the important sources of organic compounds?
26. What acids and what bases must react to form the following salts? K_3PO_4; $CuSO_4$; NH_4NO_3; $CaCO_3$.
27. Using the information on page 125, write the formulas for calcium arsenate, barium phosphate, aluminum acetate, ammonium carbonate, and magnesium chromate.
28. Name the following compounds: $CaSO_4$, $(NH_4)_3PO_4$, $Cu_3(AsO_3)_2$, $Ba_3(AsO_4)_2$, NH_4NO_3, $Hg(C_2H_3O_2)_2$.
29. Which of the following formulas are correct? K_2CO_3, CuS_3, Na_2PO_4, $Fe(C_2H_3O_2)_3$, $MgCO_3$, $Al(OH)_2$.
30. Complete and balance the following equations:

(*a*) Barium nitrate (Soluble) + Ammonium chromate → (Soluble)
Barium chromate (Insoluble) + Ammonium nitrate (Soluble)

(*b*) Ammonium phosphate (Soluble) + Calcium chloride → (Soluble)
Calcium phosphate (Insoluble) + Ammonium chloride (Soluble)

(*c*) Magnesium arsenite (Soluble) + Cupric sulfate → (Soluble)
Cupric arsenite (Insoluble) + Magnesium sulfate (Soluble)

31. What difference in chemical behavior justifies the formula of HClO for this compound of chlorine and KOH for the corresponding compound of potassium?
32. The formula for a certain compound of arsenic is usually written as H_3AsO_3 instead of $As(OH)_3$. Why should one of these formulas be preferred to the other?
33. What weight of sodium hydroxide is required to neutralize completely 200 g. of hydrogen chloride dissolved in water? Express the required weight of sodium hydroxide as gram-molecular (or formula) weights.
34. Ammonium sulfate, $(NH_4)_2SO_4$, is an important constituent of fertilizers. How much ammonia would be required to produce a ton of ammonium sulfate?
35. The anhydride of an acid contains 66.645 per cent of bromine and 33.355 per cent of oxygen. What is the simplest formula of the acid?
36. What weight of silver chloride can be made from the chloride ion available in a solution containing 100 g. of sodium chloride, assuming that an excess of silver ion is available?

REFERENCES FOR FURTHER READING

Compounds

Chapin, W. H., and L. E. Steiner, *Second Year College Chemistry.*

French, S. J., *The Drama of Chemistry.*
Hammett, L. P., *Solutions of Electrolytes*, 2d ed. New York: McGraw-Hill Book Company, 1935.
Acids, Bases, and Salts: *J. Chem. Ed.*, **7**, 782 (1930); **12**, 109 (1935).

Classification of Elements

Findlay, A., *A Hundred Years of Chemistry.*
Harrow, B., *Eminent Chemists of Our Times.*
Hatcher, W. H., *An Introduction to Chemical Science.* New York: John Wiley and Sons, Inc., 1940.
Jaffe, B., *Crucibles.*
Martin, G., *Modern Chemistry and Its Wonders*, New York: D. Van Nostrand Company, 1915.
Moore, F. J., *History of Chemistry.*
Tilden, Sir W. A., *Famous Chemists.*
Weeks, M. E., *Discovery of the Elements.*

11

INVESTIGATIONS OF THE STRUCTURE OF MATTER

1. Introduction

In Chapter 3, we summarized rather briefly current knowledge and theories of the structure of the atom and the ways in which atoms react to form compounds. We shall now describe some of the methods that have been used to investigate the structure of matter in order that we may understand the proof and evidence upon which the structure of an atom as we have described it depends. How were electrons, protons, and neutrons discovered? How were the masses of these and similar particles measured? What reasons do we have for believing that an atom has a nucleus that contains all of its protons and neutrons? These are some of the questions that we are now to consider.

The study of radioactive substances provided much of the first information that became available concerning the structure of matter and the composition of the atom. This, then, will be the first subject to which we turn our attention in this chapter.

RADIOACTIVITY

2. Introduction

Certain heavy elements display the peculiar behavior known as *radioactivity*. When these elements undergo radioactive changes, they are converted spontaneously into other elements; at the same time, certain other kinds of matter are liberated in the form of particles that can be identified because of differences in their masses, electrical charges, and velocities. Radioactivity appears, therefore, to involve the disintegration of certain kinds of atoms and should, for this reason, offer excellent opportunities for the study of the structure of matter. The particles liberated during the disintegration of atoms, for example, should throw some light upon the constitution of the atoms from which they come.

3. The Behavior of Radioactive Elements

The radioactivity of *uranium* was discovered by Becquerel in 1896. Shortly afterwards, Madame Curie and her coworkers discovered other radioactive elements including radium. Many other elements, including all of those with an atomic weight greater than that of bismuth, have since been found to be active. Radioactive isotopes of many elements not normally active have also been produced in the laboratory.

The radioactive elements were discovered by observations of the effects produced by the radiation that is emitted by the elements or their compounds. This radiation may be detected by the following methods:

(1) The rays will pass through substances which are opaque to light rays, and can be detected by a photographic plate which is

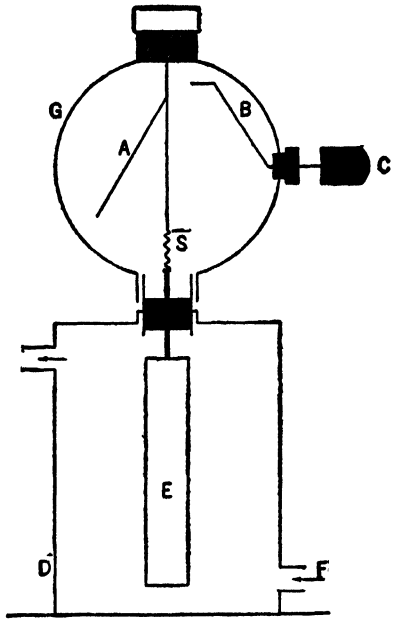


Figure 77. An Electroscope

The gold leaf (A) is held away from S because they carry like electrical charges. When the rays from radioactive material are produced in the lower compartment, they ionize the air around E and cause this metal and S to which it is attached to lose their charge. Gold leaf A then collapses to its normal position against S.

protected from the action of light by layers of black paper.

(2) The rays will discharge an electroscope (Figure 77), since they cause the air through which they pass to become a conductor of electricity.

(3) The rays cause certain substances to phosphoresce or glow. A screen coated with zinc sulfide can be used to detect the rays, because the screen glows wherever the radiation strikes it.

(4) A photograph of a space that is supersaturated with water vapor, and which is exposed to the action of radium, or some other radioactive substance, reveals the paths of the rays as straight lines (Figure 78). It is assumed that the rays convert the molecules in the space through which they pass into electrically charged particles, or ions. These charged particles then act as nuclei about which water condenses in small drops. The lines revealed by the photograph, therefore, are produced by these tiny droplets of water that form along the path of the ray. They are called *fog-tracks.*

(5) The rays emitted possess energy as shown by their ability to affect a photographic plate, to cause zinc sulfide to emit light, and to render air a conductor of electricity. Furthermore, the emission of these rays is attended by liberation of heat; one gram of radium evolves 133 calories of heat per hour, and it continues to do so hour after hour for many years. Neither the change itself nor the rate at which it occurs is influenced by the conditions that affect the speed of chemical reactions. The rate of disintegration is the same, for example, at all temperatures at which it has been possible to study it.

4. Kinds of Radiation Emitted by Radioactive Substances

Three kinds of radiation, or rays, from radioactive substances can be identified and separated by the method shown in Figure 79. The radioactive material is placed in a depression made by boring a hole in a block of lead. Since lead absorbs all three kinds of rays, only the rays emitted in an upward direction emerge from the hole, thus providing a small beam, or pencil, of the radiation. The beam is then separated into its three components by passing it between the poles of an electromagnet placed above the lead block. A photographic plate properly protected from light is placed above the block of lead. When this plate is developed, the points at which the rays strike it are revealed. The beam of rays is thus found to consist of three parts. One of these strikes the plate directly above the hole; this is not deflected. Two other fogged spots indicate that the remainder of the radiation is divided into two parts, which are deflected in opposite directions by the magnetic field. The deflections can

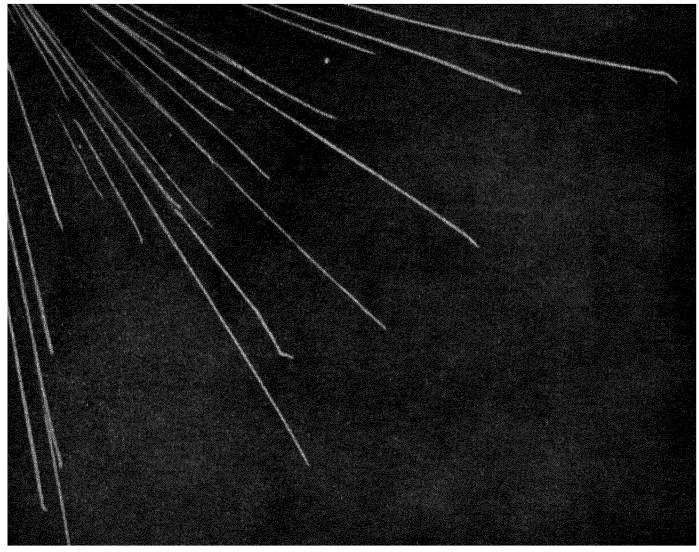


Figure 78. Fog Tracks of Alpha Rays

When alpha rays pass through space that is supersaturated with water vapor, they cause the molecules through which they pass to become electrically charged. These charged particles then act as nuclei about which water condenses in small drops. The lines shown in a photograph of this space are produced by these tiny droplets of water that form along the path of the ray.

be explained if we assume that the rays are composed of small particles that carry electrical charges, because it is a well-known fact that an electrically charged particle is deflected in a circular path by a magnetic field. The rays that are more strongly deflected act as negatively charged particles and are called *beta rays*. Those deflected to a lesser extent appear to consist of heavier, positively charged particles and are called *alpha rays*. The portion of the radiation that is undeflected by the magnetic field consists of *gamma rays*. All evidence based upon their behavior indicates that they are of the same nature and have the same velocity as light waves but have shorter wave-lengths, have more energy, and are more penetrating. As we shall learn later, not all three kinds of radiation are emitted by any one element.

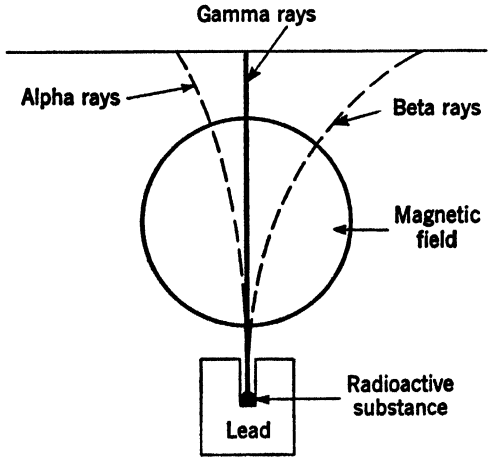


Figure 79. The Separation of Alpha, Beta, and Gamma Rays by Means of a Magnetic Field

The poles of the magnet are located at right angles to the plane of the rays.

5. Alpha Rays

These are the least penetrating of the rays emitted by radioactive substances. They can pass through a few centimeters of air or through a sheet of aluminum foil about 0.1 mm. in thickness. The fact that these rays consist of particles can be demonstrated by means of a screen covered with a phosphorescent substance, such as zinc sul-

fide. When such a screen is placed near a sample of radioactive material and observed by means of a microscope, the glow on the screen is seen to consist of numerous tiny flashes of light. The fact that the entire screen does not glow indicates that the rays that strike it are discontinuous in character. Apparently, each spot of light is produced by the impact of a single particle.

The alpha particle has a positive electrical charge as shown by the fact that a beam or stream of these particles, when passed between two plates that are electrically charged — one positively and the other negatively — is deflected toward the negative plate. The deflection of the alpha particles in a magnetic field is also in the direction in which all positively charged particles are deflected when they move through such a field.

The deflection of particles by either the magnetic or electrical field depends upon several factors, such as the strength of the field and the charge, mass, and velocity of the particles. It is possible to calculate the mass and the charge of a single alpha particle when certain information is available concerning the strength of the field, the extent of the deflection, the number of particles emitted by a radioactive sample in a definite period of time, and the total charge of these particles. The mass of a single particle has been found to be 4, as compared with 16 for an atom of oxygen, on the scale of atomic weights. Since this is the atomic weight of helium, the logical conclusion is that the alpha particle is an electrically charged atom of helium — an ion of helium.

6. Geiger Counters

This device has been one of the instruments most widely used in the investigations of the structure of matter. One of several different forms of the counter is shown in Figure 80. The needle *P* is located in an ionization chamber containing a

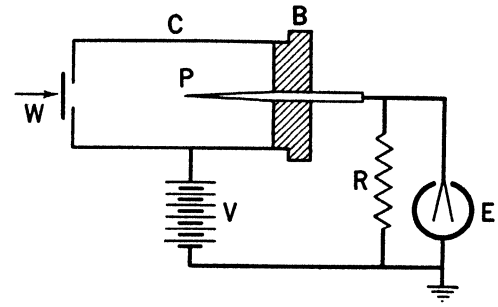


Figure 80. Geiger Point Counter

small amount of some easily ionized gas. The cylindrical walls of the chamber, *C*, and the needle are made of metal, and between them there is applied an electric potential *V*, which is just short of the potential required to produce a discharge across the space from one to the other. Alpha particles, or other similar particles that are electrically charged, enter the chamber through the window *W*, which is closed by a very thin covering that the particles can penetrate. Upon entering the chamber the particle produces ions by expelling or forcing out electrons from the molecules of the gas with which it collides. These ions are electrically charged and, therefore, they are attracted toward *P* or *C*, depending upon which has the opposite kind of charge. The ions acquire high velocities and, therefore, produce other ions by colliding with other molecules. Upon reaching *P* or *C*, the ions are discharged, a process that reduces the potential between the two electrodes. The flow of ions acts, therefore, to complete the electric circuit and allows the current to flow momentarily through *R*, producing at the same time a visible effect in the device *E*. Sometimes the current is amplified and used to actuate a loud speaker; each particle that enters the apparatus produces a clicking sound in the speaker. The effect of each particle that enters the chamber can thus be observed, and the number can be counted. The counter is useful in detecting the presence of substances that produce ionizing particles like those of alpha rays

and also in measuring the rates at which different substances eject such particles from their atoms.

7. Beta Rays

These rays consist of negatively charged particles. They travel with much greater velocities, on the average, than alpha particles, and the velocity varies with the source of the particles. Sometimes, it is almost as great as the velocity of light (186,000 miles per second). Those rays are deflected by electrical and magnetic fields, but in the opposite direction, of course, from the deflections of alpha rays. The mass of the beta particle is about $\frac{1}{1838}$ of the mass of the hydrogen atom. It is called the *electron*, and although it acts as a material particle, it must be looked upon, also, as a unit of negative electrical charge, since all *negative charges* are multiples of its charge.

8. Radioactive Elements

Radioactivity was explained by Soddy and Rutherford, in 1902, as a disintegration of the atoms of radioactive elements. In accordance with this view, radon, a gaseous element, is produced when alpha particles are liberated from atoms of radium. Pure radium does not emit any beta particles. However, if we should study a sample of the pure element, we would find that beta particles are produced, and produced in increasing numbers as time goes on, indicating that following the disintegration of radium other radioactive elements are produced, and that at least some of them emit beta rays. Some information concerning the number and nature of these elements can be obtained by studying the kinds of particles emitted and their velocities. Atoms of some of these elements emit alpha particles, and some emit beta particles. The velocities of the particles, and their ranges in the air or in other media, vary with the radioactive element that produces them.

9. Series of Radioactive Elements

All minerals that contain compounds of uranium also contain compounds of radium. In all these minerals the ratio of uranium to radium is constant — about 3,000,000 to 1. This ratio indicates that radium is produced from uranium at a very slow rate; if the change were rapid, all uranium would have disappeared from the earth long ago.

Radium is not produced directly from uranium. A study of the particles emitted from minerals containing both of these elements indicates that there are fourteen known radioactive elements in the series that begins with uranium and includes radium. See Figure 81. The *half-life* of an element refers to the length of time that must elapse before one-half of the atoms of a sample of the element disintegrate.

In addition to the radioactive elements listed in Figure 81, there are two other series; these are designated as the *actinium* and the *thorium* series, which begin with protoactinium and thorium, respectively. Each of these series, as well as the uranium series, ends with an isotope of lead.

10. Radioactive Isotopes

In Figure 81 it will be noted that uranium appears twice, thorium twice, polonium three times, bismuth twice, and lead three times. Each of the fifteen elements in the table, however, is a distinct form of matter; each is composed of atoms differing in structure from atoms of all the others. For example, the three kinds (isotopes) of polonium have the same atomic number, but their atomic weights are 218, 214, and 210, and, therefore, their atomic nuclei must contain different numbers of neutrons. These three forms of polonium are isotopes (page 37) as are the different forms of lead, bismuth and other elements of the series.

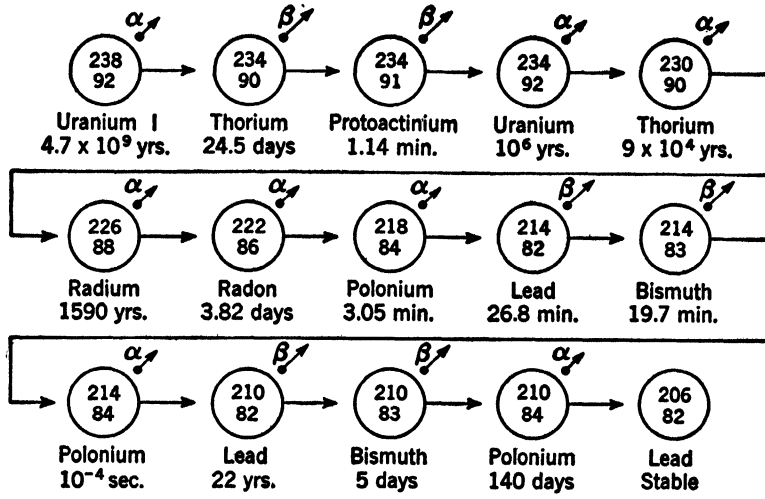


Figure 81. Transformation Series of the Uranium Family

(The upper number in each circle is the atomic mass; the lower, the atomic number. Below each circle is the name and the "half life" of the corresponding element.)

Although it has shown that atoms are not what we once thought them to be, information concerning radioactivity has probably done more than any other discovery to make atoms and molecules real to us. The observation of the path of a single alpha particle in a photograph secured by Wilson's fog-track method, or of the tiny flash of light that the impact of the particle produces on a phosphorescent screen, is an observation of an atom of helium in action. The atom that produces the fog-track and causes the tiny flash of light is a physical reality. It is as real as a bullet that we do not see, but which leaves indisputable evidence of its existence when it strikes an obstruction in its path.

ELECTRONS, PROTONS, AND NEUTRONS

11. Methods of Liberating Electrons from Matter

The beta particles emitted by certain radioactive elements are electrons. Electrons are also emitted by certain metals, or their compounds, under the influence of heat. Thus, the filament of a radio tube is heated, by a current of electricity, to a temperature at which it, or some material with which it is coated, emits electrons. Electrons are also emitted by the action of radiation upon elements or their compounds. Visible light causes very active metals, such as sodium and potassium, to emit electrons. Ultra-violet light has the same effect upon other elements, and X-rays liberate electrons from all forms of matter. Electrons emitted in this manner are called *photoelectrons*. Another source of electrons is discussed in the next section.

Whatever their source, or whatever the method by which they are liberated, electrons are identical. This, coupled with the fact that they can be liberated from all atoms, shows that they are parts of the structure of all atoms.

12. Cathode Rays

Many of their properties have been discovered by studying electrons produced during the discharge of electricity through gases under greatly reduced pressure (0.01 mm. of mercury or less). The cathode-ray tube (Figure 82) is designed for this purpose. Two wires, connected on the outside to a source of electrical potential (voltage), are sealed into the tube, which is evacuated by pumping out the air, or other gas, until the pressure is extremely low. Under these

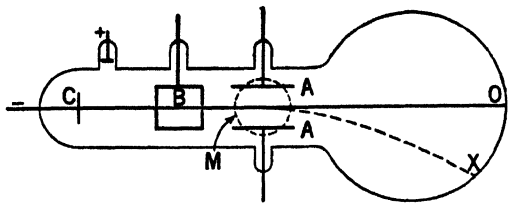


Figure 82. The Cathode-Ray Tube

Thomson used a tube of this kind to determine the ratio of the electron's charge to its mass. AA is the electrical field; M is the pole of a magnet; B is the slit system by which a pencil of rays is selected; O is the point at which the undeflected rays strike the walls of the tube; and X the point at which deflected rays strike. C is the cathode.

conditions, an electrical discharge occurs between the anode (+) and cathode (−). During this discharge, cathode rays are produced. They travel in straight lines from the cathode, and cause the walls of the tube, where they strike, to glow. They can also be detected by placing a piece of metal foil in their path; the foil becomes hot if the rays strike it. They also cause a small pin-wheel to revolve, if such a device is placed in their path. A metallic object placed in the path of the rays (Figure 83) casts a shadow upon the walls of the tube opposite the cathode. If a small pencil, or beam, of rays is selected by means of a slit in a screen, this beam is deflected (Figure 82) when it passes through a magnetic or an electrical field. The direction of the deflection is the same as that suffered by a negatively charged particle in passing through such fields. In short, the properties of the cathode rays can be explained most satisfactorily by assuming that they consist of streams of small negatively charged particles of matter — *electrons*.

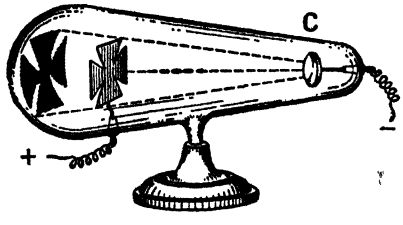


Figure 83. Cathode-Ray Tube

13. The Mass and Charge of the Electron

The velocities of the electrons composing cathode rays vary with the voltage between the terminals of the tube, and electrons possessing different velocities are deflected to different extents upon passing through the magnetic and electric fields. The deflection of an electron depends, also, upon its mass, its charge, and upon the strength of the electrical or magnetic field which deflects it.

By observing the deflections of cathode-ray particles in electrical and magnetic fields of known strength, Sir J. J. Thomson was able to determine the velocity of a group, or stream, of electrons all of which were deflected in the same manner and which, therefore, could be assumed to have the same velocity, mass, and charge. Knowing the velocity of the electrons and the strengths of the deflecting fields, he was able to calculate the ratio of an electron's charge, e, to its mass, m. He found that $\frac{e}{m} = 1.76 \times 10^7$ e.m.u. per gram. The abbreviation e.m.u. represents the *electromagnetic unit*, which is one of the units used by the physicist to express electrical charge.

14. Comparison of the Masses of Electrons and Hydrogen Atoms

Now the ratio, $\frac{e}{m}$ for the charged atom (ion) of hydrogen is known. Whenever a gram-atomic weight (m = 1.008 g.) of hydrogen is liberated by the action of an electric current upon a solution containing hydrogen ions, H^+, the quantity of electricity consumed is 96,540 units (called *coulombs*). This is used to neutralize the charges on the hydrogen ions in one gram-atomic weight, and is therefore the quantity of electricity associated with this weight of hydrogen. Since 1 electromagnetic unit is equivalent to 10 coulombs, this charge amounts to 9654 e.m.u. for 1.008 g. of hydrogen; and

hence, the ratio, $\frac{e}{m}$, for hydrogen is $\frac{9654}{1008}$ or $\frac{9578}{1}$.

Sir J. J. Thomson assumed that the hydrogen atom, when charged, possesses the same quantity of positive charge as the electron possesses of negative charge. Since the values of e are the same, the ratio of the mass of the hydrogen atom to the mass of the electron is $1.76 \times 10^7 : 9578$. Hence, the mass of the hydrogen atom is about 1837.5 times greater than the mass of the electron.

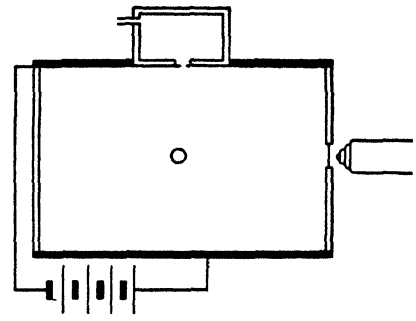


Figure 84. Millikan's Apparatus

The drop entered the space between the charged plates, from the small chamber above, through a tiny opening.

15. Millikan's Determination of the Electronic Charge

Of the many attempts to measure the charge of the electron, Millikan's method and results are best known. He observed a droplet of a liquid between two electrically charged plates (Figure 84) which form the top and bottom of an observation chamber. When the plates were not charged, the droplet fell under the influence of gravity, but when the plates were charged, the velocity of the drop was altered. Electrons and positively charged particles were produced between the plates by means of X-rays. If the droplet absorbed an electron, when the lower plate was positively charged, its fall was accelerated. But if the lower plate was negatively charged, the velocity of its fall was decreased. If sufficient electrons were absorbed to balance exactly the gravitational force, the droplet stood still, and if a still greater number of electrons was absorbed, the droplet moved upward.

Millikan found that all changes of velocity (up or down) were multiples of a certain minimum change, which corresponded to the absorption of one unit of charge — the smallest charge ever absorbed. Other changes, therefore, were produced by the absorption of two or more units of charge. He thus demonstrated the "atomic" character of electrical charge, as clearly as the law of multiple proportions shows that matter is composed of atoms.

By considering the velocity of the drop, its mass, the strength of the gravitational field and of the electrical field, and the viscosity of the air through which the drop moved, Millikan was able to calculate the quantities of charge on different drops. The smallest charge determined by these calculations represents one unit of charge, or the charge of the electron. This value was found to be 1.59×10^{-20} electromagnetic units. Since the ratio of the electron's charge to its mass is known (page 136) to be 1.76×10^7, it is possible to calculate the electron's mass. This turns out to be 9.1×10^{-28} gram, or a mass of 0.00055 on the scale of atomic weights. The present accepted value for the electron's charge is 1.602×10^{-19} coulombs.

A number so small as the mass of an electron can best be expressed by using negative exponents, e.g., 9.1×10^{-28}. This system is explained if we compare it with the well-known plan of writing large numbers as smaller numbers squared, cubed, etc.: $10 = 1 \times 10$; $100 = 1 \times 10^2$; $1000 = 1 \times 10^3$; $700 = 7 \times 10^2$; $0.1 = 1 \times 10^{-1}$; $0.01 = 1 \times 10^{-2}$; $0.001 = 1 \times 10^{-3}$.

16. Avogadro's Number

We have already shown that the mass of the hydrogen atom is 1837.5 times that of

the electron and that the mass of the latter is 9.1×10^{-28} g. We can calculate, therefore, the mass of a single hydrogen atom as $1837.5 \times 9.1 \times 10^{-28}$ gram or 1.67×10^{-24} g. The weight of a molecule of hydrogen is twice this weight, or 3.34×10^{-24} g. The number of molecules of hydrogen in a gram-molecular weight, therefore, is

$$\frac{2.016 \text{ g.}}{3.34 \times 10^{-24} \text{ g.}} = 6.02 \times 10^{23}.$$

This is the number of molecules in a gram-molecular weight of any substance, and, also, the number of atoms in the gram-atomic weight of any element. It is called Avogadro's number. A more exact value is 6.0228×10^{23}.

17. Protons as Units of Atomic Structure

If atoms contain protons, it should be possible to liberate them by causing the atoms to disintegrate. Atoms of nitrogen, aluminum, and other common elements can be decomposed by bombarding them with high speed alpha particles. When these alpha particles strike atoms and molecules, other particles are produced. These are lighter than the alpha particles, and they travel for relatively longer distances through the air or other substances before they are stopped. The ranges of at least many of these particles are about the same as those of hydrogen atoms that are struck and driven forward, when alpha particles are passed through pure hydrogen or through gaseous compounds of hydrogen. Furthermore, the ratio of the charge of one of these particles to its mass can be determined by the method that Thomson used in determining the ratio of the electron's charge to its mass. The results prove that some of the particles liberated from nitrogen, aluminum, and certain other atoms are protons. These experiments, probably more than any other direct source of evidence, indicate that the electrically positive unit of the atom's structure is the ***proton***.

18. The Neutron

Neutrons were discovered by the bombardment of atoms of beryllium and boron with alpha particles. They are uncharged, have a mass of approximately 1.009 — as compared with 16 for the oxygen atom — and travel with a velocity about one tenth of the velocity of light. At first, the neutron was thought to be composed of one proton and one electron; now, however, it is regarded as a distinct kind of particle. Yet it appears that a neutron can, under certain conditions, be changed into a proton and an electron. It appears to be likely that the beta particles emitted by certain radioactive elements are formed when neutrons in the nuclei of the original atoms are converted into protons and electrons. The belief that neutrons are a part of the structure of atoms is supported by the fact that these particles can be expelled from many kinds of atoms by bombardment.

19. Positrons

Cosmic rays constitute a very penetrating form of radiation originating somewhere in space outside the earth's atmosphere. These rays act upon certain forms of matter to liberate particles called *positrons*. These particles were discovered in 1932 during a study of the effects of cosmic rays upon matter. They are also liberated when boron and some other elements are bombarded with high energy level alpha particles. Boron is first converted into an isotope of nitrogen, which then disintegrates to produce an isotope of carbon and positrons. Each positron has the same quantity of charge as an electron, but the charge is positive instead of negative. Its mass is approximately the same as the mass of an electron.

Positrons do not appear to be capable of independent existence for any length of time. They react almost immediately with electrons, and both particles are converted into gamma radia-

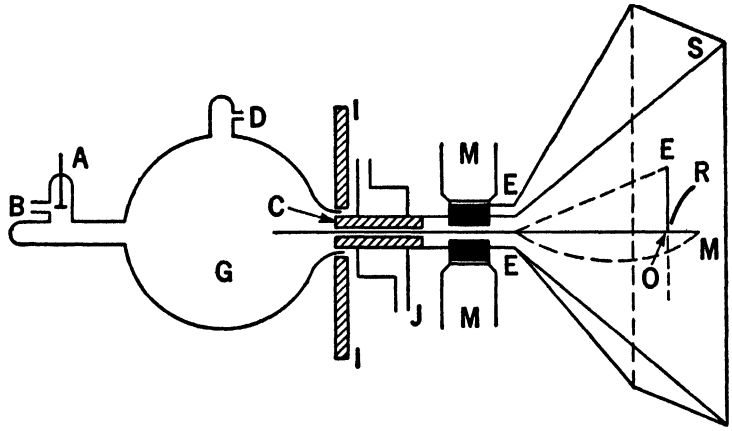


Figure 85. Thomson's Positive-Ray Tube

Positive particles are produced by collisions between electrons and molecules of gas contained in G. These positive particles pass through the opening in the cathode into the electrical field (EE) and the magnetic field (MM). J is a cooling jacket through which cold water flows. I is an iron shield to prevent positive particles in G from being deflected by the magnet before they pass through the cathode. Particles deflected by the electrical field alone strike the screen along the line E–O, and those deflected by only the magnetic field strike along M–O. Those deflected by both fields simultaneously strike along R–O.

tion. This process has been reversed by sending gamma rays through lead. The actual conversion of a small portion of the energy in the radiation into two particles, a positron and an electron, has been observed. Upon such evidence as this is based the opinion, first expressed on page 22, that there is a certain degree of *equivalence* between matter and energy, and that under certain conditions one may be converted into the other. It has been suggested that the gamma radiation of radioactivity may be produced by the reaction and mutual annihilation of positrons and electrons in the atoms of radioactive elements.

ISOTOPES

20. Positive-Ray Analysis

The discovery of cathode rays encouraged attempts to find positive rays. It was thought that these rays, if they exist, should travel in straight lines from the anode, and in a tube such as the one shown in Figure 85 that they should strike the cathode. If the cathode is perforated by a cylindrical opening, a pencil of positive rays should pass through the cathode into the region beyond. Such rays have been observed. Their deflections in a magnetic or electrical field are in the opposite directions to the deflections of electrons in the same fields. For this reason, and also because they travel toward and through the cathode, the assumption that they are made up of positively charged particles appears to be justified.

The particles composing positive rays are electrically charged atoms and molecules, or *ions*, and their masses and charges vary, therefore, with the character of the small amount of gas in the tube. They are produced by the effects of cathode-ray particles upon atoms and molecules of this gas; the impacts result in the expulsion of one or more electrons from atoms or molecules and the production of positively charged ions.

Using Sir J. J. Thomson's procedure (Figure 85), let us consider the positive particles produced in a discharge tube under the influence of a difference in potential of some thirty or forty thousand volts. After passing through the cathode of such a tube, the positive particles are deflected by passing them through an electrical and a magnetic field and finally are allowed to strike a zinc sulfide coated screen or a photographic plate, *S*. The electrical field

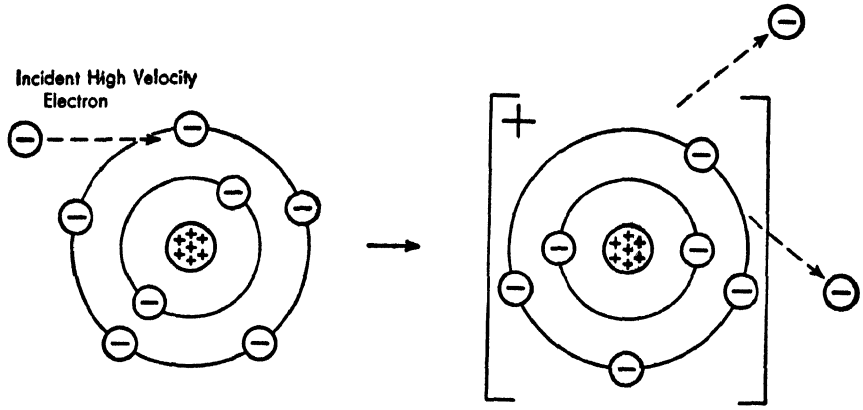


Figure 86. Ionization by Collision

Schematic diagram to indicate how a neutral nitrogen atom can form a positive ion by the loss of an electron following impact with a high-speed electron.

alone causes particles of the same mass and charge, or particles having the same ratio of charge to mass, $\frac{e}{m}$, to be deflected along the line E—E (Figure 87) above or below O depending upon whether the negatively charged plate of the electric field is above or below the beam of particles. In Figure 85 the negatively charged plate is above the path of the beam. The exact point at which each particle strikes is determined by the velocity of the individual particle. The magnetic field deflects the particles in circular paths which lie in a plane perpendicular to the field and also to the direction of the electrical deflection. This field when acting alone, therefore, will deflect similar particles along the line $M - M$ at points where the circular paths intersect the screen.

The extent of the deflection of a particle depends upon the strengths of the deflecting fields, the mass, charge, and velocity of the particle, and the dimensions of the apparatus. When acted upon by both fields simultaneously, particles possessing the same mass and the same charge (or the same $\frac{e}{m}$) will strike the screen or plate at different points, depending upon their velocities, along a curve RO that lies between $E - E$ and $M - M$. Particles possessing different masses or charges produce other similar curves, each curve representing the points at which all particles having the same ratio of $\frac{e}{m}$ strike the screen. From comparisons of the curves made by different kinds of particles, some of which are of known mass and charge, all the particles can be identified, and their masses can be determined, if their charges are known or can be calculated. This is usually not

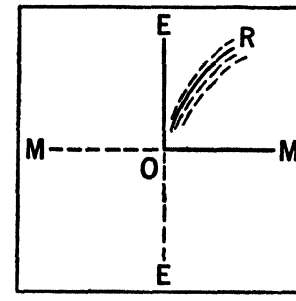


Figure 87. The Deflection of Positive Particles by Electrical and Magnetic Fields

This represents a photographic plate or screen that might be used at S in Thomson's tube, Figure 85. The point O is directly opposite the cathode. The curve R–O indicates the line along which particles deflected by both the electrical and magnetic fields strike. A different curve is observed for each kind of particle having a different ratio of e to m.

difficult because the charge of a particle is either the same as, or a small multiple of, the electron's charge.

21. Discovery of the Isotopes of the Stable Elements

During the course of his experiments with positive particles, Thomson was puzzled by the appearance of two curves whenever neon was present in the tube. Both of these curves appeared to be produced by atoms of this element, although neither corresponded exactly to the accepted atomic weight of neon, 20.2. The two curves showed that they were produced by particles which possess masses of 20 and 22, respectively, as compared to 16 for the atom of oxygen. This could mean, of course, but one thing. There must be two kinds of neon atoms, and the atomic weight, 20.2 is the weighted [1] average of these two values. The two kinds of neon are, therefore, *isotopes*.

22. Aston's Mass Spectrograph

Thompson's apparatus was considerably modified by Aston, who used it to determine the isotopes of other elements and their atomic weights. In Aston's apparatus (Figure 88), the particles are first deflected toward the negatively charged plate p_2 of the electrical field, and the original beam is separated into a number of parts because the particles differ in velocity. The deflected particles then pass into the magnetic field H, where they are again deflected. If the relative positions of the different parts of the apparatus and the strengths of the two deflecting fields are properly adjusted, the magnetic field will bring to a focus on the photographic plate P all the particles that have the same charge and mass but different velocities. By measuring the position of the spot produced by any one kind of particles, with reference to the spots formed by other particles of known charge and mass, the mass of that particle is determined.

We might expect to obtain by this method, therefore, three lines corresponding to the three isotopes of oxygen, which have relative masses of 16, 17, and 18. The intensities of these lines gives the order of abundance of the three isotopes. Because it separates particles of different masses into a spectrum, somewhat like the spectrum into which a spectrograph analyzes a beam of light, Aston's device has been called a *mass spectrograph*. It is a means of comparing directly the masses of different atoms — the atomic weights of the elements — by physical rather than chemical methods. A list showing the isotopes of some of the elements will be found in Table 2.

The atomic weights determined by this method are usually spoken of as physical rather than chemical atomic weights. Since they are based upon comparisons with the single isotope of oxygen which has a relative mass number of 16, they differ slightly from the atomic weights determined by chemical methods and based upon

[1] Weighted because the number as well as the weight of each kind of atom must be considered in calculating the average.

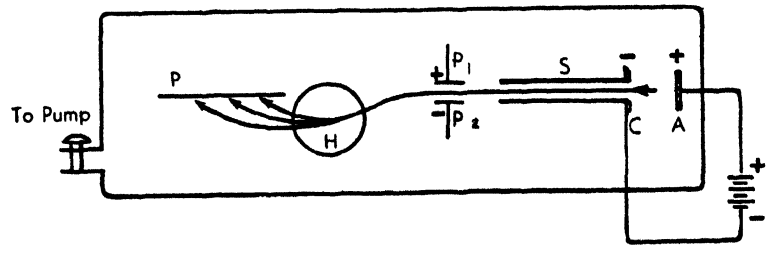


Figure 88. The Principle of the Mass Spectrograph of Aston

a comparison of the weighted average mass of all three isotopes of oxygen.

TABLE 2

ISOTOPES OF SOME OF THE ELEMENTS*

Lithium	7, 6
Boron	11, 10
Carbon	12, 13
Nitrogen	14, 15
Oxygen	16, 18, 17
Neon	20, 22, 21
Sodium	23
Magnesium	24, 25, 26
Aluminum	27
Silicon	28, 29, 30
Sulfur	32, 34, 33
Chlorine	35, 37
Argon	40, 36, 38
Potassium	39, 41, 40
Calcium	40, 44, 42, 43
Iron	56, 54, 57, 58
Zinc	64, 66, 68, 67, 70
Selenium	80, 78, 76, 82, 77, 74
Krypton	84, 86, 82, 83, 80, 78
Bromine	79, 81
Rubidium	85, 87
Silver	107, 109
Tin	120, 118, 116, 119, 117, 124, 122, 112. 114, 115
Iodine	127
Platinum	195, 194, 196, 198, 192
Gold	197
Mercury	202, 200, 199, 201, 198, 204, 196
Lead	208, 206, 207, 204

* Atomic weights are stated in the order of abundance and to the nearest whole numbers. Such values are usually called mass numbers.

THE NUCLEAR THEORY OF THE ATOM'S STRUCTURE

23. Rutherford's Experiment

According to the theory of atomic structure described on page 35, all the protons and all the neutrons of an atom are packed together in the nucleus at the center of the atom. The evidence in favor of this view was supplied by Rutherford in experiments dealing with the passage of high-speed alpha particles through thin sheets of metals, such as a very thin gold foil. On one side of the foil he placed the radioactive substance that emitted the alpha particles, and on the other a phosphorescent screen. The latter was observed with a microscope, and the number of alpha particles striking within a certain area on the screen in a certain period of time was counted.

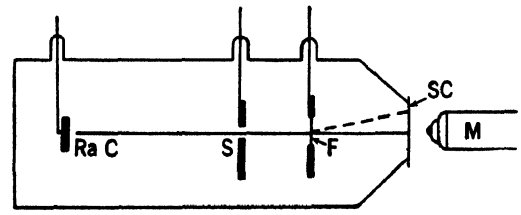


Figure 89. Rutherford's Apparatus Used in Studying the Deflections of Alpha Particles by Metallic Foils

The alpha particles were produced by Radium C and passed through the foil F, eventually striking the fluorescent screen SC, where they were observed with the aid of the microscope, M.

Rutherford found that almost all the alpha particles which passed through the foil were deflected, if at all, only slightly, since approximately the same number struck the screen, when the foil of gold was placed in front of it, as when the foil was absent. But now and then an alpha particle (one in many thousands) was deflected so strongly that it did not strike the screen at all; it was deflected through a large angle, and sometimes it was deflected backward in the same direction as its source. Such particles could be located by using other screens placed in different positions around the foil.

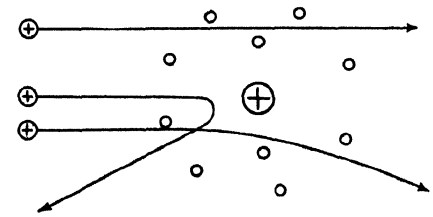


Figure 90. Deflections of Alpha Particles by an Atom

The large center circle represents the nucleus of an atom of metal in the foil. The small circles around it represent the planetary electrons.

Rutherford interpreted his results to mean that the alpha particles usually met no deflecting forces, or very small forces such as might be exerted by electrons, in their passage through the atoms of the foil. This means, of course, that most of the space occupied by the atoms of the foil is empty. The rare deflections through large angles, which sometimes caused the alpha particles to reverse their directions, indicated that only one out of a great number of such particles came close to a strongly repelling body. Since this body repelled the alpha particle it must have had a positive charge, and the rare occasions when an alpha particle came near such a body indicated very clearly that there can be relatively few locations of such positive charges in the foil — not more, for example, than one per atom.

It appears, therefore, that we may assume that all the protons of an atom are collected in a very small space somewhere within the atom. Rutherford assumed that this space is at the center of the atom, and he called it the *nucleus*.

DISINTEGRATION OF ATOMIC NUCLEI

24. Conversion of Nitrogen into an Isotope of Oxygen

As long ago as 1919, Rutherford changed nitrogen into an isotope of oxygen by bombarding the nuclei of nitrogen atoms with alpha particles of high energy level. Using the cloud chamber apparatus (page 131), he found that now and then an alpha particle collided with a nitrogen atom in such a way that two tracks were produced where there had been before only the single track of the alpha particle. A study of these tracks showed that they were produced by an oxygen nucleus of mass 17 and a proton:

$$_7N^{14} + {}_2He^4 \longrightarrow {}_1H^1 + {}_8O^{17}.$$

In this and the equations that follow the numbers written as superscripts designate the mass numbers of atoms. The subscripts at the left of the symbols indicate atomic numbers.

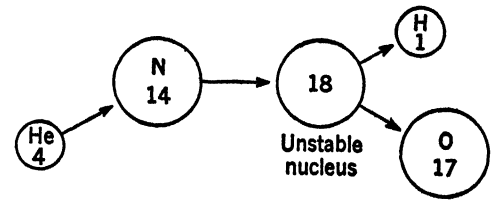


Figure 91. The Production of an Isotope of Oxygen from Nitrogen

25. Other Transmutations of Elements

Since about 1932 many other transmutations, or changes of one element into another, have been produced by similar methods. The particles used in bombarding atomic nuclei are alpha particles, $_2He^4$; electrons, $_{-1}e^0$; protons, $_1H^1$; deuterons, $_1H^2$; and neutrons, $_0n^1$. To produce high-speed particles for these bombardments of atoms, tubes producing positively charged ions and operated at several million volts are used. Other devices include the cyclotron (see below) and the betatron, which is used to accelerate electrons.

The following equations show some of the transmutations that have been accomplished:

$$_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$
$$_5B^{10} + {}_2He^4 \longrightarrow {}_7N^{13} + {}_0n^1$$
$$_3Li^7 + {}_1H^2 \longrightarrow 2\ {}_2He^4 + {}_0n^1$$
$$_4Be^9 + {}_1H^2 \longrightarrow {}_5B^{10} + {}_0n^1$$
$$_7N^{14} + {}_0n^1 \longrightarrow {}_5B^{11} + {}_2He^4$$
$$_{13}Al^{27} + {}_0n^1 \longrightarrow {}_{11}Na^{24} + {}_2He^4$$
$$_5B^{11} + {}_1H^1 \longrightarrow 3\ {}_2He^4$$
$$_6C^{12} + {}_1H^1 \longrightarrow {}_7N^{13}$$
$$_3Li^7 + {}_1H^1 \longrightarrow 2\ {}_2He^4$$
$$_8O^{16} + {}_0n^1 \longrightarrow {}_6C^{13} + {}_2He^4$$

26. The Cyclotron

This is a device by which protons and deuterons of high velocity are obtained for use in bombardments of atomic nuclei. It consists (Figure 92) of a circular brass box, built in two sections, which are connected

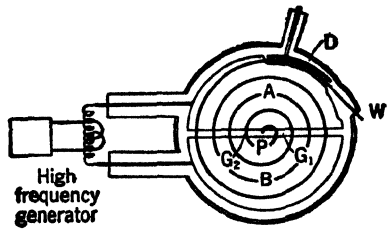


Figure 92. The Cyclotron

by means of an insulating material. The two sections are charged, one positively and the other negatively, and the box is placed in a powerful magnetic field. Protons or deuterons are introduced into the center of the box, where they move in a circular path, under the influence of the magnetic field, as all similarly charged particles do. A positively charged particle is attracted by the charge on the negatively charged section of the box (A, Figure 92), and it is repelled by the other section (B). As the particle reaches the gap (G_1) between the two sections, the charges are reversed, i.e., A becomes the positive and B the negative section. This reversal of charge produces an acceleration in the velocity of the particle and, as a result, the circular path in which the particle moves increases in radius. Since the charge is reversed each time the particle crosses the gaps, G_1 and G_2, the path becomes a spiral of ever-increasing radius. Finally, it leaves the circular box at DW with its maximum velocity, which may be as great as 25,000 miles per second, depending upon the strength of the magnetic field. The high-speed particles thus obtained are then used to bombard materials containing different elements for the purpose of producing transmutations.

27. Artificial or Induced Radioactivity

In 1934, aluminum was made to act in a radioactive manner by bombarding it with alpha particles. After the bombardment had stopped, radioactive disintegration continued for some time and indicated a half-life time for the radioactive element of three to four minutes. Tests indicated that an isotope of phosphorus, produced by the fusion of aluminum nuclei and alpha particles, was the radioactive element. Its atoms disintegrate to produce an isotope of silicon and positrons, ${}_{1}e^{0}$:

$$ {}_{13}Al^{27} + {}_{2}He^{4} \longrightarrow {}_{15}P^{30} + {}_{0}n^{1} $$
$$ {}_{15}P^{30} \longrightarrow {}_{14}Si^{30} + {}_{1}e^{0} $$

A radioactive isotope of sodium with a half-life period of 14.8 hours has been produced by bombarding sodium chloride with deuterons:

$$ {}_{11}Na^{23} + {}_{1}H^{2} \longrightarrow {}_{11}Na^{24} + {}_{1}H^{1} $$
$$ {}_{11}Na^{24} \longrightarrow {}_{12}Mg^{24} + {}_{-1}e^{0} $$

More than 600 different atomic nuclei are known, and of these some 400 are unstable.

28. Tracer Elements

The radioactive isotopes of some elements are useful as "tracers." For example, if we wish to follow the course of phosphorus through a series of reactions we can prepare a compound of the element in which both stable and radioactive phosphorus are present. Since the two isotopes have the same properties, their atoms will remain mixed in the same proportion throughout any series of reactions in which they may be involved. Wherever phosphorus appears during subsequent changes, therefore, it will consist in part of the radioactive form, which can be detected easily by means of a Geiger counter or any of the devices designed to detect the radiations emitted by such substances. Thus, by using the "radioactive isotope" of phosphorus mixed with ordinary phosphorus in the form of a phosphate that is incorporated with food material, it is possible to determine not only the time required for that element to become a part of the phosphate structure of the bones of the body, but also the time that elapses before phosphorus in food passes through the different phases of metabolism and is elimi-

nated from the body. Similarly, we may study the circulation of the blood by injecting into the blood stream a solution of sodium chloride, if some of the sodium atoms are of the radioactive isotope of that element.

Several radioactive isotopes are used in the treatment of disease, because of the beneficial effects of the radiations emitted by these substances in killing disease producing organisms or in destroying cancerous tissues. Radioactive phosphorus and strontium have been used in the treatment of leukemia, a disease in which there is a very great increase in the production of white corpuscles in the blood, and osteomyelitis, an infection of bone marrow. A radioactive isotope of iodine has been used in studying and treating diseases of the thyroid gland.

A radioactive isotope of carbon ${}_6C^{14}$ is widely used in chemical and biological research. This substance is produced by the action of relatively slowly moving neutrons on nitrogen:

$$ {}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1H^1 $$

It has a half-life period of almost 5000 years and, in this respect, is much unlike many of the other artificially produced radioactive elements which disintegrate very rapidly. It is useful in studying the mechanism of series of reactions involving the synthesis of organic compounds. For example, growing plants absorb carbon dioxide and from it synthesize carbohydrates. If some of the carbon dioxide in the atmosphere surrounding a plant contains ${}_6C^{14}$ atoms, their course may be followed from the leaves to other parts of the plant's structure. It is possible that this use of radioactive carbon may help eventually in arriving at a solution of the important problem regarding the changes involved in the production by plants of sugars and starch. The use of this isotope of carbon has stimulated and made possible many new investigations in organic chemistry.

29. Nuclear Fission

Natural uranium consists of the three isotopes, ${}_{92}U^{234}$, ${}_{92}U^{235}$, and ${}_{92}U^{238}$. These isotopes have almost identical chemical properties, but they differ considerably in the effects resulting from the absorption of neutrons by their nuclei. When a neutron is absorbed by a nucleus of U–235, that nucleus is split into two smaller nuclei of about the same size and from one to three neutrons. All of the liberated particles possess relatively large quantities of kinetic energy. A change of this kind in which an atomic nucleus is split into two fragments of about the same size is called *nuclear fission.* The nuclear fragments are nuclei of radioactive isotopes of elements having atomic numbers from 34 to 57. Figure 93 shows the fission of a uranium nucleus to form the nuclei of barium and krypton.

The neutrons ejected during the fission of a single U–235 nucleus may (1) escape into the surroundings, (2) be absorbed by the nuclei of other U–235 atoms, or (3) be absorbed by U–238 nuclei or by impurities in the sample of metallic uranium.

The neutrons that are absorbed by U–235 nuclei may cause the fission of those nuclei. The fission of each nucleus liberates from one to three additional neutrons which may be absorbed by other U–235 nuclei, thus causing the process to be repeated again and again. A self-propagating reaction of this kind is called a *chain reaction.* If more neutrons are absorbed by U–235 nuclei than

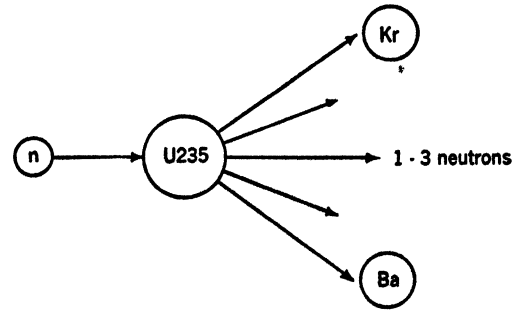


Figure 93. Fission of an Atom of U-235

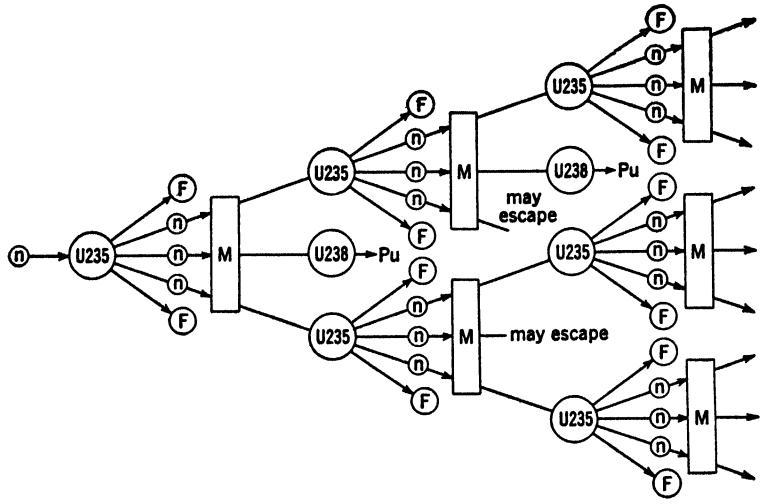


Figure 94. Chain Fission Reaction

M, moderator (graphite) to slow neutrons; n, neutrons; F, fragments of fission of U-235, atoms of elements in middle portion of periodic table; Pu, plutonium.

are lost to the surroundings or absorbed by U–238 and impurities, the fission of U–235 nuclei will continue at an increasing rate, and fission will spread throughout the whole mass of the sample of metal. The energy released is in the form of kinetic energy of the particles produced, and hence is actually heat energy. It is therefore quite likely that, unless the reaction is controlled in some way, the heat liberated will quickly become sufficient to vaporize the entire sample of uranium and even surrounding objects.

Some of the neutrons that are captured, or absorbed, by U–238 nuclei convert that element into neptunium and finally into plutonium by a series of changes which is summarized in the equations

$$_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} \longrightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$
$$_{93}Np^{239} \longrightarrow {}_{94}Pu^{239} + {}_{-1}e^{0},$$

in which $_{-1}e^{0}$ is used to designate an ordinary electron. $_{92}U^{239}$, an isotope of uranium, $_{93}Np^{239}$, and $_{94}Pu^{239}$ are all radioactive. The first two decay rapidly but $_{94}Pu^{239}$ disintegrates very slowly as follows:

$$_{94}Pu^{239} \longrightarrow {}_{92}U^{235} + {}_{2}He^{4}.$$

The rate of disintegration of plutonium, $_{94}Pu^{239}$, is so slow that we may consider it, for all practical purposes, as a stable element. When plutonium nuclei absorb neutrons they may undergo fission in the same manner as U–235 nuclei.

Neutrons liberated by the fission of U–235 have very high velocities and are not very effective in causing the fission of other U–235 nuclei or in converting U–238 into plutonium unless they are slowed down considerably. To accomplish this, the reaction may be carried out in a graphite-uranium *pile* instead of pure uranium. Graphite does not absorb neutrons to any great extent but it does retard them. A pile is a structure consisting of blocks of graphite and rods of uranium, which are placed in openings between some of the graphite blocks. After the neutrons have been slowed down by the graphite there is a higher degree of probability that, when they pass again into the uranium, they will produce fission of U–235 nuclei.

Unless it is controlled, the reaction may become very rapid, and the temperature may reach a point at which the pile and even surrounding objects may be vapor-

ized. To prevent this from happening, rods of cadmium or of some other material which will absorb neutrons may be inserted in openings in the pile. The absorption of neutrons by inactive material retards the chain reaction.

During the fission of U–235 there is a loss of mass amounting to about 0.1 per cent of the mass of the original material. This mass is converted into energy (page 9). For one pound of U–235, the loss of mass by fission is equivalent to a sufficient quantity of energy to supply all the electrical power required by a city of 25,000 inhabitants for an entire year. As a result of research now in progress, this energy should someday become available for industrial purposes.

To produce "atomic" bombs for military purposes, pure U–235 or plutonium must be used. In ordinary metallic uranium there are too many U–238 atoms which absorb most of the neutrons, thus interfering with the fission of U–235 nuclei. The separation of U–235 from U–238 is very difficult. The two isotopes have almost identical chemical properties; hence chemical methods of separation cannot be used. One method that has been used depends upon the difference in the rates of diffusion, through a barrier, of uranium hexafluoride molecules containing atoms of U–235 and U–238. Since the U–235 atoms are lighter, the molecules containing them diffuse more rapidly through the barrier than molecules containing the heavier atoms of U–238. The first portion of uranium hexafluoride to diffuse through the barrier is richer, therefore, in U–235 than the original material. This portion is allowed to diffuse again, and the process is repeated many times in order to get complete separation.

To produce an explosion, two portions of U–235 must be brought very quickly together, and the combined mass of the two portions must be such that the production of neutrons by fission will exceed the number lost by escape.

Plutonium for use in bombs is produced by the absorption of neutrons by U–238 nuclei in an uranium-graphite pile. Since plutonium is a different element from uranium, and consequently has quite different chemical properties, the two elements can be separated by chemical methods.

30. The Transuranium Elements

Elements having atomic numbers 93 to 98 are referred to as transuranium elements because they lie beyond uranium in the periodic table. The atomic number of neptunium is 93 and that of plutonium is 94. Elements 95 and 96, or at least isotopes of these elements, have been produced by the bombardment of U–238 and Pu–239 with high-speed helium ions. Element 95 is called *americium*, ${}_{95}Am^{241}$. It is radioactive, emits alpha particles and has a half-life period of about 500 years. Element 96 is called *curium*, ${}_{96}Cm^{240}$ and ${}_{96}Cm^{242}$. The two isotopes of this element are radioactive. Both emit alpha particles and have half-life periods of one month and five months, respectively. Isotopes of elements 97 and 98 have been produced recently by methods similar to those involved in the production of the others. These have been named *berkelium* and *californium*, respectively.

Studies of the properties of the transuranium elements indicate that they are the first members of a group of elements in the seventh period that corresponds to the rare-earth group beginning with lanthanum and including elements 57–71 in the sixth period. The seventh-period group begins with actinium, No. 89, and includes thorium, protoactinium, uranium, neptunium, plutonium, americium, curium, berkelium and californium.

REVIEW EXERCISES

1. What changes in our ideas concerning atoms have resulted from the discovery of radioactivity?
2. What happens to an atom which undergoes radioactive disintegration?

3. What is the nature of each of the three kinds of radiation emitted by the radioactive elements?
4. How can alpha and beta particles be detected?
5. How is radioactivity different from ordinary physical changes? How is it like and how is it different from chemical changes? Should it be classified as a physical or as a chemical property?
6. What does the half-life of a radioactive element tell us about the element?
7. What are alpha and beta particles?
8. Account for the effect of alpha and beta rays upon a charged electroscope.
9. How do alpha rays produce fog tracks?
10. What evidence is there that an alpha particle is an ion of helium?
11. Describe a cathode-ray tube. What facts concerning cathode rays indicate that they are composed of negatively charged particles?
12. By what method did Thomson determine the mass and charge of the cathode-ray particle?
13. How did Millikan demonstrate the "atomic" character of electrical charge? How did he determine the unit of charge?
14. What are some of the methods by which electrons can be liberated from different forms of matter?
15. What is a proton? Of what are positive "rays" composed and how are they produced?
16. The atomic weights of the isotopes of an element whose atomic number is 38 are 88, 87, and 86. What is the composition of the nucleus of each of the isotopes?
17. Three isotopes of oxygen are now known. The relative masses of the three kinds of atoms are 16, 17, and 18. Are the chemical methods of determining atomic weights based upon the isotope of mass number 16 or upon a mixture of all three? Would there be any considerable difference between the values of atomic weights based upon the isotope of mass 16 and those based upon the mean atomic weights of the three isotopes? Explain.
18. How can the mass of an atom of hydrogen and the number of molecules of hydrogen in one gram-molecular weight be estimated?
19. Describe the mass spectrograph. For what purpose is it used?
20. Describe Thomson's experiments which resulted in the discovery of isotopes of the nonradioactive elements.
21. How and why do "physical" atomic weights differ from "chemical" atomic weights?
22. Upon what kind of evidence is the theory of the atomic nucleus based? What is thought to be the composition of this nucleus? How do the nuclei of different kinds of atoms differ? How do those of isotopes differ?
23. What are some of the evidences that matter and energy may be converted one into the other?
24. What evidence indicates that all atoms contain electrons? protons?
25. Which of the following statements, if they appeared in your newspaper, would you (1) be inclined to accept as probably true, (2) question seriously and (3) dismiss as absurd?
    (*a*) The discovery of element 100 during laboratory experiments involving nuclear reactions.
    (*b*) The discovery of an isotope of element 16 having an atomic weight of 64.
    (*c*) The discovery of an element having a negative atomic number.
    (*d*) An announcement that inhabitants of some other planet were bombarding the earth with streams of electrons.
    (*e*) A claim that a method had been found whereby the oxygen atom could be converted into four atoms of helium.
    (*f*) That a method had been discovered whereby ordinary iron could be made radioactive.
    (*g*) That atoms are actually, as John Dalton believed, of uniform composition throughout.
    (*h*) That the atomic weight of ordinary potassium is 41 instead of 39.096.
    (*i*) That the atomic number of oxygen is really 9 thus indicating an undiscovered element in the periodic table between nitrogen and oxygen.
26. What can you suggest as the possible products of the following reactions?

$$_{12}Mg^{24} + {}_{2}He^{4} \longrightarrow$$
$$_{1}H^{2} + {}_{1}H^{2} \longrightarrow$$
$$_{7}N^{14} + {}_{2}He^{4} \longrightarrow$$

27. What do each of the following represent? $_{83}Bi^{209}$; $_{1}H^{2}$; $_{0}n^{1}$; $_{1}e^{0}$; $_{-1}e^{0}$; $_{6}C^{13}$; $_{6}C^{12}$; $_{6}C^{14}$.
28. Why has atomic energy not yet been used as a source of energy in place of coal and other fuels?

REFERENCES FOR FURTHER READING

Radioactivity

Hevesy, G. von, and F. Paneth, *Manual of Radioactivity*, 2d ed. New York: Oxford University Press, 1939.

Moore, F. J., *History of Chemistry.*

Rutherford, E. R., *Radioactive Substances and Their Radiations.* London: Cambridge University Press, 1913.

Rutherford, E. R., *The Newer Alchemy.* New York: The Macmillan Company, 1937.

Commercial Production of Radium: *Ind. and Eng. Chem.*, **18,** 2, 198 (1926).

Discovery of Radioactive Elements: *J. Chem. Ed.*, **10,** 79 (1933).

Radioactivity and the Periodic Table: *J. Chem. Ed.*, **17,** 481 (1940).

Radium and Radioactivity: *Annual Survey of American Chemistry,* **6,** 152 (1931); **9,** 113 (1934). New York: Reinhold Publishing Company.

Radium from Canadian Pitchblende: *J. Chem. Ed.*, **17,** 417 (1940); **24,** 148 (1944).

Pollard, E., and W. L. Davidson, *Applied Nuclear Physics.* New York: John Wiley and Sons, Inc., 1943.

Rice, Francis O., *The Structure of Matter*, New York: John Wiley and Sons, Inc., 1949.

Semat, Henry, *Atomic Physics.* New York: Rinehart and Company, 1946.

Smyth, H. D., *Atomic Energy for Military Purposes.* Princeton: Princeton University Press, 1945.

J. Chem. Ed., **22,** 619 (1945); **23,** 60, 423, 528 (1946); **24,** 538 (1947).

Chem. and Eng. News, **24,** 1192 (1946); **25,** 358 (1947).

12

ATOMIC STRUCTURE AND THE PROPERTIES OF THE ELEMENTS

1. Introduction

The preceding chapter dealt largely with atomic nuclei. We now turn our attention first of all to the distribution of the electrons in atoms. Later we shall study the method used to determine the atomic numbers of the elements, the periodic classification of elements based upon atomic numbers rather than atomic weights and, finally, the properties of the elements as related to their atomic numbers and to the arrangement of electrons in their atoms.

THE DISTRIBUTION OF ELECTRONS

2. The Bohr Theory

Our current conception of the behavior and arrangement of the electrons in an atom is based upon a theory developed by Bohr, who assumed that electrons move in orbits and thus can resist the pull, or attraction, of the positively charged nucleus. If they are given additional energy, the electrons may fly entirely beyond the boundaries of the atom, or if the added energy is small, they may rotate in larger orbits, farther removed from the nucleus. Under normal conditions, however, the attraction of the nucleus keeps them in rotation in what we may refer to as their "normal" orbits.

3. The Hydrogen Atom and Its Energy Levels

The hydrogen atom consists of a single electron revolving around the nucleus, which in this case is a single proton. The electron, however, may revolve in many orbits, depending on the energy which it possesses. Bohr's theory assumes that, as long as the electron rotates in the same orbit, it neither gains (absorbs) nor loses (radiates) energy. If it gains energy, the electron moves to a larger orbit. If it loses energy, it moves to an orbit of smaller radius.

Since the electron is a part of the atom, and since the electron possesses different quantities of energy when it revolves in different orbits, the *energy state* of the atom as a whole may be said to vary with the orbit occupied by the electron. Or putting the matter in another way, the different electron orbits may be said to represent different *energy levels*. If the electron lay in the nucleus, its energy would be zero, and this condition would represent the zero energy level. Hence, the orbit nearest the

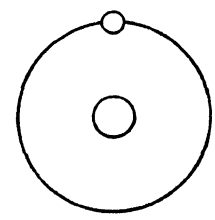


Figure 95. The Hydrogen Atom

Showing a proton in the center and the single planetary electron rotating in the orbit of smallest diameter.

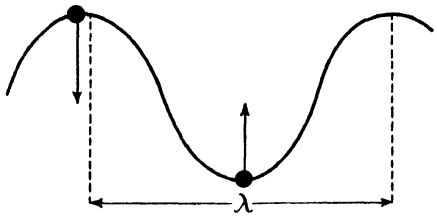


Figure 96. A Wave of Light or X-Rays is Thought to be Somewhat Like a Water-Wave

The distance from one crest to the next is a wave-length.

nucleus corresponds to the level of smallest energy and is called the first level. If the electron's energy changes, it must move from one orbit to another. An electron cannot change its distance from the nucleus and its corresponding energy continuously; only certain definite shifts are possible

4. The Evidence for the Bohr Theory

For the most part, Bohr's theory of electron orbits was based upon data obtained by studying the spectra of the light and other forms of radiant energy which atoms emit when they are made luminous by heat, by electrical discharges, or by other methods. We turn our attention at this time, therefore, to a brief discussion of *spectra*.

5. Spectra

Light and other forms of radiant energy can be considered as energy propagated through space as waves, somewhat like the waves produced in a body of water by a falling stone or some other object. Water waves consist of series of crests and troughs, and the waves travel from their origins in ever widening circles. We may think of light and X-rays as somewhat similar waves, which travel out through space in an expanding spherical shell. These waves may be considered as having crests and troughs. The distance between two successive crests is a wave-length. These wave-lengths differ for the different kinds of radiant energy — light, ultra violet and infra red light, X-rays, gamma rays, and radio rays. Thus, X-rays are composed of very short waves, while radio waves are very long in comparison to those of visible light. The frequency of the radiation (light) is defined as the velocity in centimeters per second divided by the wave-length in centimeters. The frequency is higher, therefore, the shorter the wave-length.[1]

Ordinary, or white, light is made up of all the different colors — red, orange, yellow, green, blue, and violet. Each of these colors consists of different wave-lengths, those of violet light being the shortest and those of red longest. When the beam of

[1] We cannot describe completely the nature of light and similar radiations and the theories concerning them in this book. Although light can in certain respects be considered as wave-motions, it must also be considered, if all of its properties are to be accounted for, as having some of the properties of particles called *photons* or *quanta*.

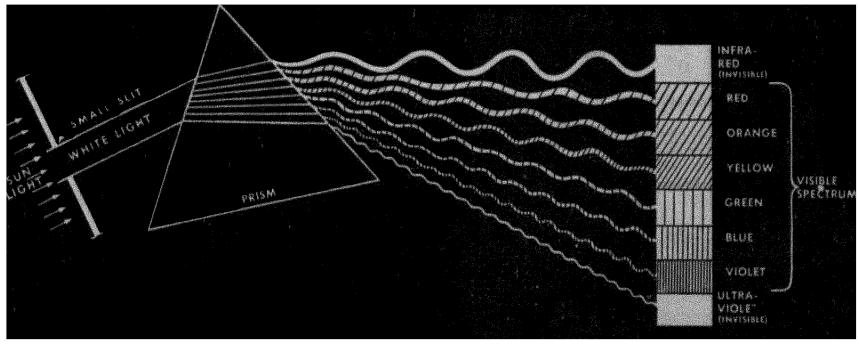


Figure 97. Formation of a Spectrum by Refraction of White Light with a Prism

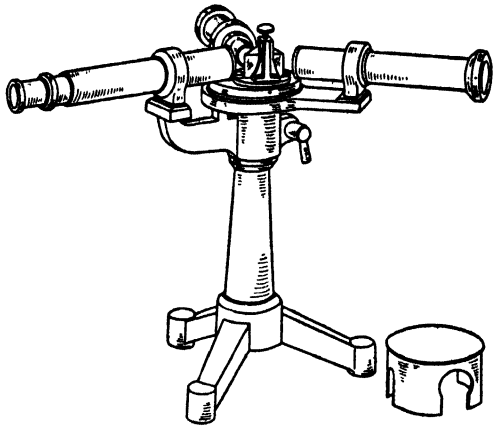


Figure 98. A Spectroscope
(Courtesy of the Arthur H. Thomas Company)

light is passed through a prism (Figure 97), each kind of wave is bent or *refracted* in a definite manner, and the different waves are refracted to different extents. Red light is refracted least and violet most.

In the *spectroscope* (Figure 99), the beam of light enters the instrument through a narrow slit. After refraction by a prism, the different colors of light give numerous images of this slit, when they fall upon a screen. Or if we substitute an eyepiece (*B*) for the screen the different images of the slit appear to the eye as bright lines on a dark field. We speak, therefore, of the *lines* of the spectrum; each line corresponds to a different wave-length or frequency. The spectroscope usually has another tube (*C*), containing a scale, which is projected upon the prism, and which is observed when one looks through the eye-piece. The different lines of the spectrum are scattered out along this scale. If the same scale is used for all spectra and if it is fixed in position, any line in any spectrum can be identified by its location on the scale.

Visible light comprises only a small part of the complete spectrum, which includes all wave-lengths of X-rays, gamma rays, ultraviolet and infrared radiation, and radio waves (Figure 100).

6. Emission Spectra

White light gives a continuous spectrum — one made up of all colors or wave-lengths of visible light. Discontinuous spectra are obtained from the light emitted when salts of the metals are volatilized in a flame, or when different gases are subjected to an electrical discharge under low pressures. The light from such sources is resolved by the spectroscope into spectra that contain only certain bright lines. These lines are characteristic of the elements in the substances that serve as the source of light. It is possible, therefore, to identify an element by means of the spectrum of the light which it emits when it is made luminous.

The common method of causing the metals to emit light, so that their spectra may be produced, consists of heating small quantities of their salts (usually the chlorides because these as a rule are most volatile) on a platinum wire in the flame of a

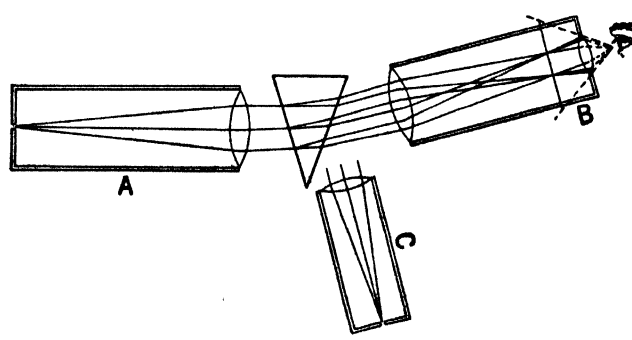


Figure 99. The Essential Parts of a Spectroscope

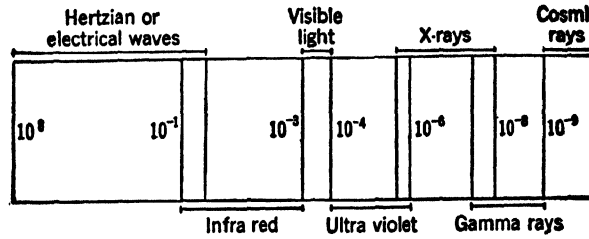


Figure 100. The Complete Spectrum
Numbers refer to wave-lengths (in mm.).

Bunsen burner. The burner is placed before the spectroscope in a position so that the light from the flame will pass through the slit. The beam of light selected by the slit is refracted by the prism; and the spectrum is observed through the eyepiece. To secure the higher temperatures sometimes required to volatilize certain substances the electric arc may be used.

Gases are usually made luminous by discharging electricity through glass tubes in which the gases are held under a pressure of about 1 mm. The central portion of the tube is usually constricted until it is of capillary dimensions (Figure 101). The tube is placed before the spectroscope, and the light emitted by the gas in the capillary portion of the tube is passed through the slit.

7. Absorption Spectra

If a transparent substance, either in the gaseous state or in a solution, is placed between the slit of the spectroscope and some source of white light, an *absorption* spectrum can be obtained. Instead of a continuous spectrum, certain brightly colored lines, depending upon the nature of the absorbing medium, fail to appear and are represented by black lines, because the wave-lengths corresponding to them are absorbed and, therefore, no light reaches these points. The positions of the black lines in the absorption spectrum correspond exactly to the bright lines of the spectrum that the same substance produces when it is made to emit light. Thus, certain black lines appear when the light from the sun is analyzed. These are called *Fraunhofer* lines; they are caused by the absorption of certain waves by the gaseous substances contained in the sun's atmosphere. By studying these absorption lines it has been possible to identify the elements producing them and, hence, the character of the atmosphere surrounding the sun.

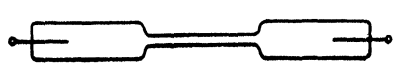


Figure 101. A Plücker Tube

8. The Hydrogen Spectrum and Bohr's Interpretation

When hydrogen is made luminous, the light that its atoms emit can be resolved into different wave-lengths. This gives the hydrogen spectrum. Bohr observed that this spectrum consists of certain well-defined series of lines. The lines of one series, for example, may be in the range of visible light, while those of another series may be in the invisible ultra-violet.

Bohr interpreted these observations as meaning that the lines of any one series are due to transitions of electrons (in different hydrogen atoms) from different energy levels to some one level near the nucleus. Thus, there would be a series of lines produced by shifts of electrons to the first level from the second, third, fourth, fifth, and higher levels, each possible transition corresponding to a definite line or wave-length. Shifts to the second level from the third and higher levels would give

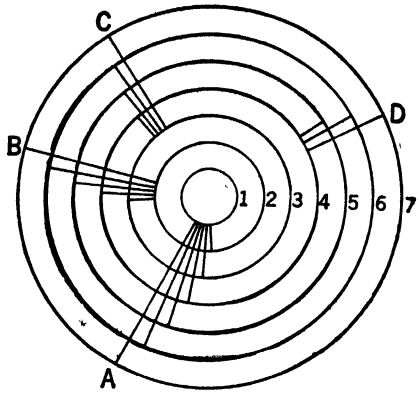


Figure 102. The Different Orbits in Which the Electron of the Hydrogen Atom Can Rotate

Depending upon its energy, the electron rotates in different orbits. Its normal orbit is the first.

a second series of lines, and so on. Since a great many hydrogen atoms are present, all the possible changes and their corresponding radiations are observed. The complete spectrum of hydrogen as now known consists of four series of several lines each. The origin of the radiations that are responsible for the wave-lengths that the lines of these different series represent is shown in Figure 102.

Bohr's theory explained the spectrum of hydrogen very satisfactorily. However, although it was considerably modified, it was not equally effective in dealing with atoms containing more than one electron. We cannot determine the exact positions that the electron occupies at different times. Instead we have come to look upon the location of an electron at any particular instant as uncertain. The electron has been found to act in such a manner that it can be dealt with theoretically as a wave. As a result there has been developed a new system of mechanics that is used in explaining the behavior of electrons and atomic systems and which is called *wave mechanics*. The electron of the hydrogen atom, instead of moving around the nucleus in a definite orbit, is probably moving very rapidly throughout all the space extending about 0.00000001 cm. from the nucleus. By wave mechanics it is possible to calculate the most probable position, within this space, at which the electron is located. This most probable distance of the electron from the nucleus has been found to be approximately the same as the radius of the orbit calculated by Bohr's theory (Figures 102 and 103). With this understanding, therefore, we shall proceed in our discussion by continuing to speak of electrons as occupying different shells around the nucleus. The shells correspond to the different regions of the greatest probability of the electron's occurrence.

9. The Structures of the Inert Gases

The numbers of electrons in the atoms of the inert gases are evidently the numbers that are required to produce very stable arrangements, because these atoms are very stable. None of their electrons can be removed without difficulty, and the atoms do not react by gaining, losing, or sharing any of the electrons that they have. If the helium atom contains two electrons in the first group, the neon atom must contain eight in the second group, because its atomic number and, therefore, its total number of electrons is ten. Since the other inert gases are very similar to neon, we may reason that they also contain eight electrons in the outermost groups of their atoms. If this is true, then it appears that the arrangement of electrons in the differ-

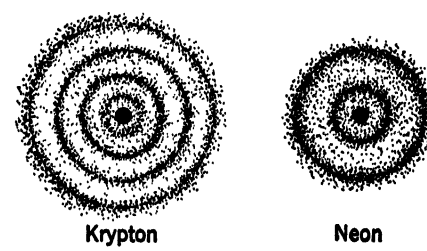


Figure 103. Distribution of Electrons in Atoms of Krypton and Neon

Circles where dots are thickest represent regions of most probable location of electrons. They correspond to different shells.

ent groups of their atoms is, likely, as follows:

Helium	2					
Neon	2	8				
Argon	2	8	8			
Krypton	1	8	18	8		
Xenon	2	8	18	18	8	
Radon	2	8	18	32	18	8

This plan gives us a general scheme of arrangement, a skeleton so to speak, that we can use in predicting the numbers of electrons in the different groups of the atoms of other elements, as, for example, those that lie between neon and argon.

10. Distribution of Electrons in the Different Shells of Atoms

We have discussed the numbers of electrons in the first three shells for the lighter elements (page 38). In Table 3 the distribution is shown for the first eighty-six of the elements.

After argon (2-8-8) the first two electrons go into the fourth level (K, 2-8-8-1 and Ca, 2-8-8-2). From scandium to copper, however, the additional electrons are used to complete the third group, which is not filled until it contains eighteen electrons (Sc, 2-8-9-2; Cu, 2-8-18-1). For the next elements (zinc to bromine) electrons are added to those already present in the fourth

TABLE 3

DISTRIBUTION OF ELECTRONS IN ATOMS

Period	Electron Shells	Periodic Groups																
		1 a	2 a	3 b	4 b	5 b	6 b	7 b	8			1 b	2 b	3 a	4 a	5 a	6 a	7 a	0
1	1	H 1																	He 2
2	1	Li 2	Be 2											B 2	C 2	N 2	O 2	F 2	Ne
	2	1	2											3	4	5	6	7	8
3	1	Na 2	Mg 2											Al 2	Si 2	P 2	S 2	Cl 2	A 2
	2	8	8											8	8	8	8	8	8
	3	1	2											3	4	5	6	7	8
4	1	K 2	Ca 2	Sc 2	Ti 2	V 2	Cr 2	Mn 2	Fe 2	Co 2	Ni 2	Cu 2	Zn 2	Ga 2	Ge 2	As 2	Se 2	Br 2	Kr 2
	2	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	8	8	9	10	11	13	13	14	15	16	18	18	18	18	18	18	18	18
	4	1	2	2	2	2	1	2	2	2	2	1	2	3	4	5	6	7	8
5	1	Rb 2	Sr 2	Y 2	Zr 2	Cb 2	Mo 2	Tc 2	Ru 2	Rh 2	Pd 2	Ag 2	Cd 2	In 2	Sn 2	Sb 2	Te 2	I 2	Xe 2
	2	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
	4	8	8	9	10	12	13	14	15	16	18	18	18	18	18	18	18	18	18
	5	1	2	2	2	1	1	1	1	1		1	2	3	4	5	6	7	8
6	1	Cs 2	Ba 2	La* 2	Hf 2	Ta 2	W 2	Re 2	Os 2	Ir 2	Pt 2	Au 2	Hg 2	Tl 2	Pb 2	Bi 2	Po 2	At 2	Rn 2
	2	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
	3	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
	4	18	18	18	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32
	5	8	8	9	10	11	12	13	14	15	16	18	18	18	18	18	18	18	18
	6	1	2	2	2	2	2	2	2	2	2	1	2	3	4	5	6	7	8

* Between lanthanum and hafnium there are fourteen elements in which the fourth shell is built up from 18 electrons to 32. For elements 87 to 98 (not shown in the table) the first two electrons enter shell 7 and then shell 5 is built up from 18 to 27 electrons (in californium).

group, until in bromine this group like the corresponding groups in fluorine and chlorine contains seven electrons (Zn, 2–8–18–2; Br, 2–8–18–7).

In krypton the fourth group contains eight electrons; and hence, the next two that are added go into the fifth level (Rb, 2–8–18–8–1; Sr, 2–8–18–8–2). For the next elements (yttrium to silver) the electrons that are added go to build up the fourth group from eight to eighteen (Y, 2–8–18–9–2; Ag, 2–8–18–18–1; Cd, 2–8–18–18–2). The fifth group is then built up until it contains seven electrons in iodine and eight in xenon (I, 2–8–18–18–7; Xe, 2–8–18–18–8). In the next two elements (cesium and barium) the two electrons that are added go into the sixth group (Cs, 2–8–18–18–8–1; Ba, 2–8–18–18–8–2). In lanthanum an electron is added to the fifth group (La, 2–8–18–18–9–2) and then from cerium to lutecium the fourth level is built up from eighteen to thirty-two (Ce, 2–8–18–19–9–2; Lu, 2–8–18–32–9–2). The fourth group is now completely filled. From hafnium to gold the electrons that are added build up the number in the fifth group to eighteen (Au, 2–8–18–32–18–1). The sixth group is then built up until it contains seven in element 85 and eight in radon (85, 2–8–18–32–18–7; Rn, 2–8–18–32–18–8): the next two electrons enter the seventh shell, and in the remaining elements the fifth shell is built up from 18 to 27 electrons.

Table 3 shows clearly that the atoms of elements having similar properties have, in general, the same electron arrangements or configurations. Especially is this true for the two outer shells of the atoms.

Table 3 is really a periodic arrangement of the elements similar to the Periodic Table on page 116, except the *A* and *B* series of elements have been placed in different columns, group 8 has been placed in the middle of the table, and the zero group has been placed on the right hand side of the table. This table shows clearly that the positions of the elements in the Periodic Table are determined by the distribution of electrons in the shells of the atoms.

In each long series the first two electrons enter a new shell on the outside of the atom. The next electrons, however, enter some unfilled lower shell. This may be explained as follows. Each electron that is added to the atomic structure enters the shell in which it will possess the lowest possible energy. For the first two electrons, therefore, it appears that the energy they possess will be less in a new, outershell than it would be if they enter a lower, unfilled shell. This must not be true, however, for more than the first two electrons, because the next that are added go invariably into a lower shell as we might expect.

11. Ionization Potentials of the Elements

The ionization potential of an element represents the strength of the electric field in volts per centimeter required to remove the most loosely bound electron from an

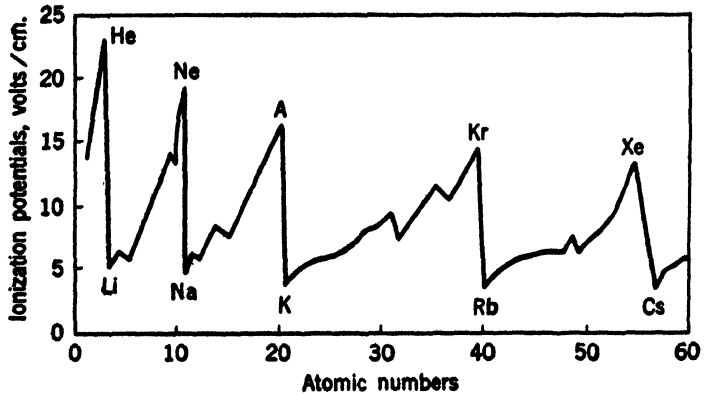


Figure 104. The Ionization Potentials of the Elements in their Gaseous States

atom of the element in its gaseous state. The ionization potentials of most of the elements are shown in Figure 104. It will be noted that the potentials required to remove one electron from an atom of each of the inert gases are relatively very high, and that it is small for each element that follows an inert gas in the order of atomic numbers. Thus, the potentials of lithium and sodium are both about five volts, while for helium and neon they are 20–25 volts. Beginning with lithium the voltage required to remove an electron from an atom increases gradually until it reaches a maximum again for neon. There is a sudden decrease at this point to another minimum potential for sodium, and this is followed by another series of increases until argon is reached. For potassium the potential again drops to a minimum, somewhat below the ionization potential for sodium. From calcium to zinc there is only a slight change in the potential, but from zinc to krypton there is another series of gradual increases, with another maximum for krypton, followed by another sudden drop to a minimum for rubidium.

The ionization potentials of the elements, therefore, support in every way the arrangement of electrons that we have previously described. The energy required to remove an electron from an atom depends upon the nuclear charge, and as the charge increases, for example from lithium to neon, the ionizing potential increases. Another factor enters the picture and dominates the situation in the case of sodium. The nuclear charge is greater than for any of the elements from lithium to neon, but the electron is far easier to remove; and hence, we must conclude that in the atom of sodium the electron that is removed must be one that is farther from the nucleus than any of the electrons in atoms of elements below sodium. It is evident, therefore, that all of the electrons that are added one by one in the atoms of the elements from lithium to neon are approximately equally distant from the nucleus. This group must, consequently, contain eight electrons.

TABLE 4

RADII OF ATOMS AND IONS

In Angstrom units. One unit equals one hundred-millionth of one centimeter.

Element	Atomic radius	Ionic radius
Hydrogen	0.37	1.36, H^-
Lithium	1.50	0.68, Li^+
Beryllium	1.112	0.39, Be^{++}
Boron	0.7	0.24, B^{+++}
Carbon	0.77	——
Nitrogen	0.53	1.71, $N^{=}$
Oxygen	——	1.40, $O^{=}$
Fluorine	0.68	1.33, F^-
Neon	1.60	——
Sodium	1.86	0.98, Na^+
Magnesium	1.595	0.71, Mg^{++}
Aluminum	1.48	0.55, Al^{+++}
Silicon	1.172	0.44, Si^{++++}
Phosphorus	1.08	2.12, $P^{=}$
Sulfur	1.06	1.85, $S^{=}$
Chlorine	0.97	1.81, Cl^-
Argon	1.91	——
Potassium	2.27	1.33, K^+
Calcium	1.97	0.98, Ca^{++}
Titanium	1.45	0.62, Ti^{++++}
Vanadium	1.313	0.59, V^{+++++}
Chromium	1.246	0.65, Cr^{+++}
Manganese	1.24	0.91, Mn^{++}
Iron	1.238	0.83, Fe^{++}
Cobalt	1.25	0.82, Co^{++}
Nickel	1.24	0.78, Ni^{++}
Copper	1.275	0.96, Cu^+
Zinc	1.33	0.74, Zn^{++}
Gallium	1.22	0.62, Ga^{+++}
Germanium	1.22	0.53, Ge^{++++}
Arsenic	1.25	2.22, $As^{=}$
Selenium	1.16	1.96, $Se^{=}$
Bromine	1.13	1.96, Br^-
Krypton	2.0	——
Rubidium	2.43	1.48, Rb^+
Strontium	2.14	1.15, Sr^{++}
Iodine	1.35	2.19, I^-
Xenon	2.2	——
Cesium	2.62	1.67, Cs^+
Barium	2.17	1.31, Ba^{++}

By similar reasoning we can determine the numbers of electrons in other groups. It is also possible to obtain additional, useful information that assists us in this matter by measuring the ionization potentials required to remove another electron, and even two or three more electrons, from the atom after the first step in the ionization has been completed by removing the most loosely bound electron.

12. Atomic Radii

The sizes of atoms, as measured by the radii of the atoms, also provide us with information that is helpful. As more electron-groups appear in the atom, we may expect that the atomic radius will also increase as each new group is added. For those atoms, as from lithium to fluorine in the order of atomic numbers, in which all the electrons that are added go into the same group, we may expect the size of the atom to decrease as the nuclear charge increases, and, therefore, pulls the electrons around it closer to itself.

Note that the sudden increases in atomic radius occur in lithium, sodium, potassium, rubidium, and cesium (Table 4) in which, as we have already assumed, the additional electron moves into a new and larger group, thus adding length to the atom's radius as compared to the atom of the inert element with the next lower atomic number. Note, also, that as the atomic radius increases from lithium to cesium, the ionization potential (Figure 104) decreases. This difference is in accord with the expectation that an electron on the outside of a large atom should be more easily removed than an electron of a smaller atom. The calculations of ionic and atomic radii have been made from data obtained in the study of X-ray diffraction by crystals.

ATOMIC NUMBERS

13. X-Rays

In 1914, Moseley found an important relationship between the atomic number of an element and the wave-lengths of the X-rays which are emitted when that element, or one of its compounds, is placed on the anticathode, or target, of an X-ray tube. These rays are produced when electrons streaming off of the cathode (−) in the evacuated tube strike any obstructing form of matter. The usual obstruction in a tube made to produce X-rays is a metallic plate called the anticathode. The rays produced in this manner are not all alike. They differ in the same manner as the components of visible light — red, orange, yellow, green, blue, indigo, and violet. It should be possible, therefore, to produce a spectrum of X-rays similar to that produced by resolving a beam of light by means of the spectroscope (page 152), if a suitable device can be found.

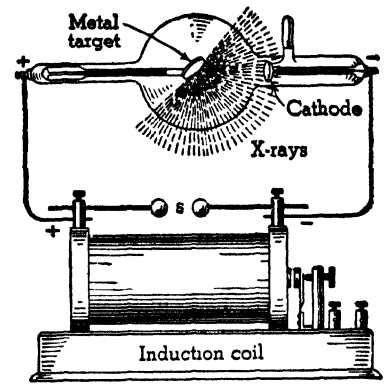


Figure 105. X-Ray Tube

14. Diffraction

Moseley selected a narrow band of X-rays by means of a slit in a box made of sheets of lead and enclosing the tube. This small band or pencil of rays was allowed to fall upon a face of a crystal, which separated the different wave-lengths of the beam of X-rays in the same manner that a diffraction grating separates the different wave-lengths, or colors, in a beam of light.

The grating consists of very closely ruled

parallel lines on a glass plate. These lines break up a beam of light that is passed through the plate into its constituent colors, or wave-lengths, thus producing a *spectrum.* To produce a spectrum, however, the lines of the grating must be spaced so that the distances between them are of the same order of magnitude as the lengths of the light waves.

A grating does not diffract X-rays because the wave-lengths are so small that even the most closely ruled lines that can be made on a glass plate are still so far apart, as compared to the size of an X-ray's wave-length, that X-rays can pass through the slits without suffering any more effect than ordinary light does when it passes through the open spaces in a picket fence.

In 1912, Friedrich and Kipping, at the suggestion of von Laue, found that a crystal can be used to diffract, or break up, a beam of X-rays into its different wave-lengths in the same manner that a ruled grating diffracts visible light. The ions, atoms, or other particles of which crystals are composed are arranged in definite planes and lines, which correspond to the lines that are ruled on a plate of glass in a grating.

The different sets of parallel, atom-bearing planes diffract a definite wave-length and cause it to strike at different positions on the screen or photographic plate (page 172) when the beam is passed through the crystal. X-rays of different wave-lengths will be diffracted by the same set of planes to different extents, thus resolving the beam into its different parts and producing a spectrum.

The apparatus used by Moseley is shown in Figure 106. A beam of X-rays is allowed to fall upon a face of a crystal *C*, which is held in a fixed position on a plate, which can be rotated about a point at the center of the crystal *C*. The X-rays pass through the surface of the crystal and penetrate through a few layers or planes of atoms, or ions, by which the rays are diffracted. The diffracted rays leave the crystal at definite angles in much the same manner as light rays are reflected by a plane mirror, and, hence, it is frequently said that the crystal "reflects" the X-rays but this is not quite true. Each plane of atoms affects the beam just as a beam of light is affected by the slit between each two lines of a grating. The rays, after being diffracted, from all the planes of the crystal that affect them, leave the crystal, and along the lines *BB* (Figure 107), where the angle with the surface of the crystal has a certain value, all the diffracted rays of the same wave-length

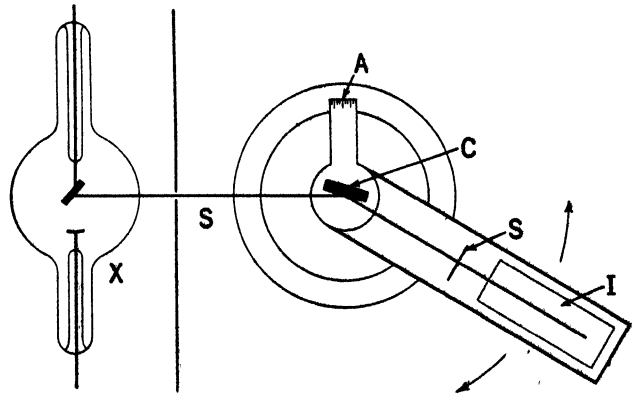


Figure 106. Apparatus Used to Study the Structures of Crystals by Means of X-Rays

The X-rays are produced in the tube X, pass through the slit S, and fall upon the crystal C. Here they are reflected by planes of atoms. The direction of the reflection is found by moving I through the arc of a circle around C. When it is in the correct position the reflected beam of X-rays enters I and ionizes the gas that it contains. The angle of reflection is then read on scale A.

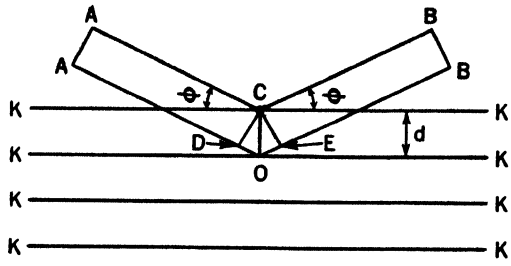


Figure 107. The Reflection of X-Rays by Planes of Particles in a Crystal

AC, the incident radiations; CB, the reflected radiation; K–K, cross-section through one set of planes of particles.

will reinforce one another; i.e., at points along the line *BB* they will meet crest to crest and trough to trough. If a suitable measuring device is set up at this angle, therefore, it will register a high intensity of X-rays. The measuring device used by Moseley consisted of a chamber *I* filled with some gaseous substance that was easily ionized. When X-rays entered the chamber, molecules of the gas were converted into ions, which caused a slight flow of current through a circuit connected with two opposite walls of the chamber. (The electrical circuit is not shown in Figure 106.) Whenever *C* was moved into a position which produced a maximum degree of ionization, as shown by the flow of current, it was known that at this angle (between the crystal's surface and the direction of the diffracted rays) reinforcement of the rays occurred, or in other words, this was



Figure 108. Equipment Used in Determining the Structure of Crystalline Compounds by the Use of X-Rays
(Courtesy of Merck and Company)

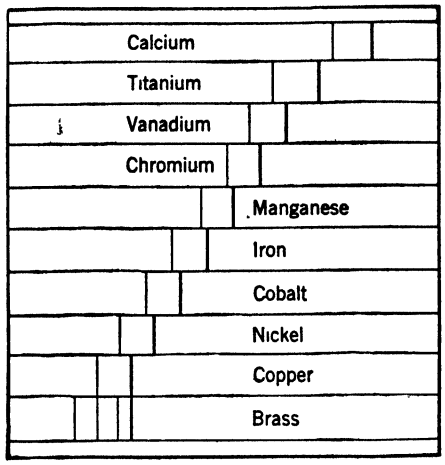


Figure 109. X-Ray Spectra Showing the Decrease in Wave-Length (toward the left) as the Atomic Numbers of the Elements Increase

the angle of "reflection." This angle could be read on the scale A. It depended upon the wave-length of the X-rays, and upon the distance between two successive layers, or planes, of atoms in the crystal. The angle of "reflection" was different for each wave-length of which the beam of X-rays was composed. By measuring the angles at which highly intensified "reflection" could be detected, and, knowing the distance between successive layers of atoms in the crystal, it was possible to determine the different wave-lengths composing the beam. These made up what Moseley called an X-ray spectrum.

15. Atomic Numbers Determined from the X-ray Spectra of the Elements

Moseley analyzed the X-rays emitted when different elements are bombarded by rapidly moving cathode-ray particles in an X-ray tube. He found that the spectra of the elements showed a continuous band of spectral lines, the shorter wave-lengths of which varied with the speed of the electrons that produced the X-rays by striking the target of the X-ray tube. In addition, however, it was found that similar lines, or pairs of lines appeared in the spectra of the X-rays produced by successive elements, as these are studied in the order in which they occur in the periodic table. The wave-lengths, or frequencies, of these characteristic lines, however, are found to vary in a regular fashion from one element to the next (Figure 109).

There is no definite relationship between the spectra of the elements and atomic weights, but when the square root of the frequency of a characteristic line — as, for example, the line represented by heavy shading in Figure 109 — is plotted against the atomic numbers of the elements, an almost straight line (Figure 110) shows that the X-rays emitted by an element depend upon the atomic number of the element rather than upon the atomic weight. If the wave-length, or frequency, of this line can be determined for an element, then the atomic number of that element can be determined directly from the curve. This method has been employed in the search for missing elements and has led to the discovery of some of them.

16. Atomic Numbers and the Periodic System

The classification of the elements in the order of their atomic numbers, as deter-

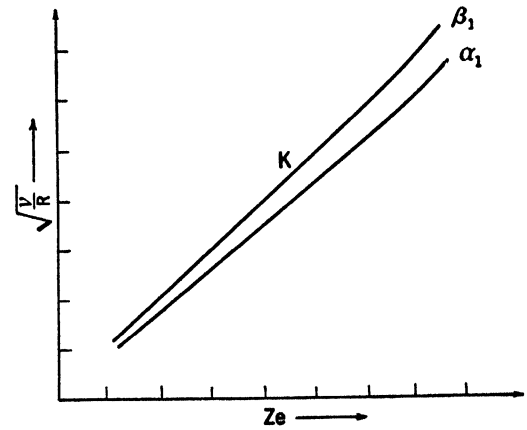


Figure 110. The Relation Between the Frequency of X-Ray Spectral Lines and the Atomic Numbers (Ze) of the Elements that Produce the X-Rays

The frequencies plotted in this figure are those of the alpha and beta lines of a series (K) in the X-ray spectrum. The greater the frequency, the shorter the wave-length.

mined by Moseley's method, has certain advantages over the classification based upon atomic weights. In the first place no exceptions, such as were made in the positions of argon and potassium in Mendeleeff's table, have to be made. In the second place, the number of elements that must be located in the Periodic Table can be fixed definitely; there can be only 98 elements between hydrogen and californium, inclusive.

The isotopes of an element have the same atomic number and very nearly identical properties. However, they have different atomic weights. Moreover, some isotopes of *different* elements may have the same atomic weights but different atomic numbers and, of course, decidedly different properties. For example, one of the isotopes of xenon, an inert gas, has the same atomic weight (130) as one of the isotopes of tellurium, an element somewhat like sulfur. All of these facts indicate that the Periodic Law (page 154) should be changed to state: *The properties of an element are a periodic function, not of the element's atomic weight, but of its atomic number.* When we consider the Periodic Table upon the basis of this statement the reasons that determine its different features become apparent. The breaks in the table, the different periods of elements, the occurrences of similar elements in the same vertical rows, the short periods and the long periods, and gradual changes in properties among the elements of the same period — all these conditions can be interpreted with at least a fair degree of satisfaction if we view the differences existing between elements as the results of different atomic structures rather than as differences in atomic weights.

17. Oxidation Numbers and the Periodic Table

The characteristic oxidation numbers of the elements in the different groups of the Periodic Table are shown in Figure 111. It

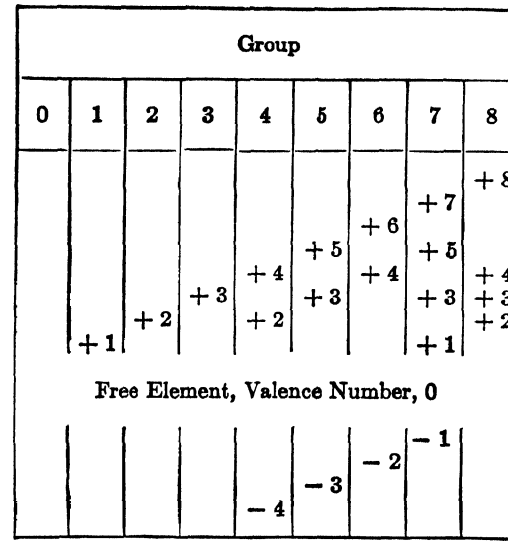


Figure 111. Oxidation Numbers in the Periodic Table

The numbers shown are those that are most prominent for the elements of each group. Not all oxidation numbers for all the elements of any group are shown.

should be remembered that all of the numbers of some of the elements are not shown in this tabulation. For example, copper in group one has a number of + 2, and mercury in group two has a number of + 1. Furthermore, some of the elements in a group may not have all of the oxidation numbers that are characteristic of that group. For example, the *B* elements of groups six and seven — chromium and manganese, for example — do not have any negative numbers.

18. Differences Among the Elements of a Family

The elements belonging to the two families of the same group differ, of course, considerably, as may be seen by comparing the lithium, sodium, potassium, rubidium and cesium family in group one with the family of copper, silver, and gold in the same group. Within a family there are also progressive changes in properties from the member at the top of the table to the one at the bottom. These changes are not as

sharp as those within a period — from left to right — in which the elements change from very active metals on the left to typical non-metallic elements on the right. Within a family, the valence of all the members is identical or nearly so. There is, however, a tendency for metallic properties to become more pronounced with increasing atomic weight. Thus, cesium (if we neglect number 87) is the most active metal in group one. Similarly, bismuth in group five (*B*) is much more metallic in character than the other elements of this family. Iodine, in group seven, although a typical non-metal, is the least active of the halogens and, in some respects, differs much less from the metals than fluorine, chlorine, and bromine.

Upon the basis of the structures of their atoms these differences in the properties of the elements of a family are readily explained. Cesium, for example, has larger atoms than sodium (see atomic radii, page 157); and hence, the single electron in the valence shell of the cesium atom is more easily removed than the electron of the sodium atom, because it is farther away from the nucleus and is held less firmly. It must be noted, however, that the nuclear charge of cesium is greater than that of sodium but, evidently, this difference is more than balanced by the difference in atomic radii. Cesium, therefore, is more active than sodium in reacting with chlorine and other elements the atoms of which can acquire electrons.

On the other hand, fluorine and chlorine are more active than iodine because their atoms are smaller than iodine atoms. The small atom of fluorine, for example, attracts the electron which it needs to complete its outermost shell very strongly and holds it very firmly, because this shell is close to the nucleus. In the iodine atom it is relatively far away from the nucleus and is held less firmly. When the atoms have acquired an electron and have become negatively charged ions, F^-, Cl^-, I^-, the iodide ion parts with its additional electron rather easily and, therefore, is readily oxidized back to the free element. The fluoride and chloride ions are more difficult to oxidize, because the electrons that they have acquired are more firmly held. Similarly, the elements of the nitrogen family (nitrogen to bismuth) become more like the metals as the atomic weight and atomic number increase, because in the larger atoms, e.g., bismuth, the electrons are held less firmly; and hence, electrons are more easily removed, thus causing the atoms to give up at least some of their valence electrons and to act as metals do in forming positively charged ions, such as Bi^{+++} and Sb^{+++}. The other elements of this family do not form such ions; they form compounds by sharing electrons.

19. Another Form of the Periodic Table

A somewhat different arrangement of the elements to show their periodic classification will be found on the inside of the back cover. As compared to Mendeleeff's table (page 116) the principal difference in the arrangement is that each of the long periods has been placed in a single row across the table. This arrangement places each family of elements in a different column. We have also placed the inert gases of the zero group on the right-hand side next to the non-metallic elements of group seven.

20. The Transition Elements

In each of the long periods of the Periodic Table the first elements (on the left) are metals, and those at the end (on the right) of the period are non-metals. Between these two groups there is a series of elements which, in general, have some of the characteristics, chemically speaking, of the metals and some characteristics of the non-metals. In the atoms of these elements the number of electrons in the outside shell is the same and the successive electrons that are added as the atomic number increases go into a lower shell that is not yet filled. Thus, in the third period, this series of elements includes all those from scandium to copper inclusive. This series of elements, or any similar series in the other periods, is called a *transition* group.

The valence, or oxidation, numbers of many of these transition elements vary considerably. Since each of their atoms con-

tains two electrons in the outermost shell, we might expect each element of the series to form ions possessing two units of charge: Cr^{++}, Ni^{++}, Fe^{++}, Mn^{++}, and so on. They also form trivalent ions, such as Cr^{+++} and Fe^{+++}, by losing not only the two valence electrons on the outside but also one electron from the unfilled shell just underneath the valence shell. They also form many compounds in which they have still higher oxidation numbers, such as Na_2CrO_4, and $KMuO_4$, by sharing electrons.

Losses of electrons from an inside shell can occur only when that group is not stable, or filled; thus, in the sodium atom the group next to the one on the outside contains eight electrons and consequently does not lose any. The sodium atom, therefore, never has any valence number other than + 1.

21. Factors that Determine the Type of Bond

From left to right in one of the periods of the Periodic Table, the elements have increasingly greater ionization potentials and smaller atomic and ionic radii, because the atoms of successive elements have larger nuclei containing more protons which draw and hold closer to themselves the different electron-groups of the atom. Thus, the sodium atom of group one in the third period has little attraction for its single valence electron, and this electron is relatively far removed from the nucleus. Sodium, therefore, easily loses its valence electron to chlorine, for example, and thus forms sodium chloride, an ionic compound. Magnesium chloride, likewise, is ionic. In aluminum chloride, however, we find a compound which, in its pure state, displays many of the properties of covalent compounds. The high ionization potential of aluminum, and its small atomic radius, as compared with sodium, would lead us to expect that the atom of aluminum would have considerable attraction for electrons, and, evidently, this attraction is sufficiently strong to cause aluminum to share electrons with chlorine instead of giving them up completely. In carbon tetrachloride, CCl_4, the positive charge of the nucleus is still greater, the atomic radius still smaller, and the tendency to yield electrons to chlorine still weaker for carbon than it is for aluminum. Although the aluminum ion, Al^{+++}, is formed and does exist as a hydrated ion — combined with molecules of water — in aqueous solutions, the carbon ion, C^{++++}, is unknown.

We see, therefore, that the type of bond — ionic or covalent — that the atoms of an element are likely to form depends upon the energy, as measured by the ionization potential, required to remove electrons from the atoms. This energy, in turn, depends upon the size of the atom, as measured by the atomic radius, and upon the magnitude of the positive charge of the nucleus. For metals ionic bonds are favored by large atomic radii and small nuclear charges. The atoms of the non-metals are more likely to form ionic bonds when their radii are small, and the charge of the nucleus is large. Hence, we might expect lithium to form ionic bonds with chlorine, whereas phosphorus or carbon would form covalent bonds with the same element.

22. The Stability of Compounds

The stability of compounds containing two elements — as measured by the energy required to liberate the elements — depends in large part upon the sizes of the atoms and the ionization potentials of the elements. In general, the stability is greatest for those compounds in which the ionization potential of the more metallic of the two elements is smallest, and the atomic radius of the more non-metallic element is smallest. On the basis of this principle we would expect, therefore, potassium to form a more stable chloride than sodium; sodium chloride to be more stable than sodium

iodide; the oxide of copper, CuO or Cu_2O, to be more stable than the oxide of silver, Ag_2O; and the oxide of zinc, ZnO, to be more stable than the oxide of mercury, HgO. In drawing such conclusions we must also consider, however, the size of the atoms and ions of the metallic elements, a factor that has an important bearing upon how closely charged atoms of the compound can approach and, therefore, how firmly they will be held together in the compound. The attraction between two electrically and oppositely charged bodies varies inversely with the square of the distance that separates them.

Let us also consider the stability of certain compounds of hydrogen. Of the halogens, fluorine to iodine in group seven, fluorine has the smallest atomic radius and iodine the greatest. Hence, fluorine attracts electrons most strongly, and hydrogen fluoride, HF, is very stable, because considerable energy is required to separate one of the shared electrons from fluorine, which must be done if the molecule of HF is to be divided into one atom of hydrogen and one of fluorine. The separation is more easily accomplished in hydrogen iodide, HI, because the large iodine atom does not exert a very firm hold upon the electrons that it shares with hydrogen. In the oxygen family the order of stability is H_2O, H_2S, H_2Se, H_2Te; and in the nitrogen family NH_3, PH_3, AsH_3, SbH_3, and BiH_3. Within a period of the table — lithium to fluorine, for example — the stability of the hydrogen compounds decreases from right to left, because this is the direction in which the atomic radius of the element combined with hydrogen increases: HF, H_2O, NH_3, CH_4; and HBr, H_2Se, and AsH_3.

Other factors have an influence upon the stability of compounds. For ionic compounds the quantity of charge per ion plays an important part, of course, in determining the attraction that the ions have for one another. The type of ion, i.e., the number of electrons in the outermost shell of the ion, is also an important factor. Several facts indicate that an ion in which there are 18 electrons in the outermost shell, e.g., silver, Ag^+, 2-8-18-18, has considerably greater attraction for electrons than an ion of about the same radius but with only 8 electrons in its outermost shell, e.g., potassium, K^+, 2-8-8. Atoms and ions like silver must have considerable attraction for electrons, because they share electrons in many compounds that they form. These ions seem also, to be able to approach negative ions, such as Br^- and Cl^-, more closely than Na^+ and K^+ ions can. Silver chloride and silver bromide are very slightly soluble in water which dissolves relatively large amounts of sodium and potassium chloride. This difference may be caused by the ability of silver ions to approach the negative ions very closely, thus forming tightly held groups of ions which are difficult for the solvent to separate.

23. The Chemical Behavior of Hydroxides

The hydroxide of an element X may participate in chemical reactions by dissociating to form X^+ and OH^- ions or to form H^+ and XO^- ions. The first of these behaviors is characteristic of the hydroxide bases, and the second of acids (page 123).

Theoretically, the hydroxide of chlorine, ClOH, might be expected to form Cl^+ and OH^- ions or H^+ and ClO^- ions. Actually, it does only the latter. On the other hand, sodium hydroxide, being an ionic compound, forms Na^+ and OH^- instead of H^+ and NaO^- ions.

The sizes of the ions are important factors in determining whether a hydroxide acts as a base or as an acid, i.e., of where in the compound the rupture is likely to occur. For the hydroxides of large ions, such as Na^+, K^+, Ca^{++}, and Ba^{++}, the break occurs between the metallic ion and the oxygen atom, because the large atom or ion has little attraction for electrons, and the oxygen atom is able to remove the valence electrons of the metal completely. The atom of chlorine, however, is smaller. It has as much or more attraction for the electrons that it shares with oxygen than oxy-

gen has. Therefore, it is difficult to break the bond between chlorine and oxygen, and the chlorine atom is held relatively close to the oxygen atom. This sharing of electrons by chlorine and oxygen decreases the effective number of electrons of the oxygen atom, or increases the effective positive charge of that atom; in other words, it makes the atom of oxygen less ready and able to share electrons with hydrogen. Hence, the hydrogen ion, or proton, is more easily separated than it would be from OH^- alone, and, consequently, ClOH acts as an acid to form H^+ and ClO^- ions.

The hydroxides of certain elements — for example, beryllium, aluminum, and zinc — dissociate both as hydroxide-bases and as acids. Thus, zinc hydroxide forms Zn^{++} and OH^- ions and also H^+ and $ZnO_2^=$ ions. In these compounds the break in the bonds may come in either place, because there is little difference between the strengths of the bonds between O and H and the metal and O. These hydroxides are classified as *amphoteric* (page 123).

REVIEW EXERCISES

1. Describe the structure of an atom of hydrogen according to Bohr's theory.
2. What is the arrangement of electrons in each of the first nineteen elements of the periodic table?
3. Why do we believe that the maximum number of electrons in the first group of orbits is two and in the second, eight?
4. How does Bohr's theory of atomic structure explain the radiation of energy by an atom? How does this theory account for the fact that some of the radiation by atoms of hydrogen is in the region of visible light and some in the region of the ultraviolet?
5. What are the probable oxidation numbers of the elements: aluminum, sulfur, fluorine, calcium, and zinc?
6. What information concerning the atomic structures of different elements can be obtained from ionization potentials?
7. Define: The atomic number of an element; X-ray spectrum.
8. How did Moseley determine the atomic numbers of the elements?
9. In what ways is the periodic system based upon atomic numbers more satisfactory than that based upon atomic weights?
10. From their positions in the periodic table, predict the formulas of oxides of the following elements: Mo, W, Si, Sn, Sb, Te, and Ra.
11. Would you expect the chloride of sulfur to resemble NaCl more closely than it does CCl_4? Explain.
12. Which element, iodine or chlorine, should react more readily with sodium? Explain.
13. Which element, nitrogen or bismuth, should react more readily with chlorine? Explain.
14. From its position in the periodic table predict the properties of sulfur as compared to those of oxygen.
15. Of the three elements, calcium, strontium, and barium, which should occupy the highest position in the activity or electrochemical series? Explain.
16. What atomic weights would you predict for elements 85 and 87?
17. Would you expect tellurium and selenium to resemble sulfur more closely than they resemble chromium? Explain.
18. Upon the basis of the atomic numbers of the elements, their positions in the periodic table, and their atomic structures, explain
    (*a*) Why sodium has a valence number of + 1 and chlorine − 1.
    (*b*) Why cesium is a more active metal than sodium.
    (*c*) Why chlorine is a more active non-metal than iodine.
    (*d*) Why chlorine and manganese, both in group seven, are so very different in properties.
    (*e*) Why there are only seven elements between neon and argon in period 3 but seventeen between argon and krypton in period 4.
19. From its position in the Periodic Table, what properties would you predict for element 85?
20. What information concerning their chemical behavior is provided by the ionization poten-

tials and the atomic radii of the elements? Explain.

21. Of what is the ionization potential of an element a measure?
22. Why is aluminum chloride a covalent compound in its pure state while sodium chloride is ionic?
23. Why is chlorine a stronger or more active oxidizing agent than bromine or iodine?
24. Why is potassium a more active reducing agent than sodium?
25. Why should HI be less stable than HCl?
26. Beryllium hydroxide is amphoteric. Explain.
27. Why should potassium hydroxide act as a base while chlorine hydroxide reacts as an acid?
28. In what portion of the Periodic Table would you expect to find: (1) the most active metals; (2) the most active non-metals; and (3) compounds that form very stable compounds with hydrogen?

REFERENCES FOR FURTHER READING

See references at end of preceding chapter.

Periodic System: *J. Chem. Ed.*, **1,** 173 (1924); **2,** 85, 107, 381, 464 (1925); **3,** 542, 1059 (1926); **5,** 57 (1928); **8,** 2052 (1931); **9,** 1593, 1605, 1625 (1932); **11,** 27, 288 (1934); **12,** 265, 475 (1935); **14,** 232 (1939); **20,** 77 (1943); **21,** 25, 111 (1944); **27,** 17 (1950); *School Science and Mathematics*, **27,** 700 (1924); *Science*, **69,** 19 (1929); **80,** 512 (1934).

13

THE LIQUID AND SOLID STATES OF MATTER

1. Introduction

The liquids that we shall study are those that are composed, at least for the most part, of molecules. These are liquids such as water and alcohol. The physical properties of such liquids are of great importance to the chemist, especially when he uses them as solvents and as media for the reactions of many substances that he dissolves in them. In studying solids we shall be most concerned with the structures of crystals. This, too, is a matter of great interest to the chemist, because the properties and uses of many crystalline substances, such as diamond, graphite, quartz, and the metals and alloys, depend in large part upon the arrangement of atoms, molecules, or ions in their crystals.

PHYSICAL PROPERTIES OF LIQUIDS AND SOLIDS

2. Changes in the Volumes of Liquids with Changes in Temperature

The use of mercury and other liquids in thermometers depends upon the expansion and contraction of the volume of the liquid with changes in temperature. The volume of a definite quantity of a liquid, generally speaking, increases with rising temperature, but the change is much less than that of gases for the same rise in temperature and is only approximately uniform over a wide range of temperature. The volume of 1 g. of water, for example, actually decreases as its temperature rises from 0° to 4° C. Between 4° and 100°, the volume increases but the change in volume is not exactly uniform for increases of 1°.

3. The Changes in the Volumes of Solids with Changes in Temperature

The extent to which solids expand and contract in volume with changes in temperature is, generally speaking, less than that of liquids, and the changes like those of liquids are not uniform for different ranges of temperature. It is almost the universal rule, however, that expansion accompanies rising temperature. For solids the linear expansion that accompanies a rise in temperature, i.e., expansion in the direction of any one of the three dimensions of a solid, is sometimes of much greater significance than the expansion of the entire volume. Thus, allowances must be provided for the expansion and contraction of railroad rails, bridges, iron pipe lines, and concrete highways.

4. Density and Specific Gravity

The density of a liquid or of a solid is the weight of the substance per unit of volume, usually the weight in grams per cubic centimeter or milliliter. Since the volume usually increases as the temperature rises, the

density decreases, i.e., a larger number of cubic centimeters weigh the same number of grams, or each cubic centimeter weighs less. There are some exceptions to this behavior; for example, between 0° and 4° C., the density of water increases as the temperature rises, but above 4° it decreases in a fairly regular manner.

Convection currents are produced if the lower portion of a liquid is heated; the colder, heavier liquid above sinks, and the warmer, lighter liquid rises. This principle is applied in hot-water heating systems, and the same principle applied to gases is used in hot-air furnaces. It also explains the action of a draft in chimneys and many natural phenomena, such as cyclones, tornadoes, and winds.

The ratio of the density of a liquid or solid to that of water under certain specified conditions is called the *specific gravity* of the substance. For example, the specific gravity of ethyl alcohol when stated as $0.793^{25^\circ}_{4^\circ}$ refers to the weight of 1cc. of alcohol at 25° as compared with the weight of 1cc. of water at 4°.

5. Surface Tension of Liquids

The molecules that lie deep within the body of a liquid are attracted by other molecules that lie all around them. This attraction is the result of Van der Waals forces (page 89). Consequently, the attraction in each direction about each molecule is balanced by an equal attraction in an opposite direction (Figure 112). But there are no molecules of the liquid above those at the surface. Molecular attraction pulls these molecules back into the liquid, and the surface tends to become smaller. Hence, we speak of the *surface tension* of a liquid. As the result of the tendency of its surface to shrink, a small mass of liquid assumes a spherical shape, since a sphere has a smaller surface than any other form of the same weight of the substance.

The surface tension of a liquid decreases as the temperature rises. A decrease in surface tension corresponds to an increase in surface, and this change calls for the expenditure of energy, since more molecules must be separated from the particles in the body of the liquid. Therefore, this change, since it requires energy, will take place more readily when the temperature is raised, and the necessary heat-energy is supplied.

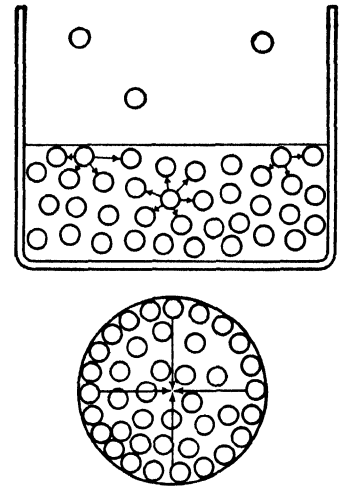


Figure 112

Diagrams showing the cause of surface tension and explaining why a small mass of a liquid takes a spherical form.

Since the molecular attraction is overcome entirely by the speed of the molecules at the critical temperature, the surface tension disappears entirely at this temperature. We may regard the critical temperature as the point at which the gas can be compressed to a volume of the same size as that which the liquid would occupy, without liquefaction resulting.

6. Viscosity

The molecules of a liquid exert attraction for one another; and hence, we should expect that there is within the liquid itself a certain resistance to the movement of molecules over and around one another, a movement usually designated as *flow*. This resist-

ance depends upon the forces of attraction among the molecules and is expressed in terms of the *viscosity* of the liquid. It is usually measured, in comparison with a standard liquid such as water, by the rate at which each liquid flows under constant pressure through a long capillary tube held in a vertical position.

The viscosities of water, alcohol, and ether are relatively small as compared with those of glycerine or lubricating oils. The former are mobile liquids, and the latter are highly viscous or less mobile. Viscosity is often an important property of liquids and even of gases. The viscosity of lubricating oils is a very important factor in determining their value, especially in automobile and airplane motors.

7. Other Physical Properties of Liquids and Solids

For some substances *color*, *odor*, and *taste* are important properties. *Thermal* and *electrical conductivity* may, occasionally, be properties of solids in which the chemist is interested. Liquids, like gases, *diffuse*, but at a very slow rate. Even solids diffuse one into another as has been demonstrated by clamping tightly together smoothly polished bars or blocks of two metals. After a long period of time, traces of one metal can be found in the other. This detection is very easy if one of the metals contains some of its radioactive isotopes.

Solid substances have definite fusion or melting temperatures, and liquids have equally definite freezing and boiling temperatures. All of these temperatures, however, vary for different conditions, especially for different pressures. Under a pressure of 760 mm. of the atmosphere above its surface, water boils at 100° C. At an elevation of 7000 feet, the boiling point is 93°, and at 30,000 feet it is about 70°. The effect of pressure upon the freezing point of water and the melting point of ice is well known to anyone who has made snowballs. The pressure produced by squeezing snow in the hands lowers the freezing point and causes some of the snow to melt. When the pressure is released, the freezing point rises once more to 0°, and the water freezes, cementing the snow or ice into a compact, hard ball.

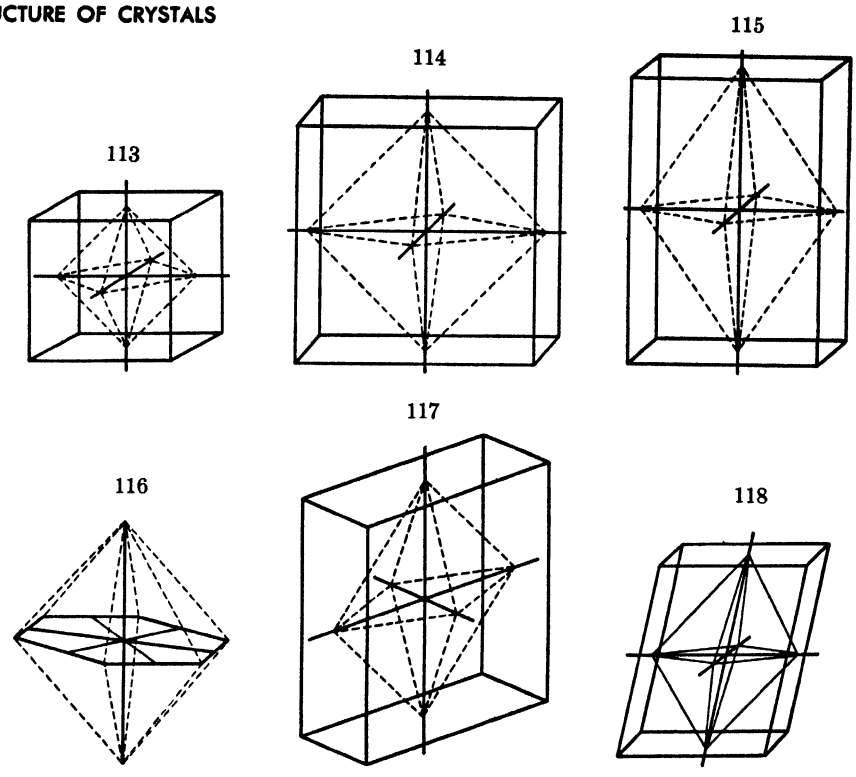
THE STRUCTURE OF CRYSTALS

8. The Forms of Crystals

Every crystal has a definite form which can be described in geometrical terms. It is bounded by plane surfaces called *faces*. These make characteristic angles with one another and are arranged in an orderly fashion with respect to certain lines which can be drawn through the crystal. These lines represent the crystal's *axes*. The axes of the crystal in Figure 113 are represented by the heavily shaded lines that are drawn perpendicularly to the faces of the cube.

Crystals are classified into six systems, depending upon the relative lengths and the arrangement of their axes. The six fundamental systems of crystals are shown in Figures 113–118. The system to which the crystals of a given substance belong is as characteristic of that substance as its other properties. The shape and appearance of the crystal may vary, but these variations do not mean that the fundamental crystalline character is different for different exterior forms. Sodium chloride, for example, may crystallize as cubes or as octahedra (Figure 113), but both of these forms belong to the regular system of crystals.

Different substances that crystallize in the same system and form crystals that have axes of the same relative lengths and inclined at the same angles are said to be *isomorphous*. On the other hand, the same substance does not always crystallize in the same system. Carbon, for example, crystallizes as diamond in the regular system and as graphite in the hexagonal system. Sulfur



Figures 113–118

The external forms of crystals depend upon the arrangement of atoms, ions, or molecules within the crystal. The six systems of crystal structure are shown above. In regular crystals (113), the axes (three lines drawn perpendicular to the faces and intersecting at the center of the cube) are equal in length and at right angles to one another. In the tetragonal system (114), the axes are all at right angles, but one axis is different in length from the other two. In the orthorhombic system (115), the axes are at right angles, but all are of different lengths. In the hexagonal system (116), three of the four axes are in one plane and make 60° angles with one another. The fourth axis is at right angles to these three. In the monoclinic system (117), the axes are of any relative lengths and one is inclined to the other two. In the triclinic system (118), three axes of any relative lengths are all inclined toward one another.

forms both monoclinic and orthorhombic crystals. These modifications are called *allotropic* forms of the substance.

9. The Use of X-rays in Studying the Structures of Crystals

Crystals are composed of atoms, ions, or molecules arranged in definite geometrical patterns consisting of many different sets of intersecting planes containing particles (Figure 119). The top and bottom faces of a cubical crystal (Figure 119) are two such planes, and between them there are many similar parallel planes. Other sets of planes are parallel to other sides of the cube, and still others intersect the faces at different angles, i.e., they cut the cube along lines that are diagonal to a face.

The different sets of planes in a crystal can be studied by means of the device described on page 159 and shown in Figure 106. The angles of "reflection" are measured just as they were in Moseley's investigations, except that this time a monochromatic (one wave-length) beam of X-rays is employed, and the crystal is rotated about different axes so as to cause the X-ray beam to be "reflected" by different sets of planes (Figure 119) and, therefore, at different angles. Many sets of parallel planes can be detected in this manner, and the distance between two planes in each set can be measured. From this information it is pos-

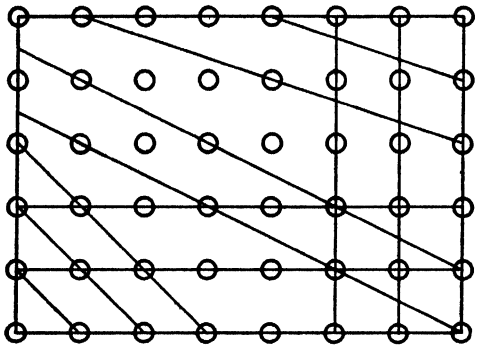


Figure 119. Some of the Sets of Planes in a Crystal that will Reflect a Beam of X-Rays

The planes of each set are separated by a definite distance between planes and, therefore, each set of planes will reflect the beam at a definite angle.

sible to draw conclusions concerning the general plan or pattern of the crystal's structure.

By Laue's method of crystal analysis, a monochromatic beam of X-rays is passed through a crystal and eventually strikes a photographic plate (Figure 120). Many different sets of planes diffract the X-ray beam, each set of parallel planes producing its own diffraction spots on the photographic plate. The distance and direction of the spots from the center depend upon the inclination of the planes with reference to the direction of the beam's path, and they depend, also, upon the spacing between parallel planes. The dark spots on the plate represent the different directions in which reinforcement of the beam occurs. The symmetrical arrangement of spots in the photograph corresponds to a similar symmetry of planes within the crystal, which can be determined by the mathematical analysis of the pattern of spots.

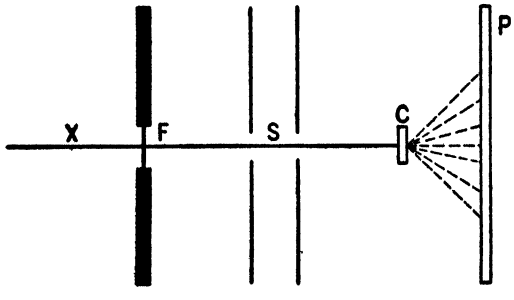


Figure 120. Laue's Method of Diffracting X-Rays by Means of a Crystal

The planes in the crystal diffract the beam, causing spots at different positions on the screen or photographic plate.

10. Crystal Lattices

The pattern of particles that compose a crystal and which is characteristic of each crystalline form of matter is called a *crystal lattice*, or, sometimes, the *space lattice* of the crystal. The smallest portion of the crystal that reveals the complete lattice pattern is called a *crystal unit*. For an illustration of what is meant by a crystal lattice, we may refer to Figure 123.

In some crystals the particles that make up the crystal lattice are ions. This is true of sodium chloride, of potassium nitrate, and of salts in general. Other substances appear to be composed of individual, uncharged atoms. Among these substances are carbon, sulfur, and the metallic elements. Most organic compounds, such as sugar and naphthalene, form crystals composed of molecules. Many substances, such as charcoal, cellulose, and rubber (when stretched), which at one time were regarded as amorphous (not crystalline), have been shown by X-ray analysis to consist of orderly arranged particles, and for this reason they must be regarded as existing in crystalline states.

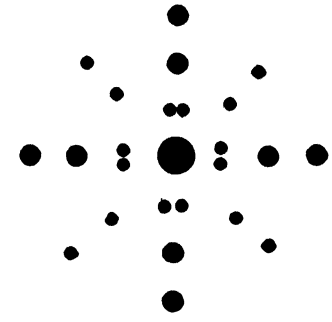


Figure 121. A Pattern of Spots Obtained on the Photographic Plate (P) of Figure 120.

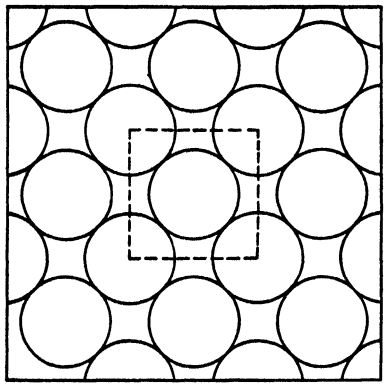


Figure 122. A Face of a Face-Centered Crystal Pattern, Showing the Packing of Atoms

11. Types of Crystal Lattices

Copper, silver, and gold crystallize in a variety of the regular system called the *face-centered lattice* (Figure 122). This drawing represents the packing of atoms in a large crystal; the space lattice — or crystal unit — is indicated by dotted lines and is also shown in Figure 123. Most of the metals that are ductile and easily beaten or rolled into thin sheets crystallize in the face-centered lattice pattern. The malleability and ductility of metals depend, of course, upon the ease with which the atoms of their crystals can slip over one another under pressure. In crystals that are based upon the face-centered lattice, planes of atoms may slide or slip over and past other planes without actual fracture of the crystal. This "slippage" of planes is not so easy in other types of crystals, such as the *body-centered lattice* (Figure 124). Crystals of chromium and one of the forms of iron are based on the pattern of the body-centered lattice. Magnesium, zinc and a few other metals crystallize in the hexagonal lattice pattern (Figure 125).

12. The Crystal Structure of Sodium Chloride; Ionic Crystals

Let us consider the structure of this substance as an example of the lattice of an ionic compound, remembering, however, that the crystals of all such compounds do not follow the same pattern for the arrangement of ions. The crystal unit of sodium chloride is a cube, and the particles composing the lattice are sodium and chloride ions, which are arranged in alternating positions (see page 42, Figure 39). The cube that acts as the crystal unit may be regarded as composed of eight smaller cubes. The ion at the center of the large cube — let us say this is a sodium ion — is surrounded by six chloride ions which occupy positions at the centers of the six faces of the cube. In a large crystal each sodium and each chloride ion, except those on the surfaces, is the center of a similar cubic-crystal unit.

The ions are held in fixed positions relative to one another in the lattice by the attraction that unlike charges exert upon

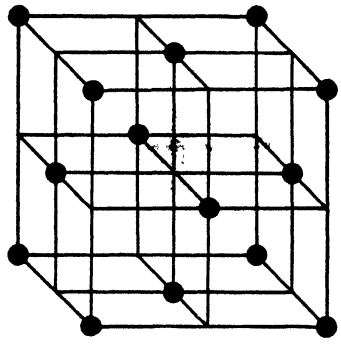


Figure 123. The Face-Centered Cubic Lattice

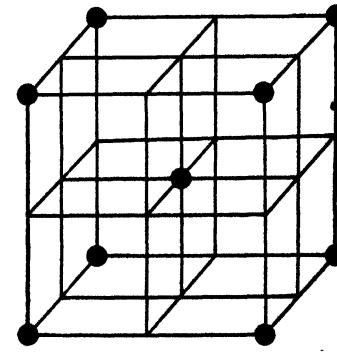


Figure 124. The Body-Centered Cubic Lattice

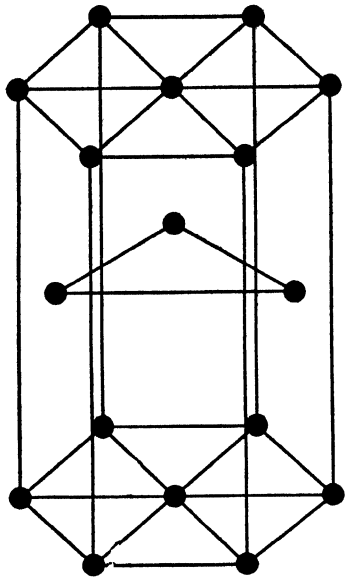


Figure 125. Hexagonal Lattice

one another. If this attraction is weakened, the crystal's structure can no longer exist. If the particles are given sufficient energy by the absorption of heat, for example, the forces which make possible the crystalline structure are overcome and the crystal melts. Then again, when salt dissolves in water, the structure crumbles because of the effect of the solvent in weakening the forces that hold the particles together.

The crystals of sodium chloride are not malleable or ductile, because one layer or

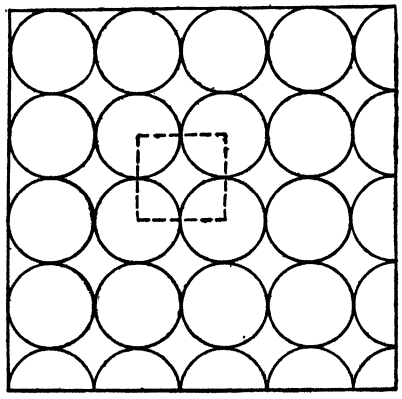


Figure 126. The Face of a Simple Cubic Pattern

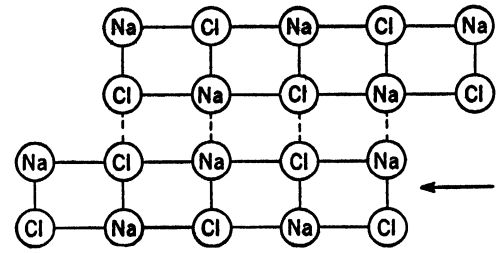


Figure 127. A crystal of an ionic compound cannot be deformed as a metal is when rolled or beaten out into a sheet, because one plane of ions cannot slip past another without bringing like ions (Na^+–Na^+ or Cl^-–Cl^-) into adjacent positions; the ions under this condition would repel each other.

plane of ions does not easily slide over other layers. If this happened the entire pattern would be disturbed, and ions of the same charge would be placed together (Figure 127), thus resulting in the repulsion of adjoining particles. Therefore, under pressure or shock the crystals shatter or break, leaving sharp edges and irregular surfaces.

Because the electrostatic forces responsible for the attraction between oppositely charged ions are relatively very strong, ionic crystals are hard, have relatively high melting and boiling points, and are not volatile at ordinary temperatures.

There are no molecules in the crystal of sodium chloride. Actually, the whole crystal may in a sense be regarded as one "giant molecule." There is some justification still for the use of the term

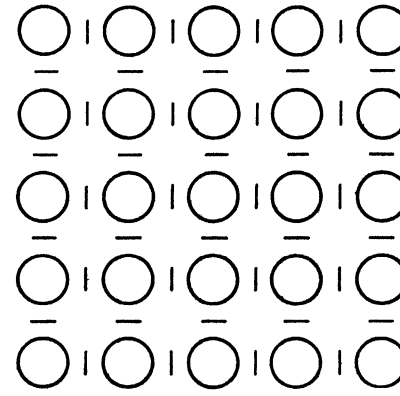


Figure 128. Metallic Crystal

The valence electrons of the atoms are scattered throughout the crystal instead of remaining with the individual atoms.

"molecule of sodium chloride," because there are good reasons for believing that in its vapor state this substance consists of molecules of NaCl.

13. Crystals of Metals

The crystals of a pure metal are composed of particles of only one kind, namely atoms of the metal. These atoms do not hold their valence electrons very firmly, and it is probable that these electrons are separated from the individual atoms and are free to migrate throughout the crystal, thus acting as a binding agent and by their electrostatic effect holding the positively charged kernels of the atoms together. (The atoms are now positively charged because they have lost their valence electrons.) When the metal acts as a conductor of electricity, these free electrons move through the solid, under the influence of a difference of electrical potential, in the direction of the positive pole.

Since all the units of the crystal are the same, a displacement of some of the atoms — as, for example, when one layer under pressure slides over another — does not result in the destruction of the general arrangement. Hence, the metals, generally speaking, are malleable.

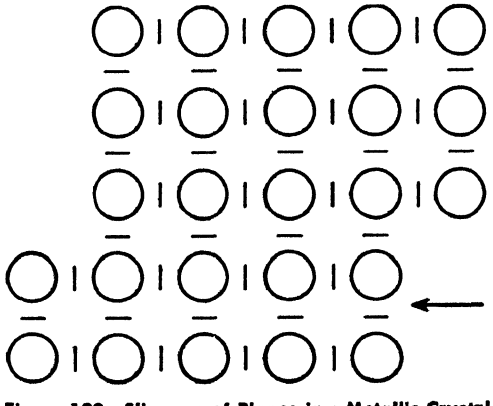


Figure 129. Slippage of Planes in a Metallic Crystal

Planes of atoms in a metallic crystal can slip along each other under pressure without changing the fundamental structure of the crystal.

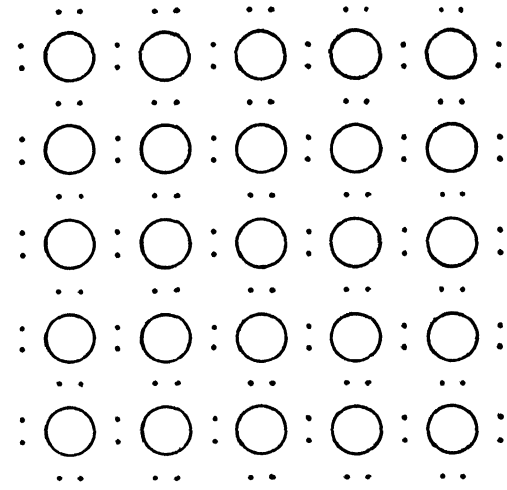


Figure 130. Crystal of Atomic Compound Such as Diamond

The atoms are held by covalent bonds. The crystal is one giant molecule.

14. Atomic Crystals

Carbon, silicon, and certain compounds of these two elements, such as silicon carbide, SiC, form crystals composed of atoms joined by covalent bonds — shared pairs of electrons. Here, too, the whole crystal can be looked upon as a "giant molecule." Like ionic crystals, these atomic crystals, because of strong bonds between their atoms, are hard, are not volatilized except at high temperatures, and have high melting and boiling points.

Certain non-metals form crystals in which the different points in the lattice are occupied by molecules instead of atoms of the element. Thus, in crystals of iodine a molecule of I_2 is found at each lattice point. In sulfur crystals the molecules that act as the building units of the lattice are molecules of S_8. Crystals of carbon and silicon, as described above, show no molecular units; they are atomic crystals.

15. Polar and Non-Polar Compounds and Their Crystal Structures

Many compounds form crystals in which

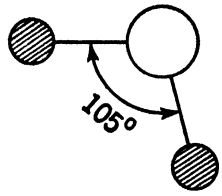


Figure 131. The Water Dipole
The two atoms of hydrogen are 105° apart.

the particles that occupy positions in the lattices are molecules. The arrangements of these lattice-patterns are of two types, depending upon whether the molecules of the compounds are *polar* or *non-polar*.

Methane, CH_4 (page 43), is a non-polar compound. In a molecule of methane the four protons (H) are arranged symmetrically around the nucleus of the carbon atom and the "centers of gravity," so to speak, of the positive and negative charges (protons and electrons) are at the same point in the molecule — the center of the carbon atom. The lattices of such substances are built up of molecules that have little attraction for one another, except a rather weak attraction, or binding force, that results from the interaction of the electrons of different molecules. Because of weak binding forces, the crystals of such substances are usually soft, they melt at relatively low temperatures, and, in general, can be vaporized readily.

Polar molecules do not have the same centers for their electrons and protons. The water molecule (Figure 131) is an example. The properties and general behavior of water indicate that the two hydrogen nuclei (protons) are not arranged symmetrically with respect to the nucleus of the oxygen atom, i.e., they are not directly opposite each other. Lines joining the protons to the oxygen nucleus make an angle of about 105° with each other. Therefore, the center of all the electrons in the molecule is the center of the oxygen atom, but the center of the protons is somewhat displaced from this point. The water molecule acts, therefore, as if it contains two poles, + and −, and for this reason it is called a *dipole* molecule.

In other polar molecules a dipole may result from differences in the attraction of the atoms of the molecule for electrons. This is the condition in a molecule of hydrogen chloride, HCl. Although in pure hydrogen chlorides the atoms are held together by shared pairs of electrons, the atom of chlorine must have far more attraction for electrons than the atom of hydrogen; the shared electrons spend more of their time in traveling around the nucleus of the chlorine atom than they spend with the hydrogen atom. This situation results in making the chlorine end of the molecule negative and the hydrogen end positive with respect to each other, and produces a dipole, or polar molecule.

The crystals of polar substances are composed of molecules which are so arranged in the general pattern, or lattice, that the positive portion of one molecule is adjacent to the negative portions of others (Figure 133). Crystals of these substances are rather firmly constructed, and because of the relatively strong attraction between molecules they have higher melting points, are harder,

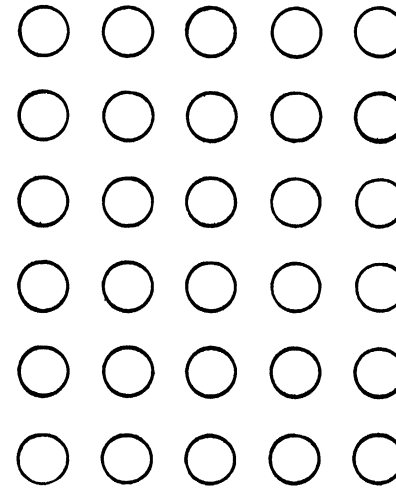


Figure 132. Crystal of Non-Polar Molecular Compound
There are no strong forces to hold the molecules in their positions in the crystal.

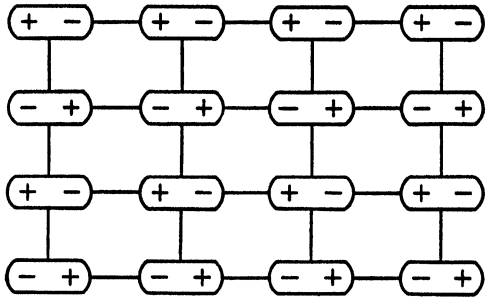


Figure 133. Crystal of Polar Molecular Compound

less easily volatilized, and less soluble in the same solvent than non-polar substances. Polar compounds do not act as conductors of electricity when melted, because they do not consist of separate positive and negative ions which can move in different directions in an electric field. In this respect polar compounds differ from ionic compounds.

CHANGES OF STATE

16. Between Liquid and Solid

In a liquid, the attraction that holds the particles of a solid in place is weakened to a sufficient extent to allow the molecules to move about more or less freely within the space occupied by the liquid. There is still, however, considerable attraction between the molecules of a liquid — more for a polar liquid than for one that is non-polar and still more between the ions in the liquid state of an ionic compound. If there were no attraction in a liquid, it would, like a gas, fill its container regardless of the size of the container or the quantity of liquid placed in it.

To change a liquid into the corresponding solid the molecules must be slowed down, a condition that can be produced by cooling. At lower temperatures molecules move less rapidly, and when the temperature is sufficiently lowered, and the velocities of the molecules are correspondingly reduced, they will no longer possess sufficient kinetic energy to resist the attraction that they have for one another. They then take up and remain in the positions of their crystal lattice, and the change to the solid state occurs. When the solid melts, heat is required to give the molecules once more the kinetic energy that they must have to overcome the attraction between them. Freezing, therefore, requires the withdrawal of heat from a body, and melting requires absorption of heat.

At 0° C., under ordinary conditions, water freezes, forming the solid state, which we call ice. In the absence of ice, water may be cooled to a temperature below 0° before freezing begins; when this happens the water is said to have been *undercooled.* Properly speaking, 0° C. is the temperature of a water-ice mixture. If heat is added to the mixture, the ice melts, and the temperature remains at 0° until all of the solid has disappeared, the added heat being used to increase the average kinetic energy of the molecules. If heat is removed from the mixture by the surroundings, the temperature remains at 0° as water changes into ice. This temperature is called the *freezing point* of water or the melting point of ice.

When one gram of ice melts at 0° C., 79 calories of heat are absorbed, and when the same weight of water freezes, 79 calories of heat are liberated. This quantity of heat is called the *heat of fusion* of ice (per gram).

Expansion occurs when water changes into ice. The amount of the expansion is about one eleventh of the volume of the water. This means that each liter of water at 0° becomes 1.09 liters of ice at the same temperature. Because of this expansion, pipes burst when the water in them freezes. For the same reason ice floats on water. For some substances the formation of the solid from the liquid is accompanied by a contraction, or decrease in volume.

17. Change from Liquid to Vapor: Evaporation

Although molecular attraction is far

greater in liquids than in gases, we cannot think of the molecules of the liquid as at rest. At a definite temperature, the *average* kinetic energy of these molecules is constant, but this does not mean that all of the molecules are moving with the same velocity. If we could examine, at some one instant, the individual molecules in a liquid, we would find that for some the velocities are considerably greater, and for others considerably less, than the average. The more slowly moving particles are held together more firmly than those that possess the average velocity, but those on the surface that have velocities greater than the average and, therefore greater kinetic energies, will not be held together at all; they will escape from the liquid into the space above its surface. This change from liquid to vapor is called *evaporation.*

Since the molecules having the greatest velocity are the ones that escape, the average velocity of those left in the liquid state decreases. This means that the temperature of the liquid also falls. Evaporation would soon cease, even in an open vessel, if the more slowly moving molecules did not acquire sufficient energy to permit them to escape from the attraction of their fellow particles in the liquid. Evaporation does not cease, however, because heat is absorbed from the surroundings, which are cooled as the liquid evaporates.

18. Equilibrium between a Liquid and Its Vapor

If sufficient water in proportion to the space above it is placed in a closed vessel, evaporation does not proceed to completion. The space above the liquid contains vapor, which exerts pressure upon the surface of the liquid and upon the walls of the container. Since the space contains air or other gases the vapor's pressure is, strictly speaking, the *partial pressure of water vapor.* The molecules that escape from the surface travel in straight lines until they strike the walls of the vessel, or until they collide with other molecules of the vapor. In these collisions some of them are deflected in a direction that carries them back, eventually, to the surface of the liquid, which they may penetrate. The number of particles that return to the liquid depends, evidently, upon the number of molecules in a definite volume of the vapor, the vapor density. At first, the partial pressure of the water vapor is small. Hence, more molecules escape into the vapor state than return to the liquid in the same period of time. The vapor density rapidly increases, and with increasing numbers of molecules above the liquid the rate at which they return to the surface and penetrate the liquid increases. Within a short time and at a definite temperature, a *state of equilibrium* is attained, when the rate at which the molecules escape from the liquid is equal to the rate at which they return. As long as the liquid and the vapor are in equilibrium, evaporation and condensation occur at the same rate; and hence, the relative numbers of molecules in the vapor and liquid remain unchanged. We must not think of either or both as ceasing; they proceed at the same rate.

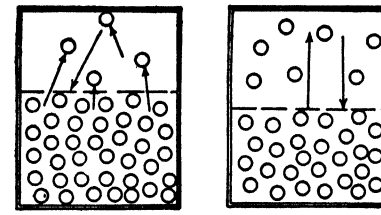


Figure 134

In a closed vessel molecules escape from the liquid into the vapor state. Some molecules of vapor also return to the liquid. Eventually, a state of equilibrium is attained (right).

19. Vapor Pressure

The vapor pressure at equilibrium balances the escaping tendency of the molecules of the liquid; and hence, it is a measure of what we may regard as the pressure

exerted by the molecules in leaving the liquid. This is a definite pressure for each liquid at a constant temperature, and exists only when the liquid is in equilibrium with the vapor of the same substance. This definite pressure is usually referred to simply as the *vapor pressure* of the liquid.

The partial pressure of the water vapor in the air — the aqueous vapor pressure — varies from time to time even at the same temperature. There are days in the summer when the humidity of the air is relatively high, and we are less comfortable than on other days, although the temperature may be about the same. On these "uncomfortable" days the partial pressure of the water vapor in the air may be relatively near the saturation value, i.e., the aqueous vapor pressure may be almost equal to the vapor pressure when liquid and vapor are in equilibrium. On such days water evaporates very slowly from the surface of our bodies, and we are without the cooling effect of its evaporation.

20. Effect of an Increase in Temperature upon Vapor Pressure

An increase in temperature causes an increase in the velocity and a corresponding increase in the average kinetic energy of the molecules. As the temperature rises, more molecules acquire the energy that enables them to break away from the other molecules of the liquid and to escape through the surface. Since the number of molecules passing through the surface is increased, more molecules must also enter the liquid from the vapor, if equilibrium is to be maintained. This condition requires that more molecules must exist in the vapor state, per unit of volume, and that the vapor pressure is increased at the higher temperature. The relation between the vapor pressure of water and the temperature is shown in Figure 135.

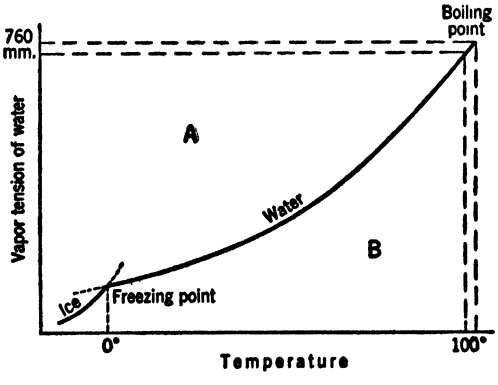


Figure 135. The Vapor Pressure of Water and Ice at Different Temperatures

21. Boiling and the Boiling Point

If water evaporates in an open vessel, water vapor diffuses and mingles with the surrounding atmosphere. The total pressure above the surface of the liquid, therefore, is the pressure of the atmosphere, which remains constant or nearly so. Finally, as the temperature of the liquid rises, the vapor pressure becomes equal to the pressure upon the surface of the liquid. The temperature at which this occurs is the *boiling point* of the liquid. When the boiling point has been reached, the temperature remains constant, and the further applica-

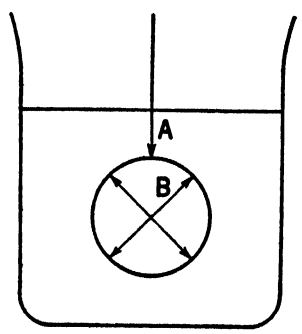


Figure 136. Boiling

In order that bubbles of water vapor may form within the body of the liquid, the pressure inside the bubble must be equal to the pressure upon the bubble. The pressure inside the bubble is the maximum pressure of water vapor at the temperature of the liquid. The pressure from without is the atmospheric pressure plus whatever pressure is produced by the liquid above the bubble. A = Pressure of atmosphere + hydrostatic pressure; B = Vapor pressure inside bubble.

tion of heat serves only to evaporate the liquid by supplying the more slowly moving molecules with sufficient energy to allow them to escape.

Boiling is a condition in which bubbles of vapor form throughout the body of a liquid. It is evident that bubbles of vapor cannot form until the pressure inside the bubbles is equal to the pressure upon the bubbles from without, namely the atmospheric pressure plus the pressure of the liquid above the bubbles. A bubble in which the pressure is less than the pressure outside would collapse immediately. See Figure 136. Hence, boiling does not occur until the vapor pressure of the liquid becomes equal to the pressure upon the surface of the liquid.

Since the temperature at which a liquid boils depends upon the atmospheric pressure, and since this pressure varies from day to day in each locality, the boiling point of a liquid is not the same at all times. The atmospheric pressure also varies with the elevation above sea level. On a mountain top, for example, the vapor pressure of water becomes equal to the external pressure at a lower temperature than it does in a neighboring valley. It is difficult to cook foods in water at high elevations, because cooking depends upon the temperature to which the food is heated, and not upon the boiling of the water. Steam pressure cookers are based upon the principle that a higher temperature must be attained before water will boil under increased pressure. At the higher temperature foods are cooked more quickly.

22. The Vapor Pressures of Different Liquids

Ethyl alcohol, ether, and similar liquids that evaporate more rapidly than water, at the same temperature, have correspondingly greater vapor pressures at equilibrium between liquid and vapor than water has. This difference arises from the small attraction that molecules of these liquids have for one another as compared to the attraction among molecules of water.

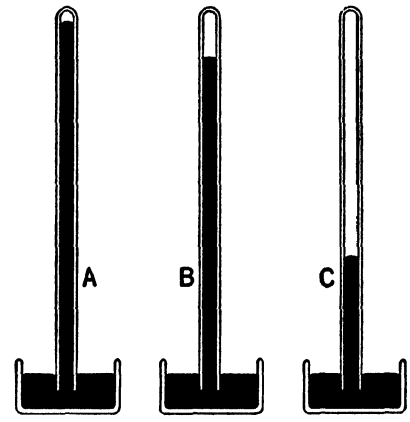


Figure 137. The Relative Vapor Pressures of Water (A), Ethyl Alcohol (B), and Ether (C), at the Same Temperature

The vapor pressure of any readily volatile liquid can be measured approximately by allowing the vapor to come to equilibrium with a small sample of the liquid contained above the mercury in a barometer tube (Figure 137). The pressure of the vapor depresses the level of the mercury in the tube and can be measured by the difference in levels in two tubes, one containing nothing but mercury, and the other containing mercury and the liquid above it.

VAPOR PRESSURE OF LIQUIDS AT 20° C.

Water	17.5 mm.
Ethyl Alcohol	34 mm.
Ether	433 mm.
Carbon Disulfide	298 mm.
Chloroform	160.5 mm.

23. The Boiling Points of Different Liquids

The fact that one liquid has a greater vapor pressure at a given temperature than another does not mean that this is true at all temperatures, but, in general, the greater the vapor pressure of a liquid and the more rapidly it evaporates at ordinary temperatures, the lower is its boiling point. Thus, ether with a vapor pressure of 433 mm. at 20° C. boils at 35°, and water with a vapor

pressure of 17.5 mm. at the same temperature boils at 100° C. (760 mm. pressure). In comparing the boiling points of different liquids, or of two samples of the same liquid, the temperatures must be corrected to the temperatures corresponding to the standard pressure or at least to the same pressure.

24. Heat of Vaporization

Energy is required to convert a liquid into its vapor, because the molecules must be separated; i.e., energy must be supplied to overcome the attraction that holds the molecules of the liquid together. The absorption of heat during evaporation explains the cooling effect of evaporation. To change one gram of water into water vapor at 100° C., 539.5 calories of heat must be absorbed. This is the *heat of vaporization* of water per gram. For the same weight of other liquids other quantities of heat are required, because of the different strengths of the attraction which different kinds of molecules have for one another.

The heat of vaporization of water is high as compared to that of other liquids, although some liquids, because they evaporate more rapidly than water and, therefore, absorb more heat in the same period of time, have greater cooling effect. Ethyl chloride, for example, when allowed to evaporate from the surface of the body evaporates so rapidly that freezing may result.

Since heat is absorbed during evaporation, it must also be true that heat is liberated when the vapor is condensed to form the liquid once again.

CHANGE FROM SOLID TO GAS

25. Vapor Tension of Ice

The molecules in ice must have a much smaller average kinetic energy than those of water. Ice, however, evaporates. Snow crystals disappear at times when the temperature is below the melting point, and they possess, therefore, a definite vapor pressure at a given temperature. Changes in the vapor pressure of ice with changes in temperature below 0° are shown by the short curve on the left-hand side of Figure 135. As the temperature rises, the vapor pressure becomes, finally, equal to that of the liquid, and at this temperature, the two phases — liquid and solid — are in equilibrium with each other. (See Figure 135.) This is the *melting point* of the solid. It is also the *freezing point* of the liquid.

26. Sublimation

Some solid substances have considerable vapor pressures and are rapidly converted into vapor at temperatures below their melting points. As the vapor is cooled it may condense to form the solid once again without, apparently, the formation of the liquid state at any time in the process. This process is called *sublimation.*

Iodine, for example, can be purified by heating the impure crystals that are first formed during its production. The solid changes into iodine vapor, which can then be condensed by holding a cold glass or porcelain surface just above the vessel in which the solid is heated. Crystals of pure iodine form on this surface, because the impurities of the original material do not sublime. As might be expected *the heat of sublimation* is equal approximately to the sum of the heats of fusion and vaporization.

REVIEW EXERCISES

1. Describe a method which can be used to measure the vapor pressure of a liquid at different temperatures.
2. Why do all liquids not have the same vapor pressures at the same temperature?
3. Describe the equilibrium that results between a liquid and its vapor in a closed vessel. How do changes in temperature affect this equilibrium?
4. Explain the cooling effect of evaporation, the cooling effect of melting ice, and the heating

effect of condensing vapors and freezing liquids.

5. Why does an increase in temperature produce an increase in the vapor pressure of a liquid?
6. Why must heat still be applied to continue the boiling of a liquid which has been heated to its boiling point?
7. Why do bubbles of vapor form in a boiling liquid? Why do they not form below the boiling point?
8. Describe the nature and cause of the surface tension of a liquid.
9. Define density and specific gravity and explain the difference between them.
10. Can you see any relation between the high specific heat of water and its use in hot-water heating systems? Explain.
11. Why does a large body of water cause near-by land to have cooler temperatures in summer than the land that is far removed from water?
12. To what property of liquids does the term viscosity refer? How is the viscosity of a liquid measured?
13. What are the six groups into which crystals are classified?
14. What are isomorphous substances?
15. How do solid allotropic forms of the same substance differ? Give an example.
16. How does a crystal act upon a beam of X-rays that falls upon one of its faces?
17. How can X-rays be used to measure the distance between parallel atom-bearing planes within the crystal?
18. Define: Crystal lattice and crystal unit.
19. Show by means of a sketch the crystal unit of sodium chloride.
20. What are the arrangements of atoms, ions, or molecules in (1) face centered, (2) body centered, and (3) simple cubic lattices?
21. Why are crystals of sodium chloride not malleable, while those of most metals are?
22. How is the attraction that holds atoms of carbon in crystals of diamond and atoms of metals in their crystals explained?
23. Define: Dipole, polar molecules, non-polar molecules.
24. What are the differences, generally speaking, in the properties of polar and non-polar substances?
25. What differences in the properties of water might be expected if the water molecule contained two protons located at equal distances from the oxygen nucleus and directly opposite to each other instead of being located as shown in Figure 131?
26. Why does a current of air blowing across the surface of water increase the rate of evaporation?
27. Why does one's eye glasses become "fogged" when one enters a warm room after being outdoors during cold weather?
28. Could water be made to boil at 0° C? Justify your answer.
29. How are atoms held together in crystals of metals? in crystals of carbon?
30. How is the electrical conductivity of metals accounted for?
31. How would you account for the fact that a small steel needle can be made to float on the surface of water?
32. Account for the fact that heat is liberated when steam is condensed and absorbed when water changes to vapor.
33. Some liquids cannot be distilled by heating them to their boiling points because they decompose at such temperatures. Can you suggest some method by which such liquids can be distilled?

REFERENCES FOR FURTHER READING

Bragg, Sir W., *Concerning the Nature of Things*, chaps. IV, V, and VI.

Linsdale, K., *Crystals and X-rays*. New York: D. Van Nostrand Company, Inc., 1949.

Meldrum, W. B., and F. T. Gucker, *Introduction to Theoretical Chemistry*.

Stillwell, C. W., *Crystal Chemistry*. New York: McGraw-Hill Book Company, 1938.

Crystal Structure: *J. Chem. Ed.*, **7**, 138, 860 (1930); **10**, 590, 667 (1933); **11**, 159 (1934); **14**, 131 (1937).

14

WATER

1. Introduction

Many of the physical properties of water have been referred to in the preceding chapter in which we frequently used the behavior of water in explaining the characteristics of the liquid state. In this chapter we shall discuss certain other physical properties of water but we shall be principally concerned with natural water, water supplies and their purification, and the chemical behavior of water. Special attention will be given to substances called hydrates, and the chapter will close with the study of the properties and methods of production of *hydrogen peroxide*, a substance somewhat related to water because it is the only other compound composed only of hydrogen and oxygen.

2. The Importance of Water to Plants and Animals

The first chemical compound which we shall study is certainly the most familiar, because of its common occurrence and because of the many uses that we find for it. All the tissues of our bodies are bathed by it. Dissolved or suspended in it, are the different substances which aid in one way or another in the digestion of food. These same foods, when digested, are carried to the various parts of the body in aqueous solutions. Likewise, many waste products are eliminated from the body as water soluble substances. Even the oxygen which we breathe must dissolve in water before it passes through the tissues of the lungs into the blood. The large amount of water in our bodies — this is about 65 per cent of the body's weight — aids in maintaining the average body-temperature. Water requires a relatively large amount of heat to raise its temperature a few degrees, and for this reason it absorbs the excess heat in the body and prevents radical changes in temperature. Water also has a relatively high heat of vaporization. More heat is required to evaporate one gram of water than one gram of most other substances. Hence, the body is cooled by the evaporation of water from the skin.

Plants depend upon water to an even greater extent than animals. The plant receives all the nutrients that it extracts from the soil in the form of aqueous solutions. In it are dissolved, also, the various products involved in the plant's biological activity. The food which is manufactured in the leaves is transported in solution to different storage places — e.g., roots, fruit, seeds. When a young plant starts to grow, this food is again dissolved and is thus carried to the growing parts of the structure. The plant also uses water in the manufacture of its foods; starch and sugar are synthesized by plants from water and carbon dioxide.

3. Occurrence

Water is present in almost all natural objects and in almost every part of the earth that man can reach. There is water vapor in the air, and water in rocks and in the soil. In addition to the water that wets them, clay and certain kinds of rocks contain it in chemical combination with other substances. Even objects that appear to be *dry*, may show a loss of weight when heated to a temperature that will evaporate the water that they contain without otherwise changing their composition. Water is present in varying amounts in all foods. Green vegetables may contain as much as 90 per cent or even more. Meat, milk, butter, and potatoes contain large percentages of water, and even bread is not "dry."

PHYSICAL PROPERTIES OF WATER

4. General Properties

Pure water is odorless and tasteless. Natural waters often possess taste and sometimes odor because of substances dissolved in them. In thin layers water appears colorless, but in thick layers it has a bluish-green color. It is a very poor conductor of electricity. It freezes at 0° C., and, when the pressure above it is 760 mm., it boils at 100° C. When one gram of water, at 100° C., changes into water vapor, 539.5 calories of heat are absorbed; this is the heat of vaporization of water per gram. The absorption of heat during evaporation explains the cooling effect of perspiration. This heat is used to separate the molecules of the liquid and to give them the additional kinetic energy which they possess as molecules of vapor. Water vapor — the gaseous state of water — is invisible. Clouds of "steam" really consist of small drops of condensed water.

The *density* of water (weight per unit of volume) varies with the temperature. The maximum density is reached at 4° C. Both above and below this temperature the density decreases. For this reason, water freezes from the top downward, rather than from the bottom upward. The water in the upper layer is cooled by the air with which it comes in contact. As it is cooled, the density increases and the water sinks. This proceeds until the water reaches a temperature of 4° C. As it cools still further, the density decreases and, hence, the colder water remains on top, where it freezes at 0°.

5. Water as a Solvent

Water is more often employed as a *solvent* than any other liquid, because of its abundance, its harmless character, and because of the great number of substances that dissolve in it. We sometimes speak of substances as "insoluble" in water. Usually, we mean to state that they are slightly soluble as compared with other substances. Thus, 6.7 gram-molecular weights of calcium chloride dissolve in 1000 grams of water at 20°, while only 0.00000001 gram-molecular weight of silver iodide dissolves in the same quantity of water at the same temperature. Relatively speaking, therefore, calcium chloride is readily soluble, while silver iodide is "insoluble," or, more strictly speaking, "very slightly soluble."

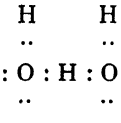
6. The Properties of Heavy Water

One gram of heavy water, or *deuterium oxide* D_2O, can be obtained from 24,280 grams of ordinary water. Its cost is about $1.25 per gram. Since it decomposes less readily than ordinary water, the residue remaining near the end of the electrolysis of a large quantity of water (containing dissolved alkalies) is richer in deuterium oxide than the original water. If this residue is electrolysed, the hydrogen oxidized, and the separation by electrolysis is repeated, the residue contains a still larger amount of D_2O in proportion to H_2O. Repetitions of the whole process finally results in the production of nearly pure deuterium oxide.

Salts have slightly different solubilities in H_2O and D_2O, and substances produced by reactions involving the two oxides (such as NaOH and NaOD) have some differences. Deuterium oxide has the following physical properties: Density, about 1.105 g. per ml. at 20°; freezing point, 3.8° C.; boiling point, 101.42° C.; vapor pressure at 100° C., 721 mm. Its heat of vaporization per gram-molecular weight is 9970 calories; its heat of fusion is 1510 calories; and its heat of formation from the elements is 70,500 calories. All of these are considerably greater than the corresponding values for water.

7. The Structure of Water

Studies of ice by means of X-rays indicate that it has a complex, rather open structure in which the oxygen atom of each water molecule acts as the center of a tetrahedron (Figure 138) with four atoms of hydrogen forming the four corners of the tetrahedron. Two of these hydrogen atoms belong to the same molecule as the atom of oxygen, and the others belong each to different molecules. Different tetrahedra are connected because all four hydrogen atoms of one tetrahedron also form the corners of other tetrahedral units. Thus, in ice the molecules of water are joined by *hydrogen bonds:* i.e., each hydrogen nucleus is attached to two oxygen atoms, one in its own molecule and one in another. To the second oxygen atom the hydrogen nucleus is joined by sharing one of the unused pairs of electrons belonging to that atom:



This is, therefore, a co-ordinated covalent bond, a bond in which both electrons of the pair that is shared belonged originally to one of the atoms. When ice melts this rather open structure is partially broken up; and hence, the molecules are packed somewhat more closely in water than in ice, causing water to have a higher density. Liquid water, however, contains some groups of H_2O molecules joined together by hydrogen bonds.

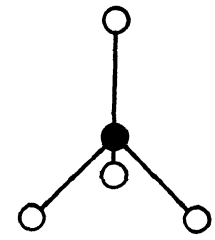


Figure 138. The Structure of Ice
Tetrahedral unit showing an atom of oxygen (●) surrounded by four atoms of hydrogen.

NATURAL WATERS

8. Impurities

The water of springs, lakes, rivers, and the sea contains varying amounts of substances either in solution or as finely divided solids in suspension. These impurities may consist of the following classes of materials:

(1) Finely divided solids in suspension. These include sand, clay, organic material (bits of plants), and organisms, such as bacteria.

(2) Dissolved salts, especially the bicarbonates, sulfates, and chlorides of sodium, potassium, calcium, magnesium, and iron.

(3) Dissolved organic compounds, many of which are produced by the decay of vegetation or are extracted by the solvent action of water from plant material.

(4) Dissolved gases, such as ammonia, carbon dioxide, oxygen, and nitrogen.

The suspended solids can be removed by filtration. If a measured weight or volume of the clear water is then evaporated to dryness, the quantity of dissolved solids in a sample of the water can be determined. Sea water contains approximately 3.5 per cent of solids, of which about 75 per cent is sodium chloride. The water from salt-lakes (Great Salt Lake, Dead Sea, etc.) contains from 20 to 25 per cent of dissolved solids, most of which is salt. Mineral waters contain relatively large amounts of different salts, such as sodium or magnesium sulfate.

9. Objectionable Impurities

Water which contains salts of calcium and magnesium is said to be *hard*. When soaps are placed in water containing calcium or magnesium salts, they react by double decomposition with the latter, and insoluble calcium or magnesium soaps are formed. Hence, the soap does not produce a lather. Hard waters can be *softened* before use by adding some substance which forms slightly soluble compounds of calcium and magnesium. Sodium carbonate, Na_2CO_3, is such a substance. Although not so common, the ions of iron are as objectionable in water as those of calcium and magnesium and for the same reasons. Also, because insoluble colored compounds of iron are likely to be precipitated on clothing, iron is even more objectionable in the laundry than the ions of other metals.

Hard waters are also objectionable in boilers. The salts of calcium and magnesium are deposited upon the walls, as the water is changed into steam. As this deposit thickens, heat losses occur, because of the thick layer of material that separates the water from the source of heat. The boiler wall must be heated to a much higher temperature than would be required, or would be possible, if the water were in direct contact with it.

Some waters are also objectionable because they contain dissolved substances, such as the carbonates of sodium and potassium, which produce foaming in boilers. Some waters have disagreeable odors and tastes because of forms of plant life called algae that grow in them. Other waters are dangerous sources of disease, because they contain certain types of bacteria, such as the typhoid bacillus, or bacteria that cause paratyphoid, dysentery, and certain other diseases.

10. The Purification of Drinking Water Supplies

The domestic water supplies of cities may come from rivers, lakes, springs, wells, or from basins which gather the "run-off" from the surrounding soil. None of these sources can be regarded as safe, regardless of precautions to exclude sewage. In fact, contamination of the supply by sewage in some cases is recognized. Proper methods of purification are therefore necessary. The bacteria in water may be killed by boiling for a few minutes, but "boiled water" is unpalatable, since it contains little or none of the dissolved gases which natural waters have in solution. Furthermore, boiling is not a practical method of purifying the water supply of a city requiring millions of gallons daily.

Nearly pure water can be prepared by *distillation*, a process in which water is first changed into vapor by heating it at the boiling point, thus separating it from all the substances except gases that are dissolved in it, and then condensing the vapor to form the liquid again (Figure 139). Distillation is, therefore, a practical method of preparing small amounts of water of a high degree of purity for scientific and medical uses.

The large-scale purification of water usually involves both filtration and chemical treatment. Bacteria are either killed by the sterilizing action of chlorine or certain compounds of chlorine, or they are removed along with other suspended material by filtration.

11. Settling and Filtration

If the water contains much mud, clay, or sand, it is first allowed to stand in a settling basin, where most of this material settles out. It then passes through the filter, which consists of layers of sand and gravel. The filter may be designed to allow the water to pass through slowly or rapidly. If filtration is to be rapid, the beds of gravel and sand are shallow, and coarse material is used. These rapid filters are not as efficient as the slow ones in removing suspended material and substances that dis-

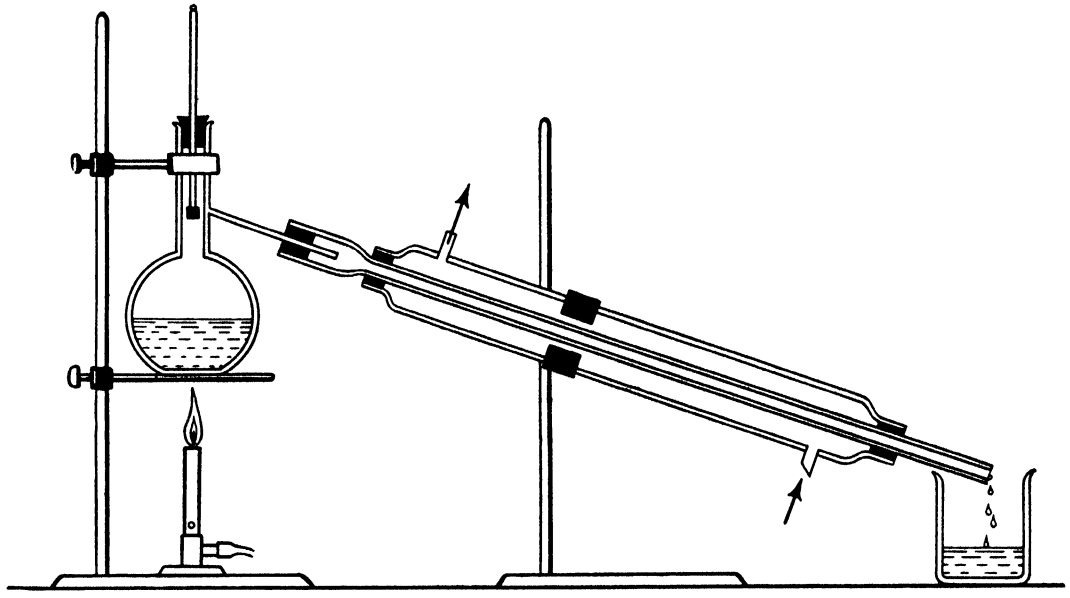


Figure 139. Distillation of Water

Dissolved and suspended solids can be separated and practically pure water obtained by distillation. Cold water is passed through the jacket of the condenser to convert steam into the liquid.

color the water. The complete removal of bacteria by filtration is not necessary, if the water is treated with chlorine. A high-speed filtration plant will supply about 125,000,000 gallons of filtered water daily per acre of surface. This is almost fifty times as much water as can be obtained from a slow filter bed of the same surface.

The construction of a filter bed designed for slow filtration is shown in Figure 140. The seepage of water through the sand leaves behind the mud, clay, and other suspended material including most of the bacteria. The slime which gathers on the surface of the sand aids materially in increasing the efficiency of the filter. The water which finally emerges from the lower layers of gravel finds its way into drain pipes made of porous tile. Through these pipes it is led to the pumping station from which it is forced out into the city's mains.

Aluminum sulfate, $Al_2(SO_4)_3$, is often added to water in the settling basins or filters. This substance reacts with water to form aluminum hydroxide, a gelatinous solid, which slowly settles, carrying down with it much of the suspended material.

$$(2\ Al^{+++} + 3\ SO_4^{=}) + 6\ HOH \longrightarrow 3\ (2\ H^+ + SO_4^{=}) + 2\ Al(OH)_3{}^1 \downarrow .$$

The aluminum hydroxide also settles out on the surface of the filter beds and aids in the removal of bacteria.

12. Purification of Water by Chemical Treatment

The use of chlorine to kill bacteria in drinking water and in swimming pools is now a common practice in almost every community of any size in this country. Its use depends upon its efficiency as a disinfectant, its low cost, and the small quantity required. Not more than 0.7 part of chlorine is required to kill all the bacteria in a million parts of water.

[1] The precipitate is probably hydrous aluminum oxide (page 126), which consists of Al_2O_3 combined with a rather indefinite quantity of water: $Al_2O_3 \cdot x\ H_2O$.

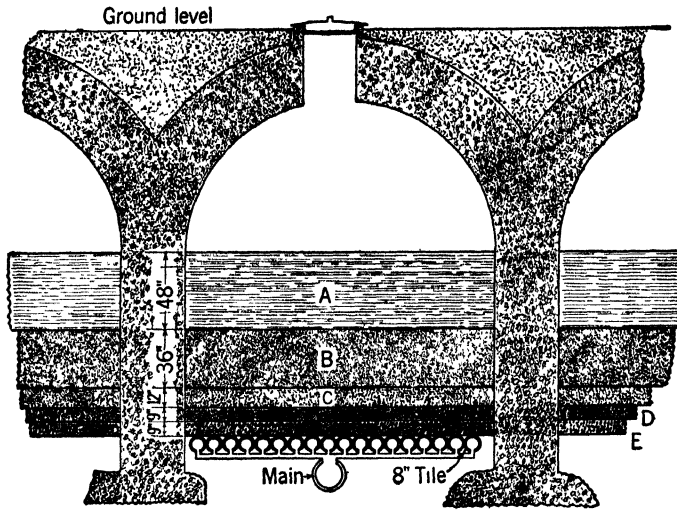


Figure 140. The Construction of a Filtration Bed
A, water; B, fine sand; C, D, E, coarse sand and gravel.

The use of chlorine for the disinfection of water in this country dates from about 1913. Prior to that time, bleaching powder ($CaOCl_2$) had been used in many places. The effect of chlorination has been most pronounced in the reduction of the death rate from typhoid fever. In many cities the death rate from this cause was reduced by 75 per cent or more immediately after treatment with chlorine was introduced. Sometimes ammonium chloride or ammonium sulfate is added along with chlorine to form *chloramine*, NH_2Cl, which also is a powerful bactericide and is said to produce less disagreeable odor and taste than sometimes result from the use of chlorine alone.

CHEMICAL PROPERTIES

13. The Stability of Water

Even at a very high temperature, heat decomposes water only slightly. If water vapor is heated in a closed tube at a definite temperature for some time, a state of equilibrium is attained when oxygen and hydrogen combine at the same rate as water vapor decomposes. At 1500° C., less than 0.2 per cent of the water vapor is decomposed under the conditions of equilibrium. As the temperature increases, the percentage of undecomposed water vapor in the equilibrium mixture gradually decreases, but even at 2000° C., only about 11 per cent is decomposed.

14. Reaction of Water with Oxides

We have previously (page 126) referred to the reaction of water with the oxides of the metallic elements to form bases,

$$CaO + HOH \longrightarrow (Ca^{++} + 2\ OH^{-}),$$

and with the oxides of non-metallic elements to form acids,

$$CO_2 + H_2O \longrightarrow H_2CO_3.$$

15. Hydrolysis

A double decomposition in which one of the reacting substances is water is called *hydrolysis*. In such reactions water reacts with certain salts and with analogous compounds of the non-metals as, for example, phosphorus trichloride:

$$2\ HOH + (2\ Na^+ + S^{=}) \longrightarrow 2\ (Na^+ + OH^-) + H_2S.$$

$$6\ HOH + (2\ Al^{+++} + 3\ S^{=}) \longrightarrow 2\ Al(OH)_3\downarrow + 3\ H_2S.$$

Since the aluminum ion, like the hydrogen ion in H_3O^+, is hydrated the exact formula of aluminum hydroxide is probably $Al(H_2O)_3(OH)_3$.

The hydrolysis of phosphorus trichloride is shown by the following equation:

$$PCl_3 + 3\ HOH \longrightarrow 3\ (H^+ + Cl^-) + P(OH)_3.$$

The hydroxide of phosphorus as shown in the above equation acts as a weak *acid* and, therefore, its formula is usually written as H_3PO_3 (page 53).

16. Water as an Acid and a Base

In reacting with the sulfides of sodium and aluminum water supplies protons which combine with sulfide ions and, therefore, may be said to react as an acid (page 121). It also acts as an acid when it reacts with ammonia, because it supplies protons which convert NH_3 into NH_4^+:

$$NH_3 + HOH \longrightarrow NH_4^+ + OH^-.$$

It acts as a base and accepts protons from an acid in forming hydronium ions in a solution of a substance such as hydrogen chloride:

$$HCl + HOH \longrightarrow H_3O^+ + Cl^-.$$

17. Water as an Oxidizing Agent

We have shown (page 60) that magnesium will burn in an atmosphere of steam, forming magnesium oxide and liberating hydrogen. Steam also oxidizes hot iron, forming the magnetic oxide of iron and hydrogen (page 70). Steam oxidizes carbon when it is passed over or through redhot coke (page 70) with which it reacts to form carbon monoxide and hydrogen in the production of water gas. These are examples of oxidation in which water acts as the oxidizing agent.

HYDRATES

18. The Composition and Properties of Hydrates

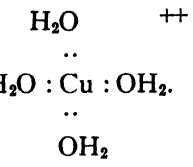
Hydrates are defined as substances containing *water molecules* combined in definite proportions with elements, ions or compounds. Most of the familiar hydrates are compounds of *salts* and water. The crystals of *blue vitriol* are composed of the hydrate, $CuSO_4.5\ H_2O$. Other examples of hydrates of salts are $ZnSO_4.\ 7\ H_2O$; $CrCl_3.\ 6\ H_2O$; $Na_2CO_3.\ 10\ H_2O$; $CoCl_2.6\ H_2O$; and alum, $K_2Al_2(SO_4)_4.24\ H_2O$. In each of these formulas the period (.) is used to indicate the chemical combination of the water with the salt.

Hydrates possess certain properties which are very much different from those of the *anhydrous* (unhydrated) compounds. Some salts combine with water to form more than one hydrate, each of which possesses specific properties, such as melting point, color, solubility, and specific gravity. Thus, anhydrous copper sulfate is a white compound, but the hydrate, $CuSO_4.\ 5\ H_2O$, is blue. Cobalt chloride is blue, when it is not hydrated, but the hydrate, $CoCl_2.6\ H_2O$, is red. The two hydrates of nickel sulfate, $NiSO_4.\ 6\ H_2O$ and $NiSO_4.\ 7\ H_2O$, are blue and green respectively. Because of these differences in properties and because of their definite composition, hydrates must be regarded as true compounds. The properties of the *solutions* of the substances are the same, however, when either the hydrate or the anhydrous compound is dissolved. Probably, only the hydrate exists in solution.

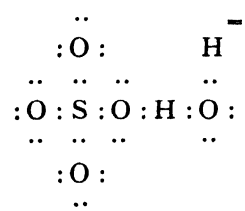
19. The Structure of Hydrates

How are the molecules of water held in hydrates? It is probable that in some hydrates of salts molecules of water are at-

tached by coordinate covalent bonds between the oxygen atoms of water and the ions of the metal. A metallic ion has no electrons in its valence shell, and, therefore, can share unused pairs of electrons belonging to the oxygen atoms of water molecules. For example, the cupric ion Cu^{++} may combine with molecules of water as shown below:



In some hydrates, no doubt, water molecules may be attached to an ion of the salt by means of hydrogen bonds. For example, in the hydrate $CuSO_4.5\ H_2O$ four molecules of water may be attached to the cupric ion in the manner described above, and the fifth molecule may be attached through a hydrogen bond to an oxygen atom of the sulfate ion:



The ions of salts are, no doubt, also hydrated when the salts are dissolved in water. However, the number of water molecules combined with each ion cannot be determined, and, therefore, it is the usual practice not to indicate any hydration when we write equations for reactions in which such ions are involved. For example, in speaking of the cupric ion in a solution of cupric sulfate, we indicate the ion by the simple formula Cu^{++}.

20. Efflorescence

When some hydrates are placed in an open vessel at room temperature (about 21° C.) they lose water to the atmosphere around them, while others do not. The hydrates that lose water to the atmosphere to which they are exposed are said to effloresce and the process is called *efflorescence.*

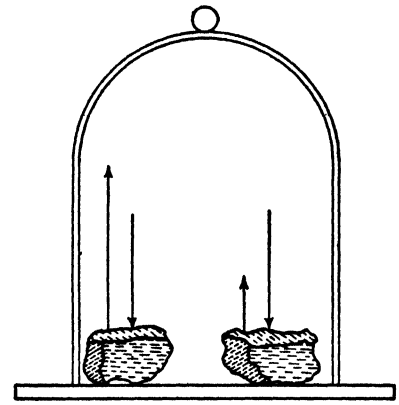


Figure 141. Efflorescence of Hydrates

The dissociation pressure of the crystal on the left is greater than the aqueous vapor pressure. This crystal will lose moisture to the air. The one on the right will not.

The different behaviors of hydrates referred to above depend upon differences in their dissociation pressures. The dissociation to which we refer here is the reaction by which the hydrate loses water and forms another hydrate containing relatively less water or the anhydrous (unhydrated) compound. If, for example, cupric sulfate pentahydrate, $CuSO_4.5\ H_2O$, is placed in a closed vessel which is evacuated, it loses water producing some of the trihydrate, $CuSO_4.3\ H_2O$. As water is lost by the pentahydrate, it collects in the vessel as water vapor thus producing a vapor pressure above and around the two hydrates. At room temperature water vapor will collect until the pressure that it exerts amounts to about 9 mm. of mercury, and the aqueous vapor pressure in the vessel containing the two hydrates is in equilibrium with them. Now if the pentahydrate is placed in an open vessel at 25° C., it is not likely that it will lose any water, because the partial pressure of the water vapor in the air at this temperature is usually higher than 9 mm. If, however, the sample of the

pentahydrate is heated, the aqueous vapor pressure required for equilibrium will soon exceed the partial pressure of water vapor in the air, at which time water will be lost, and the trihydrate will be formed.

On the other hand, crystals of sodium sulfate decahydrate, $Na_2SO_4.10\,H_2O$, when placed in the open air at 25° C., effloresces very readily. Crystals crumble, forming very small crystals or grains of the anhydrous salt, Na_2SO_4. This behavior is explained by the fact that the partial pressure of water vapor in the air is lower than the aqueous vapor pressure — the dissociation pressure of the hydrate — required for equilibrium.

The efflorescence of a hydrate, therefore, may be expected if the partial pressure of the water vapor in the air around the hydrate is less than the aqueous vapor pressure required for a state of equilibrium between the hydrate and its dissociation product.

21. Other Examples of Hydrates

Some acids and a few bases which are solids at ordinary temperatures form hydrates. Among these may be mentioned the hydrates of oxalic acid, $H_2C_2O_4.2\,H_2O$, and barium hydroxide, $Ba(OH)_2.8\,H_2O$. Many minerals are hydrated in their natural states. Ordinary clay, for example, contains large amounts of the hydrate, $H_2Al_2(SiO_4)_2.H_2O$, called kaolin. Asbestos, talc, soapstone, and mica are hydrated magnesium silicates. Carnallite, an important mineral because of its potassium content, is $KCl.MgCl_2.6\,H_2O$. Schoenite is $K_2SO_4.MgSO_4.6\,H_2O$. The mineral, gypsum, is a hydrate of calcium sulfate, $CaSO_4.2\,H_2O$, and Plaster of Paris, another hydrate of calcium sulfate made by heating gypsum, is $(CaSO_4)_2.H_2O$. Sulfuric acid forms several hydrates, one of which is $H_2SO_4.H_2O$. The element, chlorine, forms the hydrate $Cl_2.8\,H_2O$. The hydronium ion, H_3O^+, is an example of a hydrated ion.

HYDROGEN PEROXIDE

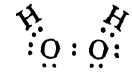
22. Peroxides

Hydrogen peroxide, H_2O_2, belongs to a class of substances called peroxides, of which sodium and barium peroxides, Na_2O_2 and BaO_2, are other examples. In the peroxides of the metals the O_2 group acts as an ion with a valence number of -2. Thus, when BaO_2 reacts with sulfuric acid,

$$(Ba^{++} + O_2^{=}) + (2\,H^+ + SO_4^{=}) \longrightarrow BaSO_4\downarrow + H_2O_2.$$

the $O_2^{=}$ ion displays a behavior very much like that of the sulfate ($SO_4^{=}$) ion. The peroxides differ in this respect from ordinary oxides, which react with acids to form salts and water. Since the O_2 group acts as a divalent radical, it is apparent that the valence of hydrogen in hydrogen peroxide is the same as in water, and that of barium in barium peroxide is the same as in the oxide BaO. There are oxides, such as MnO_2 and PbO_2, which resemble the peroxides only with respect to their formulas. They are not peroxides. The valence number of lead and manganese in these compounds is $+4$, and the oxides react with acids to form water, not hydrogen peroxide.

In terms of the electron theory of valence, the structure of hydrogen peroxide is



The angle between each of the O—H bonds and the O—O bond is 110°.

23. Production

A dilute solution of hydrogen peroxide in water can be prepared by the action of sulfuric or phosphoric acid upon barium peroxide:

$$3\,(Ba^{++} + O_2^{=}) + 2\,H_3PO_4 \longrightarrow Ba_3(PO_4)_2\downarrow + 3\,H_2O_2.$$

Since barium sulfate and barium phos-

phate are only slightly soluble, they can be removed by filtration. The hydrogen peroxide remains in the filtrate. A concentration of 25–30 per cent of hydrogen peroxide can be obtained by cautiously distilling this solution under greatly reduced pressure. In the laboratory such procedures may be very dangerous and should not be undertaken by the student.

Hydrogen peroxide is also produced by the electrolysis of a solution of sulfuric acid at a low temperature. In this reaction HSO_4^- ions ($H_2SO_4 \longrightarrow H^+ + HSO_4^-$) are probably converted into persulfuric acid, $H_2S_2O_8$, which then reacts with water to form sulfuric acid and hydrogen peroxide. Hydrogen peroxide is also produced from the potassium and ammonium salts of persulfuric acid, e.g., $(NH_4)_2S_2O_8$. Hydrogen peroxide can be extracted from its aqueous solutions by ether in which it is much more soluble than in water. Evaporation of the ether leaves nearly pure hydrogen peroxide.

24. Properties

Above its melting point (0.89° C.), pure hydrogen peroxide is a slightly blue, syrupy liquid. As compared with water, its density is 1.44 times as great. Its boiling point at 760 mm. is 151° C.

Chemically, the substance is characterized by its limited stability. It decomposes readily into water and oxygen:

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2 + 47{,}800 \text{ calories.}$$

The rate of decomposition depends upon the concentration, the temperature, and the presence of certain catalysts. The pure compound may decompose explosively. Decomposition is very slow at room temperature in dilute solution. For this reason, it is usually supplied for use as a 3 per cent solution. This solution usually contains a small amount of an acid or an organic compound (often acetanilide), which acts as a retarder of decomposition. A base, such as sodium hydroxide, acts as a positive catalyst in the decomposition. Finely divided platinum, manganese dioxide, silver, saliva, and blood, also accelerate the decomposition.

Hydrogen peroxide is a vigorous oxidizing agent, and is frequently used as a bleaching agent for silk, wool, ivory, fats, feathers, and hair and as a germicidal agent and antiseptic. Illustrations of its oxidizing action are shown by the following equations:

$$H_2S + H_2O_2 \longrightarrow S + 2\ H_2O.$$
$$PbS + 4\ H_2O_2 \longrightarrow PbSO_4 + 4\ H_2O.$$

The oxidation number of oxygen in hydrogen peroxide is -1; one pair of electrons is shared by the two atoms of oxygen. When H_2O_2 acts as an oxidizing agent, oxygen is reduced to -2. In a few reactions oxygen is liberated as the free element. In such cases, hydrogen peroxide acts as a reducing agent. The most familiar example of this behavior is the reaction:

$$2\,(K^+ + MnO_4^-) + 3\,(2\,H^+ + SO_4^{=}) + 5\,H_2O_2 \longrightarrow$$
$$2\,(Mn^{++} + SO_4^{=}) + 5\,O_2 + (2\,K^+ + SO_4^{=}) + 8\,H_2O.$$

The oxidation number of oxygen is increased from -1 in H_2O_2 to 0 in free oxygen, while the oxidation number of manganese is reduced from $+7$ to $+2$.

Hydrogen peroxide also acts as a weak acid to form both an acid salt and a normal salt:

$$H_2O_2 + (Na^+ + OH^-) \longrightarrow (Na^+ + HO_2^-) + H_2O$$
$$H_2O_2 + 2(Na^+ + OH^-) \longrightarrow (2\ Na^+ + O_2^{=}) + 2\ H_2O.$$

25. Test for Presence

When hydrogen peroxide is added to a solution of potassium dichromate acidified with sulfuric acid, a bright blue compound, probably peroxychromic acid, is produced. The blue compound is extracted from the aqueous solution by ether in which it is more soluble and also more lasting. Hydrogen peroxide also liberates iodine from an iodide; and hence, the test for ozone (page 56) may also be used to detect its presence.

REVIEW EXERCISES

1. What weight of water at 100° C. can be evaporated by the heat that is liberated when 10 pounds of water freeze?

2. How does the density of water vary at temperatures between 0° and 100° C.? Why does a body of water freeze from the top downward?
3. What kinds, or classes, of impurities are found in water? What are the sources of these substances?
4. What impurities are objectionable? Why are they objectionable?
5. What is "hard" water? Why does soap not produce a lather in it?
6. Describe the process called distillation.
7. Why does live steam produce more serious burns on the flesh than boiling water?
8. How does aluminum sulfate react with water? How is it used in the purification of water supplies?
9. How does water react with sodium sulfide and aluminum sulfide? Define hydrolysis.
10. Define hydrate. How does a hydrate differ from a hydroxide?
11. What evidence shows that hydrates are definite compounds?
12. What weight of water is contained in one pound of sal soda, or washing soda, $Na_2CO_3 \cdot 10\ H_2O$?
13. What loss in weight occurs in converting a ton of pure gypsum into Plaster of Paris?
14. A sample of hydrated magnesium sulfate weighing 15 g. was heated until all the water was expelled. The anhydrous magnesium sulfate weighed 7.32 g. What is the formula of the hydrate?
15. How would you explain his loss to a grocer who bought washing soda at 8 cents per pound, stored it in an open bin, sold it all at 10 cents per pound, but lost money?
16. What nine kinds of water molecules are present in ordinary water?
17. What is the maximum volume (measured at 0° and 760 mm.) of oxygen that could be obtained from 100 g. (approximately 100 cc.) of 3 per cent hydrogen peroxide solution?
18. Why is sulfuric acid preferred to hydrochloric in preparing hydrogen peroxide from BaO_2?
19. How does a peroxide differ from an ordinary oxide? Why should manganese dioxide, MnO_2, not be called manganese peroxide?
20. What weight of hydrogen peroxide can be produced by treating 500 g. of barium peroxide with sulfuric acid?
21. By what experimental method other than those mentioned in Section 25 could you readily determine that a liquid is a solution of hydrogen peroxide rather than pure water?
22. Suggest possible ways in which the molecules of water in the following hydrates may be combined with the ions of the salts:
    $Mg\ Cl_2.6\ H_2O$; $Mg\ SO_4.7\ H_2O$.
23. Why do some hydrates lose moisture when they are exposed to the atmosphere while others do not?
24. When hydrogen peroxide decomposes into water and oxygen what changes in oxidation numbers occur?

REFERENCES FOR FURTHER READING

Dorsey, N. E., *Properties of Ordinary Water.* New York: Reinhold Publishing Company, 1940.

Suckling, E., *Examination of Water and Water Supplies.* Philadelphia: P. Blakiston's Son and Company, 1943.

Woodman, A. G., and J. F. Norton, *Air, Water, and Food,* 4th ed. New York: John Wiley and Sons, 1930.

Hydrogen Peroxide: *Chem. Age,* **39,** 291 (1938); *Chem. Products,* **1,** 150 (1939); *J. Am. Chem. Soc.,* **44,** 2472 (1922); *J. Ind. Eng. Chem.,* **14,** 181 (1922); **22,** 1234 (1930); *J. Chem. Ed.,* **21,** 300 (1944).

Water: *J. Chem. Ed.,* **5,** 1163 (1928); **16,** 440 (1939); **18,** 18 (1941); **25,** 401 (1948); (Heavy Water) **18,** 552 (1941); *Chem. and Met. Eng.,* **38,** 516 (1931); **48,** 100 (1941); *J. Ind. Eng. Chem.,* **29,** 615 (1937); **33,** 1046 (1941); *J. Soc. Chem. Ind.,* **43,** 41 (1938); **44,** 266 (1939); *Chem. and Eng. News,* **21,** 1046 (1943).

15

SOLUTIONS

1. Introduction

In this chapter we shall study the physical properties and general nature of solutions, the effects of the dissolved substances upon the properties of the substance in which they are dissolved, and some of the ways in which solutions can be made to serve in the work of the chemist.

2. Solutions are Mixtures

There are several reasons why solutions must be classified as mixtures rather than compounds, but, perhaps, it will be sufficient at this time to mention only one of these. The composition of a solution is not definite. Thus, we may dissolve 1 g. or any amount up to about 36 g. of salt in 100 g. of water, and we can dissolve 1 ml., or 100 ml., or any volume for that matter, of water in 100 ml. of alcohol, because these two substances are miscible in all proportions.

A solution is defined, therefore, as a mixture, but it is evident that it is a special kind of mixture. It is composed of molecules, or molecules and ions, of two or more substances. A mixture of sand and water or one of sugar and sand is *non-homogeneous*. This means that one sample removed from such a mixture is not exactly like another sample. The two components are not distributed uniformly throughout the mixture. The composition of a solution, however, is *homogeneous*, for all practical purposes, because we cannot observe and we cannot separate the molecules of a solution as we can the large particles of sugar and sand in a mixture of these materials. A solution is not actually homogeneous in the same sense as a compound, which is composed of a single kind of molecule.

A solution can be defined, therefore, as a homogeneous mixture of two or more substances, the proportions of which can be varied usually only within certain limits. We have carefully used the phrase "varied *usually* only within certain limits." A solution of salt in water can be varied in composition up to about 37 g. of sodium chloride in 100 g. of water at 30° C., but in a solution of ethyl alcohol and water the two liquids can be mixed in any proportions.

Our definition of a solution does not mean that all solutions of sugar and water, for example, have the same composition; a sample of *one* solution of sugar in water, however, does have the same composition as any other sample of that solution provided the components have been thoroughly mixed, or the solution has been allowed to stand until the sugar has diffused throughout the volume of the solution. Another solution of sugar, however, is likely to have an entirely different composition.

3. The Components of a Solution

The components of a solution are referred to as the *solvent* and the *solute*. The

former is the component of the mixture that is present in the greater amount. We also think of the solvent, in most cases, as the medium in which the molecules of the solute are scattered and which has the same physical state as the solution. Sometimes, however, it is impossible to say which of the components is the solvent and which the solute. This question arises, for example, in a solution of water and alcohol containing 50 per cent of each. The terms are used only for convenience and there is no fundamental difference in the rôles that solute and solvent play in forming the solution.

4. Classes of Solutions

Usually, when we speak of solutions, we have in mind solutions of solids in liquids. However, since solutions are homogeneous mixtures, their composition is not limited to mixtures of these two states of matter. Theoretically, we should be able to produce the following kinds of solutions, which are distinguished by differences in the physical states of the solutes and solvents:

(1) Gases in gases.
(2) Gases in liquids.
(3) Gases in solids.
(4) Liquids in liquids.
(5) Liquids in solids.
(6) Solids in solids.
(7) Solids in liquids.
(8) Liquids in gases.
(9) Solids in gases.

Examples of these nine classes of solutions are listed below:

(1) All mixtures of gases are solutions, since they are homogeneous.

(2) The water that we drink contains oxygen, nitrogen, and carbon dioxide in solution.

(3) The hydrogen absorbed by platinum and palladium may be thought of as dissolved in the metals.

(4) Water and ethyl alcohol are miscible in all proportions.

(5) Mercury dissolves in gold to form a solution of a liquid in a solid.

(6) A solution of a solid in a solid is called a *solid solution*. Gold and silver form such a solution when they are melted together, and the solution is allowed to solidify. Many alloys contain solid solutions of metals in one another, and some minerals are solid solutions of compounds.

(7) Solutions of solids in liquids are well known.

(8) We may regard a mixture of air and water vapor as a solution of a liquid in a gas, since at the temperature of the air water is normally a liquid.

(9) A mixture of air and sulfur vapor may be regarded as a solution of a solid in a gas.

CONCENTRATION OF SOLUTIONS

5. Concentration and How It is Expressed

The *concentration* of a solution may be expressed as the quantity of solute in (1) a definite volume of the solution; (2) a definite volume of the pure solvent; or (3) a definite weight of the solvent. Thus, we may express the weight of the solute as grams in 100 ml. of the solution, in 100 ml. of the pure solvent, or in 100 g. of the solvent.

6. Molar Solutions

Concentration is very often expressed as the number of gram-molecular weights of the solute in one liter of the solution. A solution containing one gram-molecular weight of any solute in one liter of solution is a *molar* (*1 M*) solution. It is evident, of course, that a solution containing two gram-molecular weights in two liters has the same concentration as a solution containing one gram-molecular weight in one liter or one tenth of a gram-molecular weight in one-tenth liter. A solution of which one liter contains two gram-molecular weights of solute is a two molar (2 M) solution, and one containing one tenth of a gram-molecular weight in one liter is a one-tenth molar (0.1 M) solution.

7. Normal Solutions

When we *compare* one solution with another, we must express the concentrations so that equal volumes of solutions of the

TABLE 5

THE NORMALITY OF SOLUTIONS

Substance	Concentration 1 N		Other Solutions		
	Mol. Wt.	Weight per Liter of 1 N Solution	Weight per Liter	Normality	Molar Concentration
Barium hydroxide ($Ba(OH)_2$)	171.39	85.695	21.424	$\frac{1}{4}$ N or $\frac{N}{4}$	$\frac{1}{8}$ M
Sodium sulfate (Na_2SO_4)	142.064	71.032	7.103	$\frac{1}{10}$ N or $\frac{N}{10}$	$\frac{1}{20}$ M
Sodium chloride (NaCl)	58.46	58.46	29.23	$\frac{1}{2}$ N or $\frac{N}{2}$	$\frac{1}{2}$ M
Sulfuric acid H_2SO_4	98.06	49.008	9.8	$\frac{1}{5}$ N or $\frac{N}{5}$	$\frac{1}{10}$ M

same concentration are equivalent in the sense that they will react with the same quantity of a third substance. This is not true of all molar solutions; one liter of molar sulfuric acid, for example, is equivalent to two liters of molar hydrochloric acid solution in the reaction with sodium hydroxide. If concentration is expressed as the number of *equivalent* weights of the solute per liter, equal volumes of the solutions of different substances will react with each other or with the same volume of the solution of a third substance. A solution containing one gram-equivalent weight of the solute per liter is a *normal* (*1 N*) solution. Concentrations are usually expressed according to this system as N, 2 N, 10 N, 0.1 N, or $\frac{N}{10}$, etc.

8. Molal Solutions

Concentration is also expressed as the number of gram-molecular weights, or the fraction of a gram-molecular weight, of the solute dissolved in 1000 g. of solvent. A solution containing 1 gram-molecular weight in 1000 g. of solvent is said to have a concentration of one *molal* (1 m). In very dilute solutions one liter of (aqueous) solution and 1000 g. of water are almost identical, but in concentrated solutions there is considerable difference between the two.

9. Standard Solutions and Titrations

A *standard solution* is one that contains a definite and known concentration of solute. The use of standard solutions is illustrated by the following example. Let us say that we wish to find the concentration of a solution of hydrochloric acid, i.e., we wish to find the *normality* of the solution. A definite sample of the solution is measured out in a beaker from a burette, Figure 143, or a pipette, Figure 144. A few drops of the solution of an indicator are then added, and a standard solution of a base is added until the change in color of the indicator shows that the acid has been neutralized.

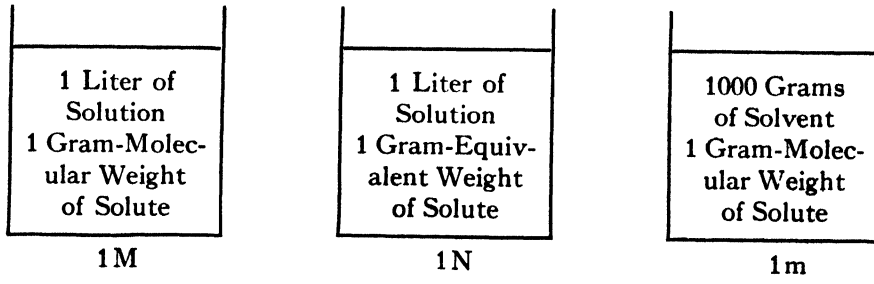


Figure 142
Comparison of 1 Molar, 1 Normal, and 1 Molal Solutions

If the sample of acid consists of 20 ml. and if 40 ml. of normal sodium hydroxide solution are required for the neutralization, the solution of the acid is obviously twice as concentrated (2 N). As another example, let us say that 20 ml. of the solution of the acid are neutralized by 15 ml. of the normal solution of NaOH. From the volumes of the two solutions it is evident that the concentration of the acid (expressed in terms of normality) is $\frac{15}{20}$ that of the base, or $\frac{3}{4}$ N, or

$$\frac{\text{Volume of solution of base}}{\text{Volume of solution of acid}} = \frac{\text{Normality of acid}}{\text{Normality of base.}}$$

The process of analyzing a solution in this manner is a common *volumetric* analytical method and is called *titration*. The *end-point* of the titration is reached when chemically equivalent quantities of acid and base have been brought together.

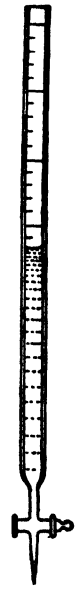


Figure 143. A Burette

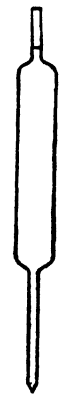


Figure 144. A Pipette

SATURATION

10. Equilibrium between Solution and Undissolved Solute

A solute reaches a state of equilibrium with its solution, if it is added in excess of the quantity that will dissolve. Let us consider the solution of a solid in a liquid. Molecules, or other particles, enter the solution from the surface of the solid (Figure 145). As a result of collisions with molecules of the solvent and with the walls of the vessel, the particles of the solute move in all directions within the solution, and, therefore, some of them eventually come into contact with the surface of the solid, and of these a certain number will be caught and held by the same forces that originally held them in the crystal. Equilibrium between the solid and its solution is reached when particles enter the solution and return to the solid from the solution at the same rate.

11. Saturated Solution: Solubility

The equilibrium between the undissolved portion of a substance and its solution requires that the solute be present in both conditions, dissolved and undissolved. A

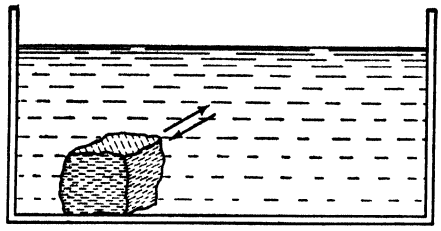


Figure 145. The Conditions Required for Saturation: The Equilibrium between the Solution and Undissolved Sodium Chloride

saturated solution is defined, therefore, as one that is in equilibrium with the undissolved solute. The quantity of solute, per unit volume, of a saturated solution is called the *solubility* of the solute and is expressed, usually, as grams per 100 ml. or as gram-molecular weights per liter. It varies with the temperature, and for solutions of gases in liquids especially, depends upon the pressure.

12. Supersaturation

If a solution saturated with a solid solute at a moderately high temperature is separated from the excess of solute, and cooled to a lower temperature, it will then contain, usually, more of the solute per unit of volume than corresponds to the solubility. We should expect the excess of the solute to separate from the solution as the temperature falls, and in most cases this occurs. If it does not, the solution at the lower temperature will contain more of the solute than a solution that is saturated at the same temperature. The condition of the solution is then described as *supersaturated.*

Supersaturation is not difficult to understand, when we take into consideration the character of the solid, crystalline state. As previously shown, particles of the solid are arranged in regular patterns. Now if a small crystal of sodium chloride (Figure 146) is in contact with a solution, particles of the solute may leave the solution and join the structure already existing. But if there is no such structure, then a certain number of particles must simultaneously come into the positions required to establish the first unit of crystalline growth. Until a portion of the solid structure is begun it is evident, therefore, that the solution may contain at least for a time a greater concentration of the solute than corresponds to the actual solubility. The addition of a very small crystal of the solute starts crystallization. Small particles may break away from the first crystal that forms and act as units of crystallization in other parts of the solution. The addition of other kinds of crystals — especially those having the same type of lattice — shaking the solution, and scratching the inner wall of a glass vessel containing the solution are other methods sometimes used to start the separation of the solid. A scratch on the vessel's walls may leave an irregular array of molecules that attract molecules of the solute from the solution in the same manner that crystals of the solute, itself, attract them.

CONDITIONS THAT INFLUENCE SOLUBILITY

13. Effect of Pressure and Temperature upon the Solubility of Gases and Liquids

The only solutions in which the quantity of solute that dissolves in a definite volume or weight of the solvent is influenced appreciably by pressure are solutions of gases

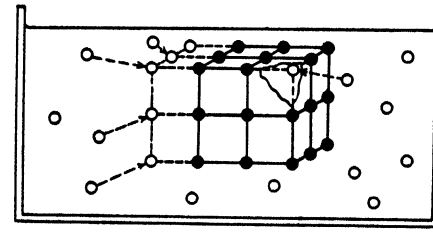


Figure 146. Supersaturation is Impossible in the Presence of the Undissolved Solute

Sodium and chloride ions in this solution of sodium chloride may join the ions composing the crystal that already exists, thus causing the crystal to grow and making a supersaturated solution impossible.

TABLE 6

SOLUBILITY (IN GRAMS) OF GAS IN 100 GRAMS OF WATER (PRESSURE, 760 MM.)

Gas	0°	10°	20°	40°	60°	80°	100°
Nitrogen	0.00294	0.00231	0.0019	0.0014	0.0011	0.00066	0.0000
Oxygen	0.00695	0.0054	0.00434	0.0036	0.00227	0.0014	0.0000
Hydrogen	0.00019	0.00017	0.00016	0.00015	0.00012	0.00008	0.0000
Carbon dioxide	0.335	0.232	0.169	0.126	0.058		
Hydrogen sulfide	0.707	0.511	0.385	0.236	0.148	0.076	0.0000
Sulfur dioxide	22.83	16.21	11.28	5.41			

dissolved in liquids or in solids. Henry's Law states the effect of the pressure of a gas upon its solubility in a liquid with which it is in contact: *The weight of any gas that dissolves in a definite volume of a liquid is directly proportional to the pressure that the gas exerts above the liquid at a constant temperature.* For every gram of a gas that dissolves in 100 ml. of water under one atmosphere of pressure, temperature remaining constant, 10 g. will dissolve if the pressure is increased to 10 atmospheres. The effect of pressure is greatly modified if a chemical reaction occurs between the gas and the solvent. Henry's law applies with a fair degree of accuracy for gases that are not very soluble.

The most familiar example of the effect of increased pressure upon the solubility of a gas in a liquid is *soda water* or any other carbonated beverage. The quantity of gas that dissolves in a definite volume of the liquid is increased by forcing the gas into the liquid under pressure. When the solution is bottled, the cap prevents the escape of carbon dioxide and maintains the pressure of the gas in the space above the surface of the liquid. When the cap is removed, the gas escapes from the space above the liquid, thus reducing the pressure. The gas in solution then escapes as bubbles, because it is not as soluble when the pressure is reduced.

The quantity of a gas that dissolves in a definite quantity of a liquid decreases as the temperature of the liquid rises. For example, bubbles of air collect on the inside walls of a vessel containing cold water that is brought into a warm room and allowed to stand until the water reaches the temperature of the room, because more air was dissolved in the water when it was cold than can dissolve at the higher temperature. If the liquid is heated to the boiling point, almost all of the dissolved gas is rapidly expelled along with the steam. The solubilities of different gases in water at different temperatures are shown in Table 6 on this page. When a gas is dissolved in a liquid, its physical state is changed to that of the liquid. You will recall that energy is absorbed when a liquid evaporates and is liberated when the vapor condenses. Hence, the solution of a gas in a liquid is an endothermic process, and, therefore, we should expect gases to be less soluble as the temperature rises.

The effect of temperature upon the solubility of liquids in liquids is, generally speaking, rather slight but it may be said that two liquids which are only partially miscible will dissolve one in the other to a slightly greater extent as the temperature increases. When two such liquids are mixed, since both are in the same state, there is little if any absorption or liberation of energy unless a chemical reaction occurs. Therefore, heat has little effect upon solubility in the formation of such solutions.

14. The Effect of Temperature upon the Solubility of Solids in Liquids

The same rise in the temperature of the

solvent may cause great increases in the solubility of some solids, slight increases of others, and even decreases for some. Thus, a change from 0° to 70° causes the solubility of potassium nitrate to change from about 12 g. in 100 g. of water at 0° to 140 g. at 70°. For sodium chloride the solubility over the same range of temperatures varies from 36 g. to 38 g. For calcium hydroxide the solubility in 100 g. of water at 100° is 0.08 g., and at 20° it is 0.165 g.

Variations in the solubilities of different substances with changes in temperature are shown by the curves of Figure 147. For most solutions the curves are smooth, indicating gradual changes in solubility as the temperature increases. This is not always true, however, as shown by the curve for sodium sulfate. At low temperatures the solubility of this substance increases as the temperature increases, but at a temperature of 32.4°, the solubility begins to decrease. This temperature is the transition point at which the hydrate, $Na_2SO_4 \cdot 10\ H_2O$, and anhydrous sodium sulfate, Na_2SO_4, are in equilibrium. The two curves represent the solubilities of two different substances at different temperatures. If a solution of sodium sulfate is evaporated at temperatures below 32.4°, crystals of the hydrate are formed; at higher temperatures, crystals of the anhydrous salt are produced. Breaks in the solubility curves may also result from changes in the crystal structure of the same substance.

In general, the solubility of a solid in a liquid increases as the temperature increases. This behavior is what we might expect, because in dissolving the solid is changed to the liquid state. This change requires an absorption of energy and, therefore, we may expect it to occur more readily when heat is supplied. Sometimes, the solute reacts with the solvent, and heat is liberated in quantities that exceed the quantity absorbed when the solid is changed to the liquid state of the solution. In these solutions, solubility of the solute decreases as the temperature increases.

15. Fractional Crystallization

Variations in the solubilities of different solids in a liquid with the temperature are used in separating the soluble components of a mixture. Let us consider, for example, an aqueous solution containing potassium nitrate and sodium chloride.

How can one of the substances be obtained in a fair state of purity from such a mixture? The solution is evaporated at about 100° until crystallization begins. Since it is least soluble at the high temperature, the crystals that form first are composed of sodium chloride. They are removed by filtration. The filtrate is then cooled to a low temperature, let us say to 0°. Now the solubility of potassium nitrate in 100 g. of water drops from 246 g. at 100° to about 12 or 13 g. at 0°, but the solubilities of the other substances that might crystallize (NaCl, KCl, $NaNO_3$) although they decrease as the temperature is lowered, do not decrease nearly as greatly as the solubility of potassium nitrate. Hence, the first batch of crystals that forms, as the temperature drops, will consist principally of potassium nitrate. If these are dissolved in water, and the solution is again evaporated, filtered, and cooled, the crystals that form will again consist largely of potassium nitrate and will be more nearly pure than those first obtained. By a repetition of this process, almost pure potassium nitrate can be produced. This process is called *fractional crystallization*; it is often used to purify substances that are readily crystallized from solutions.

THE PROPERTIES OF SOLUTIONS

16. Introduction

The properties to which we refer in this section are *vapor pressure, boiling point, freezing point, and osmotic pressure.* We

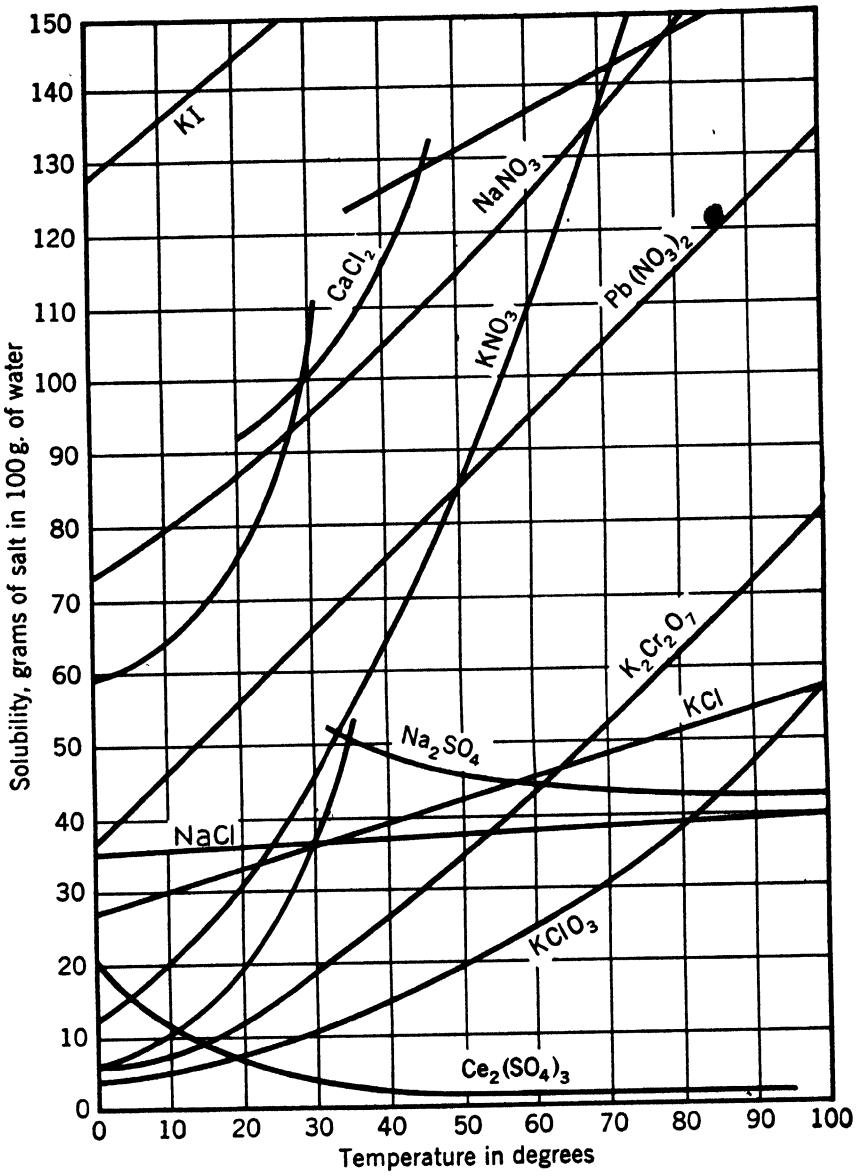


Figure 147. Solubility Curves for Solutions of Salts in Water

might expect these properties to vary from solution to solution, but, strangely enough, the important condition that determines these properties appears to be the *number of particles* of the solute that is mixed with a definite number of molecules of the solvent. Usually, the weight of the solvent is fixed as 1000 g. In 1000 g. of water, for example, there are $\frac{1000}{18} = 55.5$ gram-molecular weights, and therefore $55.5 \times 6.023 \times 10^{23} = 3.34 \times 10^{25}$ molecules. *Now if one gram-molecular weight* (6.023×10^{23} *molecules*) *of any non-electrolyte is dissolved in this weight of water, we find that certain properties of the solution are the same, regardless of the nature of the solute, provided that no change occurs*

except a mixture of the two kinds of molecules.

This statement cannot be applied to solutions of ionic compounds, or to solutions of any electrolyte, because the number of particles in such solutions does not correspond to the number of gram-molecular (or gram-formula) weights of solute dissolved. Thus, a gram-molecular weight of sodium chloride contains $2 \times 6.023 \times 10^{23}$ particles, half of them Na^+ and the other half Cl^- ions.

17. The Vapor Pressure of Solutions

Since a solution is not a chemical compound, it cannot have a characteristic vapor pressure of its own. We should expect the water molecules in an aqueous solution, therefore, to behave very much as they do in the pure solvent, subject of course to certain physical conditions resulting from the presence of the solute, and provided, too, that the solute and solvent do not react and that their molecules have no more attraction for one another than molecules of each kind have for one another. Thus, the water molecules in a solution escape through the surface to produce water vapor, and equilibrium is set up between the vapor and the water in the solution. At a given temperature, however, the pressure of the vapor at equilibrium is always less than the pressure of the vapor in equilibrium with the pure liquid. We assume here that the solute has only a negligible vapor pressure. In dealing with solid solutes this assumption is almost always justified.

Why is the tendency of water to evaporate from a solution less than the tendency of pure water to evaporate? Let us consider a solution of sugar in water. The water molecules that strike the surface probably have almost as much chance of escaping as do those of the pure solvent, if the solution is dilute. It is true, of course, that the chance will not be as great, if the attraction between molecules of water and sugar is strong — stronger than the attraction of water molecules for one another; this attraction, however, does not affect the behavior of water molecules to an extent that is very important so long as the solution is dilute.

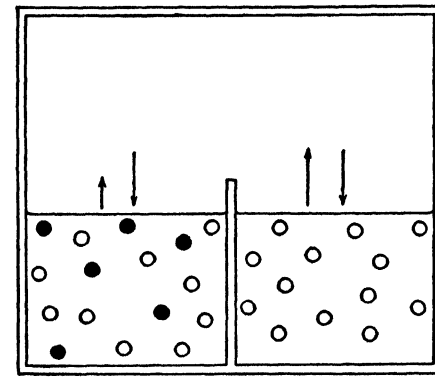


Figure 148. The Vapor Pressures of a Solution (left) and Pure Solvent (right)

Probably of greater significance, in dilute solutions, is the simple effect of sugar molecules in impeding the motion of water molecules, thus decreasing the number that reach the surface in a certain period of time. The sugar molecules do not escape through the surface to form vapor; they act, therefore, as obstacles in the paths of water molecules. If this is a primary cause of the decrease in the vapor pressure of water, the kind of solute molecules has little to do in determining the extent of the effect; and, furthermore, the decrease in vapor pressure should be proportional to the number of molecules of solute that is mixed with a definite number of molecules of solvent.

18. Deliquescence

When crystals of ionic compounds are placed in moist air, some water will condense to form a film of moisture on the surface. If the ions of the crystal have a tendency to form hydrates, such substances will be produced by combinations between the ions on the surface of the crystal and water. If the aqueous vapor pressure of this hy-

drate is small as compared with the partial pressure of the water vapor in the air, moisture will continue to condense, and this water will dissolve the salt, if it is soluble, forming a saturated solution. If the pressure of the water vapor in the air is still greater than the aqueous vapor pressure of the solution, water will continue to condense, diluting the solution and thus allowing more and more of the salt to dissolve. In some instances, solution is complete. Thus, grains of anhydrous calcium chloride form drops of a solution of calcium chloride when they are exposed to the air. Substances which act in this manner to remove moisture from the air, thus forming aqueous solutions, are said to be *deliquescent.* Deliquescence cannot be regarded as the reverse of efflorescence, because it involves, fundamentally, the formation of solutions. Only soluble substances — and not all of them — undergo deliquescence in moist air.

Table salt does not become moist and, therefore, does not "cake" in its container if it contains nothing but pure sodium chloride, which is not deliquescent. The tendency of some samples of salt to become moist is caused by small quantities of impurities which are deliquescent.

19. Raoult's Law

This law is stated as follows: *The lowering of the vapor pressure of a solvent is directly proportional to the weight of the solute dissolved in a definite weight of the solvent.* Raoult's law is also stated sometimes as follows: The vapor pressure of the solvent in a solution is directly proportional to the *mole fraction* of that substance in the solution. The mole fraction of the solvent refers to the fraction (of the whole number of molecules present in the solution) that consists of solvent molecules. Thus, the mole fraction of water molecules in a molal sugar solution (1 g.-mol. wt. of sugar per 1000 g. of water) is $\frac{55.5}{55.5+1} = 0.983$. The vapor pressure of the water in this solution is, consequently, only 0.983 of the vapor pressure of pure water.

20. Ideal Solutions

Raoult's Law as stated above holds exactly only for what we may call *ideal solu-*

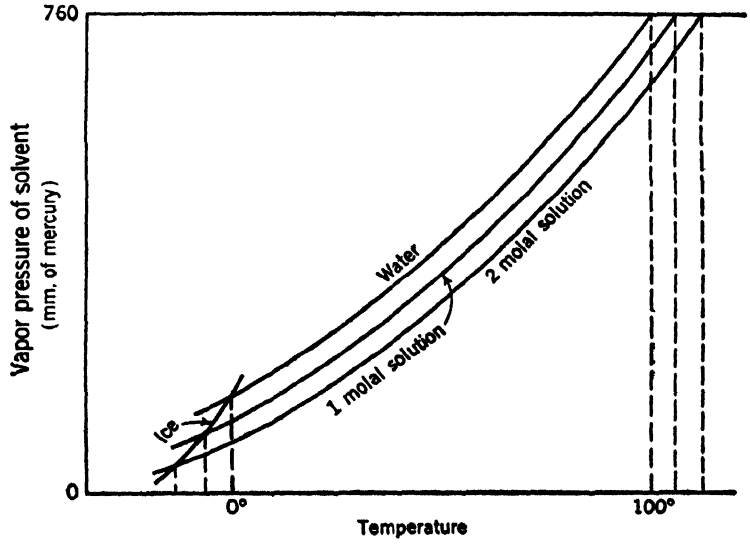


Figure 149. The Effect of a Solute upon the Vapor Pressure of a Solvent

tions; i.e., solutions in which the molecules of solute and solvent are subject to forces no different from those that each kind of molecule exerts upon its own kind.

Needless to say, an ideal solution exists only in the realm of theoretical possibilities, because unless there were some attraction between molecules of solute and solvent, as there is between molecules of the solvent themselves, there would be no reason why the molecules of the solvent should form a mixture with molecules of the solute. There must be some attraction between solute and solvent or they would separate into different layers instead of forming a homogeneous mixture.

There are, however, some solutions that closely approach ideal behavior. Usually, these are solutions in which the molecules of solute and solvent are very much alike, and, therefore, the molecules of the mixture have about the same attraction for one another as the different molecules of each substance have for one another.

21. Vapor Pressures of Mixtures of Liquids: Fractional Distillation

The vapor pressure of a solution composed of two liquids, A and B, varies, at constant temperature, with the composition of the mixture. An ideal solution of this kind would follow Raoult's Law exactly, and there would be a gradual, regular change from the vapor pressure of pure A to that of pure B as shown by the line a in Figure 150. This behavior is approached for certain solutions, especially if they are dilute. Deviations from Raoult's Law sometimes cause the vapor pressure to vary as shown in b; i.e., there is a minimum vapor pressure for some definite composition of the solution; sometimes there is a maximum vapor pressure as shown in c. Curves of the c type may be expected if the two liquids of the solution differ greatly in the polarity of their molecules, because such molecules will not be held together very tightly by their mutual attraction, and, therefore, the partial vapor pressures of the two liquids are relatively high. On the other hand, the deviation may be such as to produce a curve of the b type if the molecules of the two liquids have more attraction for one another than the molecules of each have for their own kind. When this is true, the molecules of the solution have less tendency to pass into the vapor state than do the molecules of each pure liquid.

The boiling point of a solution containing two liquids is the temperature at which the total vapor pressure of the mixture becomes equal to the pressure of the atmosphere. The boiling points of a mixture for which the vapor pressure varies regularly with composition (a of Figure 150) lie along

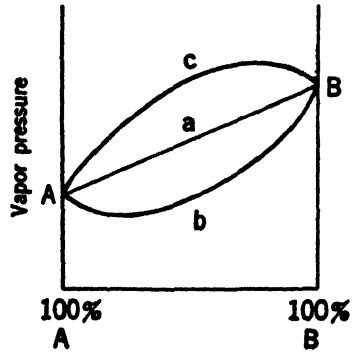


Figure 150

Vapor Pressure at Constant Temperature of a Mixture of Liquids

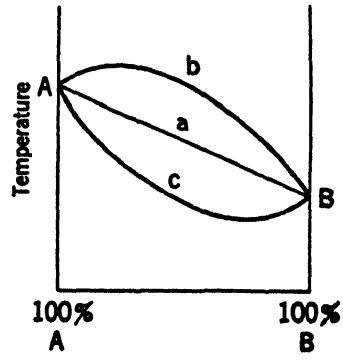


Figure 151

Boiling Temperatures at Constant Pressure of a Mixture of Liquids

a straight line that connects the boiling points of the two pure liquids. For those mixtures that show minima and maxima of vapor pressures (*b* and *c*, Figure 130) for definite compositions of the solutions the boiling point curves (Figure 131) also pass through minima or maxima.

Let us consider a mixture of two liquids for which the vapor pressure varies with composition as shown by *a* (Figure 130). This mixture will begin to boil at a temperature slightly above the boiling point of the lower boiling component, *B*. The vapor produced at the lowest boiling point contains both components but is richer in the lower boiling component than the original mixture. The composition of the mixture is changing continually, and this means that the boiling point also changes. This change is always toward the higher boiling substance, *A*. The vapor contains, therefore, more and more of this component, as the boiling temperature rises, and less and less of the more volatile component, *B*. If these vapors are condensed in different fractions, corresponding to different boiling points, the first fractions will be richer in the component *B*, and the last fractions in *A*. The first and last fractions may be collected and separately distilled again to obtain another fractional separation of the vapors evolved at different temperatures. If this process is repeated, perhaps several times, relatively pure samples of the two liquids are eventually obtained. Because of the separation of the distillate into fractions, this process is called *fractional distillation*. It is used, for example, in producing solutions of alcohol that contain larger relative amounts of alcohol than the solutions resulting directly from fermentation. It is also used to separate the different mixtures of hydrocarbons in petroleum into gasoline, kerosene, lubricating oil, etc.

22. Constant Boiling Solutions

Let us next consider a mixture of two liquids for which there is a maximum on the boiling point curve (Figure 131) corresponding to a minimum vapor pressure for a definite composition. This maximum boiling point corresponds to a constant boiling mixture; i.e., it will produce, by boiling, vapor of the same composition as the mixture of the liquids, and the temperature of the mixture will remain the same until the entire mixture has been changed into vapor.

When a concentrated solution of hydrochloric acid is heated to the boiling point, the vapor consists almost entirely of hydrogen chloride. The solution remaining in the distilling flask contains, therefore, relatively more water than at first, and the percentage of hydrogen chloride decreases as boiling continues. The temperature at which the solution boils changes, also, and finally becomes higher even than the boiling point of water. Finally, when the percentage of hydrogen chloride is 20.24, the mixture boils at a constant temperature (110° at 760 mm.), and produces vapor of the same composition as the liquid in the still. This is called a *constant boiling solution*; it represents the concentration of the solution that has the lowest vapor pressure and the highest boiling point of all the different mixtures of solvent and solute.

23. The Lowering of the Freezing Point of the Solvent

When an unsaturated solution is cooled to a sufficiently low temperature, freezing produces crystals of the pure solvent, not of the solution itself. The temperature at which these crystals form is below the freezing point of the pure solvent. We use aqueous solutions of alcohol, glycerine, and other substances instead of pure water in automobile radiators, because they freeze at lower temperatures. The water of the car's storage battery does not freeze, because it contains sulfuric acid in solution.

Let us consider the freezing points of pure water and of the water in a sugar solu-

tion, Figure 149. It will be seen that pure water and ice have the same vapor pressure at 0° C., but this is not true of ice and the water in a solution. At 0° C. the vapor pressure of ice is greater than that of the water in the solution; hence, if the two were placed together, the ice would melt, and the solution would become more dilute. At a temperature somewhat lower than 0° the vapor pressure of water in the solution is the same as that of ice, and at this temperature the solution and ice are in equilibrium. This temperature corresponds to the point of intersection of the two curves, one representing the vapor pressure of ice and the other the aqueous vapor pressure of the solution. It is the freezing point of the solution, or, more accurately, that of the water of the solution.

The freezing point of water in a solution containing one gram-molecular weight of a non-electrolyte in 1000 g. of water is − 1.86° C., and for two gram-molecular weights of the solute in the same weight of water the freezing point is approximately twice as far below 0°, or − 3.72°.

24. Freezing Mixtures

If salt, for example, is mixed with ice, a temperature lower than the melting point (0° C.) of ice can be produced. As ice melts, salt dissolves in the water, forming a solution that has a lower vapor pressure than water or ice. Hence, solution and ice are not in equilibrium. The ice consequently melts and, since this process requires about 80 calories of heat for each gram of ice that changes to liquid, the temperature of the mixture falls.

This withdrawal of heat may be employed to freeze a liquid in a vessel immersed in the bath of ice, salt, and water. It is for this reason that a salt and ice mixture is used to freeze and to pack ice cream. For the same reason, streets and sidewalks can be freed of ice by sprinkling salt upon them.

25. Eutectic Mixtures

As the pure solvent freezes out of a solution, the concentration of the solute must become greater. The increase in concentration leads, of course, to a lower freezing temperature. The solution may eventually become saturated with the solute. When this happens, both solvent and solute will crystallize upon further cooling, and the solid form of each will be in equilibrium with the solution. The concentration of the solution remains constant as the two substances crystallize together.

A solution that acts in this manner is called a *eutectic* mixture, and the eutectic temperature may be defined as the temperature at which both solvent and solute separate as solids from the mixture. This temperature is the lowest freezing point of the solution.

26. Elevation of the Boiling Point of the Solvent

A solution must be raised to a higher temperature than the pure solvent, before the vapor pressure of the solvent becomes equal to a constant atmospheric pressure, and the solution boils. This condition may be easily understood by inspecting Figure 149. The boiling point is raised the same amount by equal numbers of molecular weights, or equal fractions of the molecular weight, of different solutes. For example, one gram-molecular weight of sucrose ($C_{12}H_{22}O_{11}$) and one gram-molecular weight of glucose ($C_6H_{12}O_6$), in 1000 g. of water, form solutions that have the same boiling points. (These two substances are both sugars.) A solution containing one gram-molecular weight of any non-electrolyte, as solute, in 1000 g. of water has the same boiling point as the sucrose and glucose solutions. This is another way of stating Raoult's law (page 203). It does not hold for electrolytes because they do not act as single, pure substances in solutions,

but as mixtures of their ions, with each ion producing the same effect as a molecule of any non-electrolyte.

27. Osmosis

Osmosis refers to the unequal rates of diffusion of a liquid in two directions through a membrane. To demonstrate it we can place the pure liquid on one side of a separating wall or membrane of the proper kind while on the other side we place a solution in which the same liquid acts as solvent; or a dilute solution may be separated from a more concentrated solution containing the same solvent. The separating wall must consist of a membrane that is permeable to the solvent but impermeable to the solute. Different animal and vegetable membranes act in this manner.

To explain osmosis, let us refer to Figure 153. It is evident that the concentration of water is less on the solution side of the membrane than on the other side where there is nothing but water. This means

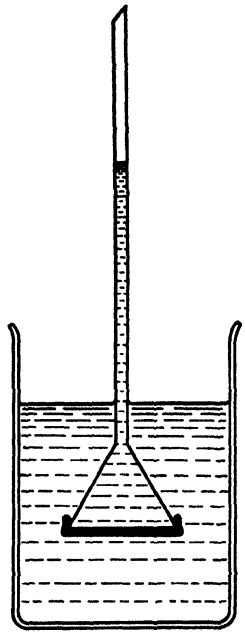


Figure 152. Diagram of Apparatus Used to Demonstrate Osmosis

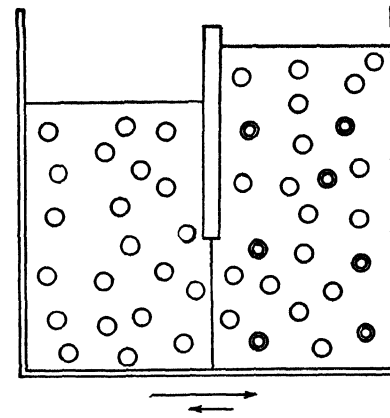


Figure 153. An Explanation of Osmosis
The solution is on the right-hand side.

that of the molecules in contact with the membrane, all are water molecules on one side, while on the other a certain percentage are sugar molecules. The latter do not pass through the membrane, while the former will diffuse through the membrane in the two directions at unequal rates because more of them are in contact with the membrane on the pure water side. The difference in the rates of diffusion depends upon the percentage of molecules of sugar in the solution, because the greater their number the more they will replace molecules of water in contact with the membrane. Hence, water passes through the membrane into the solution, and the column of the solution continues to rise, until its hydrostatic pressure becomes equal to what is commonly called the *osmotic pressure* of the solution.

28. Osmotic Pressure

Let us refer to Figure 152. As the liquid enters the funnel and the long glass tube attached to it the column of the solution rises. This column exerts pressure against the membrane as well as upon the walls of the funnel. If the tube of the funnel is long enough the column of liquid will, after a time, reach a height at which its pressure will tend to force water molecules back

through the membrane into the outer vessel to the same extent as the water molecules tend to pass through the membrane in the opposite direction; i.e., into the funnel. The pressure required to balance in this way the flow of solvent through the membrane and into the solution is the *osmotic pressure* of the solution. For solutions containing the same number of gram-molecular weights of any non-electrolyte in 1000 g. of water the osmotic pressure is the same at the same temperature.

29. Determination of Molecular Weights of Substances in Solution

It has been found that one gram-molecular weight of sucrose, glucose, or glycerine, dissolved in 1000 g. of water lowers the vapor pressure of water 0.31 mm., lowers the freezing point 1.86° C. elevates the boiling point 0.515° C., and produces an osmotic pressure at 0° C. of approximately 22.4 atmospheres.

It is evident, therefore, that the molecular weight of any *non-electrolyte* can be determined from the properties of its solution as compared with those of a solution containing one gram-molecular weight of sucrose or any other non-electrolyte dissolved in 1000 g. of the same solvent. The comparison is often made by considering freezing points. Let us say that 10 g. of a substance, which we shall call x, when dissolved in 200 g. of water, lower the freezing point of the water 0.372°.

The molecular weight of the substance is that weight which when dissolved in 1000 g. of water lowers the freezing point 1.86°. Hence,

1) 50 g. of x lower the freezing point of 1000 g. of water 0.372°.

2) $\frac{1.86°}{0.372°} \times 50 \text{ g.} = 250 \text{ g.} =$ molecular weight of x.

The general equation is as follows:

The gram-molecular weight of the solute =

$$X\text{g. of solute} \times \frac{1000 \text{ g.}}{W\text{g. of water}} \times \frac{1.86°}{T°},$$

in which X represents the grams of solute, W the grams of water in which the solute is dissolved, and T° the number of degrees the freezing point of water is lowered below 0°. This equation may also be used to determine the molecular weights of substances dissolved in solvents other than water if 1.86° is replaced by the lowering of the freezing point (Table 7) which is produced by one gram-molecular weight of any substance in 1000 g. of the selected solvent. This equation can also be used for calculations of the molecular weight from boiling point data by substituting such data in the above equation in place of freezing point data.

Let us say that 10 g. of solute X dissolved in 100 g. of water elevates the boiling point of the

TABLE 7

LOWERING OF FREEZING POINTS AND ELEVATION OF BOILING POINTS OF DIFFERENT SOLVENTS

Solvent	Boiling Point of Pure Liquid (° C., 760 mm.)	Boiling Point Elevation — 1 g.-mol. wt. per 1000 g. of solvent	Freezing Point of Pure Liquid (° C.)	Lowering of Freezing Point — 1 g.-mol. wt. per 1000 g. of solvent
Water	100°	0.515°	0.0°	1.86°
Benzene	80.2°	2.57°	5.5°	5.12°
Ether	34.6°	2.16°	−117.0°	1.79°
Carbon tetrachloride	76.8°	5.03°	−22.6°	2.98°

water 0.129°. Then the gram-molecular weight of X is $10 \times \frac{1000}{100} \times \frac{0.515}{0.129} = 10 \times 10 \times 4 = 400$

30. Extraction of Dissolved Substances by Another Solvent

To recover a substance from a solution that may contain several other substances we may add a solvent in which that substance is more soluble. For example, we may wish to remove iodine from an aqueous solution. If we add ether and shake the mixture, the iodine will distribute itself between the two solvents so that its concentrations in them will be in the same ratio as its solubilities in them. Since ether and water are only slightly soluble in each other, they separate into two layers, and the ether layer will contain most of the iodine, which is much more soluble in ether than in water. By evaporating the ether, the iodine can be recovered in a pure state. This principle is used in preparing and purifying many substances, especially certain organic compounds.

HOW SOLUTIONS ARE FORMED

31. How Ionic Compounds Dissolve

The attraction between two electrically charged (+ and −) metallic plates depends, in part, upon the substance between the plates. Some substances, such as water, greatly decrease the attraction and are said to have greater *dielectric constants* than air or other substances that have little effect. Water exerts a similar influence upon the attraction of positive and negative ions in a substance such as sodium chloride.

When a crystal of sodium chloride is placed in water, the water dipoles (page 176) orient themselves around sodium and chloride ions on the surface of the crystal as shown in Figure 154. The negative ends of the molecules are attracted to the positive sodium ions, and the positive poles of other

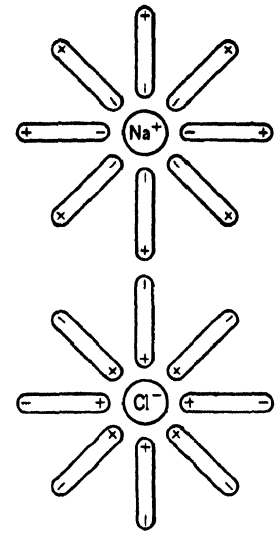


Figure 154. Water Dipoles Separating Sodium and Chloride Ions

molecules are attracted toward the negative chloride ions. Because of the orientation of water molecules around each ion, the attraction of each ion for those of the opposite charge is decreased. If the attraction is sufficiently decreased, the ions will no longer be held in the positions that they occupy in the crystal lattice, and, therefore, the crystal's structure will gradually disappear as the surface ions are removed and become scattered in the solution.

Whether or not an ionic compound dissolves in a liquid depends upon so many factors that no hard and fast rules can be given by which solubilities can be predicted or explained. Evidently, the dielectric constant and the action of molecules of the solvent as dipoles (see above) are important. Sodium chloride does not dissolve and, therefore, liberates no ions in solvents whose molecules do not act as dipoles. Methane (page 43) if liquefied, would be such a solvent. Molecules of this substance have no effect upon the ions of a crystal, because they would not be attracted by the charges of the ions.

Other factors that are important in determining the solubility of an ionic compound are: (1) The extent to which the ions combine with molecules of the solvent to form compounds, e.g.,

hydrates, and the energy released in this process; (2) the sizes of the ions and how closely they are packed in the crystal lattice; (3) the quantities of electric charge upon the ions; (4) the number of electrons in the outermost shells of the ions, especially of metallic ions, e.g., Ag^+ has 18, and K^+ has 8; (5) the structure of the solvent, e.g., molecules of water, even in the liquid state, appear to be at least partially bound together by hydrogen bonds (page 185), which, of course, must be severed before molecules of a solute can mix with molecules of the solvent, and (6) the melting point of the solid solute which determines at least in part the energy required to separate the ions of the crystal and change them into the liquid state.

32. The Solubility of Covalent Compounds

The miscibility of gases in all proportions is possible, no doubt, because of the very weak attraction of their molecules for one another. If molecules of oxygen, for example, possessed considerable attraction for one another, they would tend to cling together in the presence of other gases, such as the nitrogen of the air, and mixtures could not be formed. Now if molecules of a solute in a solution behave similarly to those of a gas, we must conclude that they, too, possess little attraction for one another and so are more or less free to mingle with other equally free molecules in forming solutions. Furthermore, we must conclude that the molecules of the solvent do not exert very strong attraction for one another; otherwise, it would be impossible for molecules of the solute to force them apart and form a homogeneous mixture.

In general, solids composed of molecules will dissolve in a liquid whose molecules have similar fields of force around them, and which are of the same general nature as their own molecules. We would not expect methane, for example, to be soluble in water and, for the same reasons, we would not expect naphthalene, $C_{10}H_8$ to dissolve. Their molecules and those of water are entirely unalike; one is a dipole and the other is not; and one contains an atom with unused pairs of electrons that can be used in forming hydrogen bonds, and the other does not. Naphthalene, however, is soluble in benzene, C_6H_6, a compound whose molecules resemble its own; neither of these compounds has much attraction even for molecules of their own kind, and, therefore, there is little resistance to the mixing of the two kinds of molecules. Sugar, whose molecules contain hydroxyl, OH, groups like those of water, does not dissolve in benzene, but it is very soluble in water. Its OH groups act as dipoles and its oxygen atoms, with unused pairs of electrons, can act as those of water in forming hydrogen bonds.

REVIEW EXERCISES

1. How could you prove that a sample of a liquid is a solution and not the pure solvent?
2. From the data given on page 199, calculate the weight of oxygen that will dissolve at 10 atmospheres of pressure in 100 g. of water (0° C.).
3. Describe the method commonly used to separate two miscible liquids.
4. Describe the nature of the distillate and the changes in temperature that you would expect to occur, when a mixture containing hydrogen chloride (35 per cent) and water is distilled.
5. How are solubility curves similar to those on page 201 constructed?
6. How many grams of sodium nitrate will dissolve in 500 ml. of water at 30°? Obtain data from the solubility curve.
7. How many grams of solid potassium chloride will separate from a solution that is saturated at 70°, if the solution is cooled to 30°, and if the solution contains 200 g. of water?
8. From which substance, $NaNO_3$ or NaCl, could KNO_3 be more easily separated by fractional crystallization? Explain.
9. What is meant by an *ideal* solution?
10. What is a solid solution? Give examples.
11. Define: Solute, solvent, saturated solution, supersaturated solution.
12. Define: Concentration, molar solution, normal solution, molal solution.
13. For what kinds of solutes are a 1 M and a 1 N solution identical? Under what conditions is the molality of a solution almost the same as the molarity?

14. How many grams of the following substances are contained in 1 liter of (*a*) 0.2 M and (*b*) 0.1 N solutions? HNO_3, $Ba(OH)_2$, NaCl, $CaCl_2$?
15. Why does the solubility of any gas in a liquid decrease with rise in temperature?
16. How does a saturated solution differ from a concentrated solution?
17. What volumes of the following liquids are required to give 1000 g. of each?

Liquid	Specific Gravity
Benzene	0.878
Ethyl alcohol	0.785
Carbon tetrachloride	1.584
Ether	0.720
Carbon disulfide	1.293

18. How many gram-molecular weights of each of the above solvents are present in 1000 grams?
19. State Raoult's law. Why does a solution of a non-volatile solute have a lower vapor pressure than the pure solvent?
20. Apply Raoult's law to the boiling and freezing points of solutions. Why do solutions have higher boiling points and lower freezing points than the pure solvents?
21. A solution containing 20 g. of a substance in 150 ml. of benzene has a freezing point of 2.7° C. What is the molecular weight of the substance?
22. In what ways is a substance in solution like a gas?
23. How could you determine whether a given solution is unsaturated, saturated, or supersaturated?
24. Can 1 molar solutions of all salts, acids, and bases be prepared?
25. The formula for ethyl alcohol is C_2H_5OH. Knowing that it resembles sugar in its effects upon the properties of a solvent, calculate the volumes of alcohol and water which should be mixed to fill an automobile radiator holding 15 liters, if the freezing point of the mixture is to be − 15°. Assume that no change (this is slight) in volume occurs when the two liquids are mixed. The weight of 1 ml. of pure alcohol is 0.79 g.
26. How could you determine the approximate molecular weight of a substance from the osmotic pressure of its aqueous solution?
27. Why are the osmotic pressure and the vapor pressure of solutions of equal molal concentrations in the same solvents approximately independent of the nature of the solute, provided that the solute is a non-electrolyte?
28. Suggest a cause for the failure of Raoult's law when applied to solutions of electrolytes.
29. The formula of glycerine is $C_3H_5(OH)_3$. If 54 g. of glycerine is dissolved in 300 g. of water, what will be the freezing and boiling points of the solution? What will be the approximate osmotic pressure of this solution at 0° C.?
30. What volume of 2 N sodium hydroxide solution is required to neutralize 200 ml. of 1 N sulfuric acid solution?
31. Ten milliliters of a solution containing 3.0 g. of sodium hydroxide per liter are required to neutralize 30 ml. of a solution of hydrochloric acid. What is the normality of the solution of the acid?
32. A solution containing 0.23 g. of glycerine in 10 ml. of water freezes at − 0.465°. What is the approximate molecular weight of glycerine?
33. How would you proceed in the laboratory to produce the pure solvent from a liquid solution containing (*a*) a gas, (*b*) another liquid, and (*c*) a solid?
34. How many grams of the following substances should be dissolved to produce 1 liter of an aqueous solution having a concentration of (*a*) 0.1 M and (*b*) 0.5 N : HCl, H_2SO_4, NaOH, H_3PO_4?
35. 15 ml. of a solution of H_2SO_4 are completely neutralized by 32 ml. of a solution of 0.5 N NaOH. What is the concentration of the solution of the acid in terms of (*a*) its normality and (*b*) the number of gram-molecular weights per liter?
36. Why is water a better solvent for potassium nitrate than benzene, C_6H_6?
37. Why does sugar dissolve in water but not in benzene or liquid methane?
38. Can you suggest a reason for the greater solubility of ethyl alcohol, C_2H_5OH, than benzene, C_6H_6, in water?
39. Why is a polar compound, like water, generally not very soluble in a non-polar solvent, like carbon tetrachloride, CCl_4?

40. Why is the melting point of a solid to some extent an indication of its solubility in a liquid?
41. Why does the solution (Figure 152, page 207) finally cease to rise in the tube? Why does it rise at all above the level of water in the beaker?
42. Why does salt sprinkled on an icy sidewalk cause the ice to melt?
43. Why is alcohol not entirely satisfactory as an antifreeze in a car's radiator? In what way is it preferable to a solution of salt?
44. Why must a membrane permeable to the solvent but impermeable to the solute be used in demonstrating osmosis?
45. Why must all mixtures of gases be regarded as solutions?
46. What are some of the kinds of evidence that indicate the occurrence of chemical reactions in the formation of many solutions?
47. Why do some substances, like sodium hydroxide, become moist when exposed to the air? Why is this more likely to happen for very soluble substances than for very slightly soluble substances?
48. Why can deliquesence not be regarded as the opposite of effloresence?
49. What harmful effects might be expected to result from drinking salt water?

REFERENCES FOR FURTHER READING

Chapin, W. H., and L. E. Steiner, *Second Year College Chemistry.*

Clarke, B. L., *Marvels of Modern Chemistry.*

Findlay, A., *The Spirit of Chemistry.*

Tilden, Sir W. A., and S. Glasstone, *Chemical Discovery and Invention in the Twentieth Century,* chap. IX.

Osmotic Pressure: *J. Chem. Ed.*, **6,** 98 (1929); **7,** 2170 (1930); **8,** 149 (1931); **10,** 234 (1933); **12,** 24 (1935); **13,** 153 (1936).

16

SOLUTIONS OF ELECTROLYTES

1. Introduction: Ions

At different times in the earlier chapters we have referred to *ions*, which we have defined as *atoms or groups of atoms that possess electric charges*. In this chapter we are returning to the study of ions once again for the purpose, primarily, of dealing with the properties of the solutions of electrolytes and the theories that have been offered at different times to explain these properties.

THE THEORY OF ARRHENIUS

At one time, it was thought that all substances are composed of molecules, and that all reactions, in solutions as well as elsewhere, occurred between such particles.

In 1887, Svante Arrhenius put forth a theory based upon the idea that salts, acids, and bases dissociate into ions when they dissolve in water or in certain other solvents. For several years his theory served as the sole guide to the investigations of the behavior of electrolytes and their solutions. At present, it is still extremely useful and important, although some of the original assumptions have been replaced by new ideas.

2. A Brief Summary of the Theory

The following statement is an outline of the theory of ionization advanced by Arrhenius. *Let us bear in mind, as we consider it, that he believed all compounds to be composed of molecules.*

(1) Ions are produced by the dissociation of *molecules* of salts, acids, and bases (hydroxides) when these substances are dissolved in water and in certain other solvents.

(2) Ions are electrically charged. When a molecule dissociates it produces one or more positively charged ions and one or more negatively charged ions. The sum of the charges on the positive ions is equal to the sum of the charges on the negative ions produced by the same molecule:

$$HCl \longrightarrow H^+ + Cl^-$$
$$H_2SO_4 \longrightarrow H^+ + H^+ + SO_4^{=}.$$

The solution, therefore, remains electrically neutral.

(3) The ions produced in a solution make that solution an electric conductor. Those compounds whose aqueous solutions do not conduct the electric current do not produce any ions.

(4) The ionization of an electrolyte is not complete except in extremely dilute solutions. In ordinary solutions, the ions are in equilibrium with undissociated molecules.

$$HCl \rightleftharpoons H^+ + Cl^-.$$

The percentages of molecules of different electrolytes that must ionize to establish equilibrium differ widely. We say that different substances ionize to different extents.

Let us turn now to the properties of elec-

trolytes and their solutions in order that we may understand some of the evidence upon which this theory was founded. As we approach this problem, let us place ourselves in this position: We do not know whether substances like sodium chloride exist in solution as molecules or as ions. What facts will guide us toward the true solution of the problem?

EVIDENCE SUPPORTING THE THEORY OF ARRHENIUS

3. A Comparison of the Reactions of Electrolytes and Non-Electrolytes

All electrolytes — salts, acids, and hydroxide-bases — participate readily, and usually almost instantaneously, in double decomposition reactions when solutions containing them are mixed. In these reactions the same electrolyte always provides the same particles. Thus, cupric sulfate always reacts in aqueous solutions, whenever it takes part in a double decomposition, to form a new copper compound and the sulfate of some other element:

$$(Cu^{++} + SO_4^{=}) + (Ba^{++} + 2\ Cl^{-}) \longrightarrow (Cu^{++} + 2\ Cl^{-}) + BaSO_4 \downarrow$$

Substances whose solutions do not conduct the electric current do not enter readily into double decomposition reactions, and most of them do not react in this manner at all.

Furthermore, the reactions that occur between non-electrolytes are much slower, as a rule, than reactions between electrolytes. This difference indicates that solutions of electrolytes contain ions that can and do combine as soon as the substances are mixed. For non-electrolytes, however, the molecules must meet and then, perhaps, each molecule must undergo considerable change before the products are formed.

An illuminating example of the difference between electrolytes and non-electrolytes is shown in the behavior of sodium chloride as compared with carbon tetrachloride, CCl_4, or chloroform, CH_3Cl. Any soluble chloride, such as NaCl, reacts immediately in solution with silver nitrate to form silver chloride, which precipitates, but when silver nitrate is added to carbon tetrachloride or to chloroform, there is no precipitate, and silver chloride is not formed. The chlorine is not free to react with silver; and, consequently, silver chloride cannot be produced.

4. The Boiling Points of Solutions of Electrolytes

We might, naturally enough, expect a solution containing one gram-molecular weight (or the weight corresponding to the formula, NaCl) of sodium chloride in 1000 g. of water to boil at the same temperature as a sugar solution of the same concentration, namely 100.52°. This solution of sodium chloride boils, however, at 100.97°. The elevation (0.97°) of the boiling point is almost twice the elevation produced by a gram-molecular weight of sugar dissolved in the same weight of water. How can this be? Arrhenius answered this question as follows: The boiling point of the salt solution indicates that this solution contains almost twice as many particles of solute as the sugar solution. Most of the molecules of salt — if salt is composed of molecules — break up in the solution, each molecule forming two particles, each of which has the same effect upon the boiling point of the solvent as a molecule of sugar. The fact that the elevation of the boiling point is not quite twice as great as the elevation caused by an equal number of sugar molecules indicated to Arrhenius that not all of the molecules of salt break up in the solution.

The elevation of the boiling point for a solution containing one gram-molecular weight of calcium chloride ($CaCl_2$) in 1000 g. of water is between two and three times as great as the elevation produced by one gram-molecular weight of sugar. Arrhenius believed, therefore, that almost all of the

molecules of calcium chloride break up into three ions each:

$$CaCl_2 \longrightarrow Ca^{++} + Cl^- + Cl^-.$$

For other compounds the elevation of the boiling point is only a little more than the normal elevation of 0.52°. Arrhenius concluded that only a few of the molecules of the solute were ionized in these solutions.

5. Freezing Points of Solutions of Electrolytes

Molal aqueous solutions of sucrose, glucose, glycerine and other non-electrolytes freeze at − 1.86°. The freezing point of a solution containing one gram-molecular weight of sodium chloride in 1000 g. of water is − 3.42°, which is almost twice the normal lowering of the freezing point in a molal solution. Here again, we must assume that almost all of the molecules in the gram-molecular weight of salt — if it is composed of molecules — break up to form two particles (ions) each.

6. Percentage of Ionization

From the data presented above, it is possible to calculate — upon the basis of Arrhenius's theory — the percentage of sodium chloride molecules in the molal solution that ionize and the percentage of those that do not. If the solution froze at − 1.86°, it would be evident that none of the molecules in this solution is ionized. To take the other extreme, if the freezing point of the solution were − 3.72°, it would appear that each molecule produces two ions, and that all the molecules are ionized. Actually, the freezing point is − 3.42°, which is between − 1.86° and − 3.72°. Hence, a number of molecules, somewhere between zero and 100 per cent of the entire number present, appears to be ionized. The apparent percentage of ionized sodium chloride can be calculated easily from these facts. If the solute were completely ionized, the lowering of the freezing point *in excess of the lowering produced by the same concentration of a non-electrolyte* would have been 3.72° − 1.86° = 1.86°. Instead, the freezing point is lowered 3.42° − 1.86° = 1.56° more than it would be if no sodium chloride were ionized. The percentage of ionized solute is, therefore, $\frac{1.56}{1.86} \times 100 = 84$ per cent.

THE ELECTROLYSIS AND ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF ELECTROLYTES

7. Electrolysis: The Electrical Charges of Ions

When a direct current of electricity passes between two platinum electrodes dipping into a solution of hydrochloric acid, HCl, hydrogen is evolved at the cathode (−) and chlorine at the anode (+). The liberation of the elements at the electrodes can scarcely be explained unless we assume that electrically charged hydrogen [1] and chloride ions exist in the solution. Why should hydrogen move toward the negative electrode, unless its atoms are positively charged? Similarly, must not the chlorine atoms possess negative charges, since they migrate toward the positive electrode? If the atoms are charged in the solution, the changes at the electrodes are changes that discharge them and convert them into atoms of the free elements.

8. Faraday's Law of Electrolysis

One of the most important of Faraday's contributions is his Law of Electrolysis. This law states the following general principle: *Equal quantities of electricity liberate equivalent quantities of all ions from their solutions during electrolysis.* The unit of the quantity of electricity is the *coulomb*.[2]

[1] These may be simple hydrogen ions, H^+, or they may be the hydrated ions, such as H_3O^+, resulting from the combination of H^+ with molecules of water, H_2O. The explanation that follows does not depend upon the exact character of this ion.

[2] The coulomb is the quantity of electricity carried by a current of electricity of one ampere in one second. A current of 15 amperes flowing through a conductor for 10 minutes amounts to 9000 coulombs. A coulomb can also be defined as the quantity of electricity required to deposit 0.001118 g. of silver from a solution containing silver ions.

To liberate 1.008 g. of hydrogen from any acid 96,500 (actually 96,494) coulombs — called one *faraday* — of electricity must be used. The same quantity of electricity will liberate one gram-atomic weight of any *univalent* element. For *divalent* elements, 96,500 coulombs liberate one half of an atomic weight, for *trivalent* elements one third of an atomic weight, and so on.

When 96,500 coulombs discharge 1 gram-atomic weight of hydrogen at one electrode, there will also be discharged 1 gram-atomic weight of chlorine at the other electrode, from a solution of hydrogen chloride.

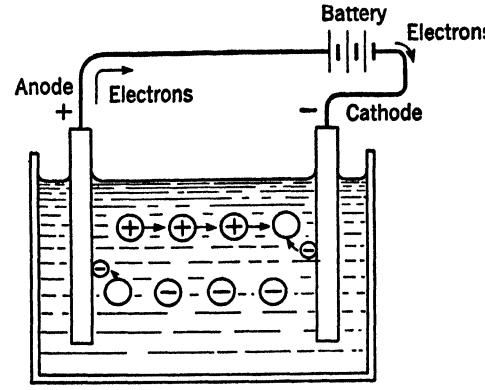


Figure 155. Electrolysis

When we recall that the atoms of all univalent elements lose a single electron each, it is not surprising that the same quantity of electricity is required to liberate an equal number of atoms of any of these elements since each ion that was produced by the loss of one electron must remove one electron from the cathode when it is discharged. The atoms of a divalent element lose two electrons each. The same quantity of electricity, therefore, liberates only one half as many atoms of a divalent element as of a univalent element. To liberate one gram-atomic weight of hydrogen, or of any element whose ions carry one unit of positive charge, one electron is required for each atom, or 6.023×10^{23} electrons for all the atoms in one gram-atomic weight.

9. Explanation of Reactions Occurring During Electrolysis

Let us first consider the electrolysis of an aqueous solution of sodium hydroxide. Let us assume that the direct current of electricity used to electrolyze an aqueous solution of sodium hydroxide is supplied by a storage battery, whose poles (or terminals) are connected to *electrodes* of the cell. As a result of chemical changes occurring in the battery, the number of electrons on the cathode of the electrolytic cell is increased. At the same time, the changes in the battery remove electrons from the anode. There is thus produced a difference in the distribution of electrons in the two parts of the cell, that is, a difference of electric potential between the cathode and the anode. In order to restore the normal, equal distribution of electrons throughout the system, the cathode tends to lose electrons and the anode to gain them. Thus the cathode may be expected to yield electrons easily to anything that can accept them — to a positively charged ion, for example. The anode, on the other hand, will remove electrons from anything, such as a negatively charged ion, that can supply them.

The aqueous solution of sodium hydroxide contains sodium (Na^+) and hydroxyl (OH^-) ions from the sodium hydroxide. Water, which produces a relatively small number of ions, supplies some hydroxyl and hydrogen (H^+) ions. The sodium and hydrogen ions, both of which carry a positive charge, migrate toward the cathode, where the hydrogen ions remove one electron each and are converted into the free element. Sodium ions are not discharged, because a greater difference of potential is required to convert sodium ions into the free element than is required to discharge hydrogen ions. Even if sodium were liberated, it would in turn react with water (page 69) to form hydrogen and sodium hydroxide.

The reaction at the anode probably involves the conversion of hydroxyl ions into oxygen and water:

$$4\,OH^- \longrightarrow O_2 + 2\,H_2O + 4\,e.$$

The electrons of the ions are removed by the anode. The reactions that occur at the electrodes result, therefore, in the conversion of the water of the solution into hydrogen and oxygen.

In the electrolysis of an aqueous solution of hydrogen chloride, hydrogen is liberated at the cathode by reacting with electrons to form hydrogen atoms, which, in turn, combine to form molecules. At the same time chloride ions are con

verted into chlorine atoms at the anode by giving up one electron each to this electrode. However, in any solution of a chloride in which the chloride ion's concentration is very small, oxygen is liberated at the anode from OH^- ions as shown above. The hydroxyl ions are those produced from water.

In the electrolysis of a solution of sulfuric acid, H_2SO_4, in water the reaction at the cathode is

$$2\,H^+ + 2\,e \longrightarrow H_2$$

and at the anode

$$H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e.$$

Since the sulfate ion is not liberated, the total reaction, therefore, involves only the decomposition of water into hydrogen and oxygen. The reaction at the anode resupplies the hydrogen ions discharged at the cathode, and, hence, the sulfuric acid remains in the solution.

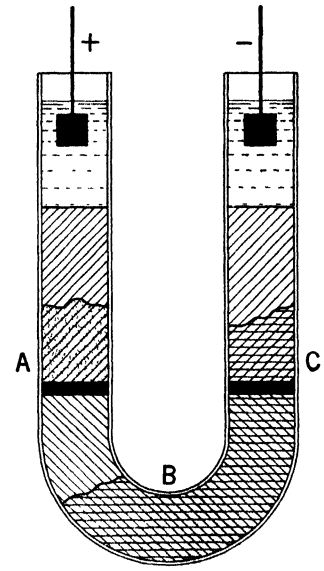


Figure 156. An Experiment to Demonstrate Differences in the Migration Velocities of Ions

The U tube is filled with gelatine or agar. The lower half of the jelly contains cupric sulfate in each arm of the tube. In the upper half of the left arm (A) there is present a small amount of barium chloride. When a current flows through the solution, the cupric ions, which are colored blue, migrate toward the cathode, thus extending the region of blue color in this direction. The rate at which this change occurs is a measure of the migration velocity of the cupric ion. The sulfate ions migrate toward the anode and at A react with barium ions to form insoluble barium sulfate. The formation of this precipitate allows us to follow the migration of the sulfate ion in this arm of the tube.

10. Electrical Conductivity

To measure the conductance of a solution, we determine its electrical resistance by comparing the solution with a metallic conductor for which the resistance is accurately known. The unit of resistance is the *ohm*, and the unit of conductivity is the *reciprocal ohm* $\left(\frac{1}{\text{number of ohms}}\right)$. The quantity of current carried by the solution in a given period of time is determined by the number of ions that reach the electrodes; this number depends, in turn, upon the number of ions in the solution and upon their velocities.

Differences in the velocities of different ions can be shown by means of the experiment pictured in Figure 156. The relative distances which the ions travel in the same period of time are shown by the changes in color or by the formation of precipitates as the ions migrate through the solution.

Hydrogen (or hydronium H_3O^+) ion, which has the highest velocity, migrates 11.74 cms. per hour in a very dilute solution under the influence of one volt; hydroxyl ion has a velocity of 6.5 cms. per hour; and sodium ion 1.6 cms. per hour.

11. Specific and Equivalent Conductances of Solutions

Let us assume, as Arrhenius did, that an aqueous solution of any salt, acid, or base contains both ions and undissociated molecules. These are in equilibrium with each other (page 213). Let us start with a solution containing one equivalent weight of solute per liter. The conductance of 1 ml. of this solution, when measured between platinum electrodes which are 1 cm. square, 1 cm. apart, and under a potential of one volt, is called the *specific conductance* of the solution. The product of the specific conductance and the total number of milliliters of solution containing one equivalent weight of the solute gives the *equivalent*

conductance. For a 1 N solution the equivalent conductance is obtained when the specific conductance is multiplied by 1000, for a 0.1 N solution by 10,000, and so on.

We may define the equivalent conductance as the current that would be carried, at some definite temperature, by a solution containing one gram-equivalent weight of the solute if the entire solution were contained between two parallel, flat electrodes 1 cm. apart and under a potential of one volt.

12. Change in Equivalent Conductance with Dilution

Let us start with one liter of a 1 N solution of hydrochloric acid; this liter is then diluted to two liters. If the total number of hydrogen and chloride ions remains the same, the number of ions in each milliliter of the more dilute solution is one half of the number in 1 ml. of the 1 N solution. Since the ions act as the carriers of the current, the specific conductance should be one half of its original value. When this specific conductance is multiplied by the number of milliliters (2000) that contains an equivalent weight of the solute, the equivalent conductance *should be the same* as it is for the 1 N solution. The equivalent conductance should not vary, therefore, with the dilution, *provided that the total number of ions does not change.* Experimentally, we find that the equivalent conductance *does increase* with dilution. This result can be interpreted — as Arrhenius thought — as meaning that the ionization of the electrolyte becomes more nearly complete as the solution is diluted. There is, however, a different interpretation which will be discussed in connection with another theory of ionization (page 219).

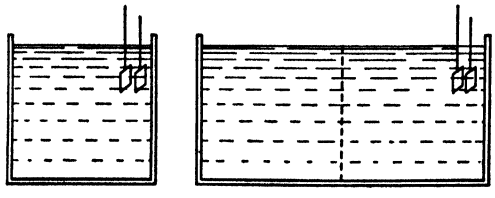


Figure 157. The Total Conductivity of a Definite Weight of Solute Increases as the Solution Is Diluted

The volume of the solution between the electrodes is the same in both cases. If no more ions were produced upon dilution the conductivity of 1 cc of the solution (between the electrodes) in the solution (right) would be one-half of the conductivity of the same volume of the first solution. But there are twice as many cubic centimeters in the second solution; hence, the total conductivity should not change upon dilution, unless the solute is ionized to a different extent.

13. Measuring the Percentage of Ionization

As the dilution increases, a condition is reached, finally, when the equivalent conductance does not increase as more of the solvent is added. At that time, the degree of ionization of the electrolyte in terms of the theory of Arrhenius is said to be 100 per cent, and the solution is said to be *infinitely dilute.* The equivalent conductance of an infinitely dilute solution is called the *limiting conductance* and corresponds, of course, to the maximum conductivity of all the ions that the solute can liberate. If the equivalent conductance of a solution of definite concentration of the solute is 50 per cent of the limiting equivalent conductance (of the infinitely dilute solution) of the same solute, we may assume that this solution contains in all 50 per cent as many ions and is, therefore, 50 per cent ionized.

The increase in conductivity as a solution is diluted can be explained — or so Arrhenius believed — if the reaction by which ions are produced, is reversible:

$$NaCl \rightleftarrows Na^+ + Cl^-.$$

When the solution is diluted the ions are further separated, and their recombination to form molecules is less likely to occur. As the dilution is increased, the ions are scattered, finally, to such an extent that the chances of recombination are negligible. The solute is then said to be completely ionized, and the solution is infinitely dilute.

MORE RECENT THEORIES OF IONIZATION

14. Reactions of Strong Electrolytes

Let us consider the effect of mixing solutions of potassium chloride and sodium nitrate. The following equation is sometimes written to explain the changes that occur:

$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl.$$

If the two salts in the beginning and those at the end of the reaction exist as molecules, we should expect some temperature change to be evident as the reaction takes place. However, dilute solutions of these two substances can be mixed without any observable temperature change at all. Furthermore, the properties of the mixture are the same as those of any mixture of potassium, sodium, chloride, and nitrate ions made, for example, by dissolving sodium chloride and potassium nitrate in the same solution. We must conclude, therefore, that no reaction occurs when the dilute solutions of these substances are mixed. We must think of the separate solutions as containing K^+ and Cl^-, and Na^+ and NO_3^-, ions. When the solutions are mixed, all four ions remain just as they were in the separate solutions, and there is no combination of them to form molecules of KNO_3 and NaCl. It is only when the solution is concentrated by evaporation that crystals of sodium chloride form, and they are formed just as they would be if a solution of sodium chloride alone were evaporated.

A similar explanation applies to the neutralization of strong bases by strong acids:

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-) + HOH + 13{,}700 \text{ calories.}$$

$$(H^+ + NO_3^-) + (K^+ + OH^-) \longrightarrow (K^+ + NO_3^-) + HOH + 13{,}700 \text{ calories.}$$

The heat change is the same in both reactions. We conclude, therefore, that the same reaction occurs in both cases; this reaction is the combination of H^+ and OH^- to form HOH. Both acids and both bases were ionized in the beginning, and both salts (NaCl and KNO_3) are ionized at the end of the reactions.

Such facts as these cause us, as they did others long ago, to question the assumption of Arrhenius that the ions and molecules of every electrolyte exist in equilibrium with each other in all except infinitely dilute solutions.

15. Is Sodium Chloride Completely Ionized in Solution?

Crystals of certain substances are shown by X-ray analyses of their structures to consist only of ions. Sodium chloride, for example, is completely ionized even before it is dissolved. There is no reason to believe that sodium and chloride ions combine in a solution to form molecules, since in solution, and in the fused state, the ions are separated farther and are more nearly independent than they are in the crystal. It is much more satisfactory to think of the ions in the solution as no longer rigidly oriented with respect to one another but as exerting to some extent the same kind of attraction for each other as they exert in the crystal. The difference is one of the strength rather than the nature of this attraction.

16. The Debye-Hückel Theory of Strong Electrolytes

Our present ideas concerning solutions of strong electrolytes are in agreement with our information concerning the crystalline states of substances like sodium chloride. Most of these ideas are embodied in the *Debye-Hückel Theory*. Although the assumption is made that a strong electrolyte is 100 per cent ionized, we may think of them as existing in the solution in somewhat the same condition as they exist in the crystal, i.e., each ion attracts those of the opposite kind in all directions. This con-

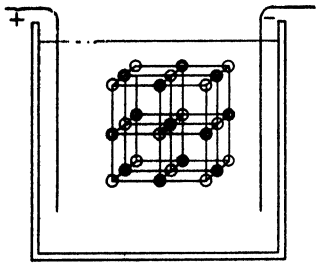


Figure 158

dition results in what we may consider as a field of the opposite kind of charge around each ion; that is, in the field surrounding an ion there will be more ions that carry the opposite charge than there will be of those that carry the same kind of charge. When an ion migrates toward one of the electrodes in a cell, the electrostatic attraction existing between it and the field around it must be overcome, and this attraction retards the mobility of the ion. An extreme case of the same sort exists in a crystal of the substance. Imagine a small crystal of sodium chloride, such as the one shown in Figure 158, between two terminals of a battery. The ion at the center has zero mobility since it is surrounded by six ions of the opposite kind, and these are urged by the potential between the electrodes to migrate in the opposite direction. In a solution of sodium chloride, the crystal's structure, of course, has disappeared, but the attraction, between oppositely charged ions still exists, although it is considerably weakened by the effect of the solvent (page 209). This attraction restricts the independent action, and particularly the movement, of the ions.

17. An Explanation of Apparent Degrees of Ionization

Now the conductance of a solution depends upon the number of ions in a solution and upon the velocity with which they migrate toward the electrodes. If they did not move, the conductance would be zero. If the ions were absolutely independent of all forces that restrict their movement, the conductance of the solution would be proportional to the number of ions in the solution. But if their migration is retarded or hindered in any way, the conductance of the solution will be decreased by an amount that depends upon the extent to which they do not act as independent particles.

Let us imagine, for convenience, that a solution contains 100 ions each of sodium and chlorine. If these ions were entirely free of attraction in their solution, they would show a certain maximum conductivity, and this would represent the condition which, in the Arrhenius theory, is called complete ionization. But if these ions attract each other and are retarded somewhat as they tend to migrate toward the electrodes, the observed conductivity of the solution should be less than the maximum. Let us say that it is 90 per cent of this maximum. In terms of Arrhenius's theory, we would say that the solute is only 90 per cent ionized, and that 10 per cent of the solute exists as undissociated molecules. In terms of the Debye-Hückel theory, we would say that 100 ions of each kind, which are restricted in action by the attraction that they exert upon one another, can produce the same conductivity as 90 ions of each kind that are completely free and unobstructed in their individual actions.

We see, therefore, that it is possible to explain the measurements upon which *apparent degrees of ionization* are based without assuming that any portion of a strong

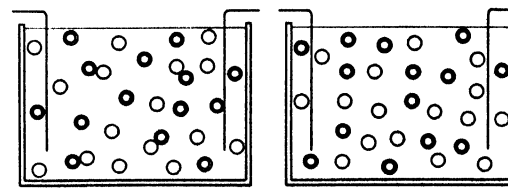


Figure 159. A Comparison of the Arrhenius Theory and the Theory of Debye and Hückel

In one case, the solution is assumed to contain both molecules and ions of the solute: in the other case the solution is assumed to contain only ions.

electrolyte such as sodium chloride exists in solution as undissociated molecules. As the concentration of a solution of an electrolyte is increased, the ions are crowded closer together, and they consequently exert greater attraction for one another. The total conductance of the solution decreases, and the lowering of the freezing point and the elevation of the boiling point become more nearly the same as the effects of equal concentrations of a non-electrolyte. Likewise, the effect of dilution can be explained, not by the ionization of an increased number of molecules, but by the greater degree of freedom possessed by individual ions in the more dilute solution. Each ion acts more nearly as an individual the more dilute the solution becomes, because the ions are more widely scattered and exert weaker attraction for one another.

18. Other Factors that Influence the Behavior of Ions

The independent action and behavior of ions in solution are restricted by several other factors in addition to those resulting from their mutual attraction and repulsion because of their electrical charges. It is possible that for some ions and under certain conditions two oppositely charged ions may team-up, at least for a very short time, to form a molecule, i.e., an *ion-pair*. Many ions are probably hydrated in aqueous solutions, and the extent of hydration is not the same for all ions. Hydration not only affects the size, general character, and velocity of the ion, but it also affects the total number of independent water molecules in the solution. In some instances, ions may combine to form more *complex ions*. Silver ion, Ag^+, in a solution containing cyanide ion, CN^-, forms a complex ion, that contains, both of them, namely the silver cyanide, or argento-cyanide, ion $Ag(CN)_2^-$. All these factors alter the behavior of ions in solutions, and they also alter the properties of the solution, such as its conductance, which depend upon the number of ions, their velocity, and the number of molecules of the solvent in a definite volume.

19. Ionization of Weak Electrolytes

The objections which may be raised against Arrhenius's theory apply, on the whole, only to solutions of strong electrolytes. For solutions of weak electrolytes it is still possible, and indeed necessary, to regard the undissociated molecules as well as ions as realities. The weak electrolytes are usually acids, such as acetic, or bases, such as ammonium hydroxide. A few substances usually classed as salts must be included; thus, mercuric chloride has a very small apparent degree of ionization in solutions of the usual concentrations, and pure, liquid aluminum chloride is a non-conductor of the current.

The structures of weak electrolytes are thought to depend, for the most part, upon covalence instead of electrovalence. In some of these compounds we may account for the production of ions by considering the possible reactions of the solvent molecules with the molecules of the solute (page 120). Thus, aluminum chloride, a non-electrolyte in the pure, fused state, may react with water to form hydrated aluminum and chloride ions:

$$AlCl_3 + 6\,H_2O \longrightarrow Al(H_2O)_6^{+++} + 3Cl^-.$$

It is probable that similar changes in solution are responsible, also, for the production of ions by some strong electrolytes. Hydrogen chloride, for example, in the pure state appears to be a typical covalent compound and is a non-conductor. In aqueous solution ionization may depend upon the reaction of molecules of water with the hydrogen of the acid to form the hydronium ion (H_3O^+) and chloride ion (page 120). This reaction must be almost complete, because hydrochloric acid shows about the same apparent degree of ionization as sodium chloride. It is entirely possible, and even probable, however, that at least an occasional proton will leave the hydronium ion and recombine with the chloride ion by sharing a pair of electrons. In con-

centrated solutions of the acid this event becomes more than probable; it actually happens, as shown by the definite vapor pressure of the hydrogen chloride in these solutions.

20. Production of Ions Depends upon the Solvent

The ions of other substances may be produced by reactions similar to the one described above. This behavior, however, appears to be confined largely to certain types of substances, notably to salt-like substances, such as aluminum chloride (page 164); certain covalent compounds that have basic properties, such as ammonia, NH_3,

$$NH_3 + HOH \longrightarrow NH_4^+ + OH^-;$$

and acids such as HCl (page 120).

It should be noted, also, that only certain solvents can produce ions from covalent compounds in this manner. The solvent molecule must contain one or more atoms capable of sharing electrons in the same manner that the oxygen atom, in the illustration given, is thought to share them with the hydrogen ion from HCl. Thus, HCl dissolved in a solvent such as liquid methane, CH_4, or a similar compound, could not react to form ions, since the carbon atom of the methane molecule has no pair of electrons through which the union can be brought about (page 43). A solution of HCl in liquid methane, or in similar solvents is, therefore, a non-conductor of the electric current.

21. The Ionization of Weak Acids

In solutions of weaker acids, such as acetic, we may think of the following reversible reaction with the solvent as occurring:

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^-.$$

This reaction is by no means as complete as the reaction between HCl and water. In the latter, we may assume that the proton forms a much stronger covalent bond with the oxygen atom of water than with chlorine. In the acetic acid solution, we may assume that the covalent linkage between hydrogen and the oxygen atom of the acid is stronger than the bond between the proton and the oxygen atom of the water molecule.

There are relatively few ions in the solutions of weak electrolytes at ordinary concentrations. Hence, the attraction between ions is negligible, or almost so, and the effects which we observe for strong electrolytes, and which are explained upon the basis of interionic attraction, are absent, or are very small. Arrhenius's theory holds very well for the solutions of these substances.

REVIEW EXERCISES

1. Summarize the different kinds of evidence which show that salts, acids, and bases produce ions in aqueous solutions.
2. How many coulombs of electricity are required to deposit 10 g. of copper from a solution of $CuSO_4$?
3. A solution contains 60 g. of $CaCl_2$ in 1000 g. of water. If the degree of ionization of the salt is 75 per cent, what is the freezing point of the solution?
4. For what reason did Arrhenius assume that molecules of sodium chloride are in equilibrium with sodium and chloride ions in an aqueous solution of that substance?
5. We now believe that sodium chloride in an aqueous solution is completely ionized. If this is true, why does the conductivity method of measuring the degree of ionization show that this substance (in .1 N solution) is only 84 per cent ionized?
6. What data must be available for the calculation of the degree (percentage) of ionization of an electrolyte from the conductivity of its solution?
7. Define an infinitely dilute solution in terms of the theory of Arrhenius. How would the same condition be explained by the Debye-Hückel theory?

8. The equivalent conductivities of acetic acid solutions of different concentrations are given below. Calculate the degree of ionization for each concentration.

10	N	0.05 reciprocal ohms
1	N	1.32 reciprocal ohms
0.1	N	4.6 reciprocal ohms
0.01	N	14.3 reciprocal ohms
Infinite dilution		352 reciprocal ohms

9. Compare the quantities of electricity required to deposit the same weight of iron from solutions containing ferrous and ferric ions.
10. Explain the meaning of the following statement: The acetic acid ($HC_2H_3O_2$) in a 0.1 N solution is 1.3 per cent ionized.
11. Explain the effect of diluting a solution upon the equivalent conductance of the solution in terms of (1) Arrhenius's theory and (2) the Debye-Hückel theory.
12. If acetic acid (.1 N) is 1.3 per cent ionized, what weight of pure acetic acid and what volume of solution would be required to furnish one gram-ion of $C_2H_3O_2^-$?
13. What is the principal difference between the theory of Arrhenius and that of Debye and Huckel as regards strong electrolytes?
14. The freezing point of a solution containing 4 grams of sodium hydroxide in 200 g. of water is – 1.674°. What is the apparent percentage of ionization of the sodium hydroxide?
15. What should be the freezing point of a solution containing 0.1 of a gram-molecular weight (or formula weight) of sodium chloride in 1000 g. of water, if the sodium chloride is apparently 90 per cent ionized?
16. What changes occur at the electrodes during the electrolysis of a solution of hydrogen chloride in water?
17. Why is the reaction between ethyl alcohol and acetic acid slower than the reaction of sodium hydroxide and acetic acid?
18. Why can molecular weights of electrolytes not be determined by the freezing or boiling point methods?
19. The apparent percentage of ionization of cupric sulfate, $CuSO_4$, is much smaller than that of sodium chloride. Both are completely ionized according to the Debye-Hückel theory. Can you suggest an explanation?
20. A solution containing 6.6 g. of sodium chloride in 100 g. of water boils at 101.11°. What is the apparent molecular weight of the solute? Account for the difference between the apparent molecular weight and that corresponding to the formula, NaCl.
21. A tenth normal solution of an electrolyte which we shall represent as AB has an apparent ionization of 90 per cent. What are the freezing point, boiling point, and osmotic pressure of the solution?
22. How can one account for the fact that acetic acid, or any other weak acid, is less ionized, in an aqueous solution, than hydrochloric acid?
23. Why is the assumption that *all* electrolytes are completely ionized in aqueous solutions not sound?
24. Why does chloroform, $CHCl_3$, not form a precipitate of AgCl when it is mixed with a solution of silver nitrate?
25. What are some of the kinds of evidence that indicate weaknesses or failures of Arrhenius's theory?
26. Give at least one reason that may have led Arrhenius to believe that:
    (*a*) Ions of all electrolytes are produced by the dissociation of molecules.
    (*b*) At infinite dilution an electrolyte is completely ionized.
    (*c*) Ions carry electrical charges.
    (*d*) When an electrolyte ionizes the sum of all the charges on positive ions produced by that substance is equal to the total charge on the negative ions.
27. Can you think of any facts that were known or might easily have been determined in Arrhenius's time that would have cast doubt upon the accuracy of any statement in his theory?

REFERENCES FOR FURTHER READING

Alembic Club Reprint, No. 19, "The Foundations of the Theory of Electrolytic Dissociation."
Hammett, L. P., *Solutions of Electrolytes.*
Jaffe, B., *Crucibles*, "Life of Arrhenius."
J. Chem. Ed., **5**, 1425, 1639 (1928); **6**, 1716 (1929); **7**, 782 (1930); **8**, 1493 (1931); **12**, 11, 24, 109, 567 (1935); **14**, 316 (1937); **17**, 124, 128, 131 (1940); **18**, 206 (1941); **22**, 575 (1945).

17

THE COLLOIDAL STATE

1. Introduction

If an insoluble solid is finely powdered and is then thoroughly mixed with water, it may remain suspended for some time. But the particles of the solid are usually visible; they can be separated from the liquid by filtration; and if more dense than water, they will settle to the bottom of the container after some time. Between this kind of a suspension and a solution there are other mixtures that contain one substance dispersed in an extremely fine state of division in another substance. The particles of these mixtures are not visible; they cannot be separated by filtration; and they do not settle out of the mixture. This kind of a suspension is called a *colloidal dispersion*, and the dispersed substance is said to be in the *colloidal state*. The substance in which the particles are suspended is called the *dispersing medium*, and the two substances together make a *colloidal system*.

It is evident that there is no definite dividing line between the colloidal state and true solutions, on the one hand, and the colloidal state and ordinary mixtures of particles of solids and liquids (or any other states of matter) on the other. The differences between the three kinds of mixtures depend largely upon differences in the sizes of the particles of the substances which make up the mixture. When the particles of the dispersed substance are smaller than one millionth of a millimeter (*one millimicron*, mμ) in diameter, the mixture begins to exhibit the properties of a true solution. Colloidally dispersed particles are, in general, those whose diameters lie within the range of 1 mμ to 200 mμ. Above 200 mμ, the particles become visible with the aid of a powerful microscope, and the mixtures behave as ordinary suspensions.

2. The Colloidal State of Matter

The form and physical characteristics of colloidally dispersed particles vary widely. They may be grains, droplets, bubbles, or even films and filaments, if the films are thin enough and the filaments are small enough in diameter to come within the range of colloidal dimensions. Colloidal suspensions *appear* to be homogeneous, but they differ widely from true solutions. Such mixtures have negligible osmotic pressures, and their freezing and boiling points are approximately the same as those of the pure liquid in which the suspensions exist.

The name colloid was suggested by Graham (1861). The word comes from the Greek word *kolla*, which means *glue*. Graham used this term to distinguish certain substances from *crystalloids*, which form true solutions. We now know that the colloidal state is not peculiar to any one group of substances. If sodium and chloride

ions form sodium chloride in a liquid in which salt does not dissolve, the product may be obtained as a colloidal dispersion. Even ice may exist as a colloid when the water dissolved in certain organic liquids is cooled below its freezing point. In general, there is but one limitation: The colloidal state of one substance cannot be produced in another in which it is soluble.

A colloidal dispersion in a liquid is called a *sol*, and when the liquid is water, the dispersion is a *hydrosol*. An *organosol* is a sol in which the liquid is an organic compound, e.g., alcohol or ether. An *aerosol* is a sol in which the medium is air or some other gas. When a sol is coagulated, it is then called a *gel* or *jelly*. We thus may have *hydrogels* or jellies, *organogels* or jellies, *aerogels*, etc.

3. Kinds of Colloidal Dispersions and Their Importance

Suspensions in which a liquid acts as the dispersing medium are most familiar and most important, but in other cases the dispersing medium may be a gas or a solid, and the dispersed substance may be a liquid, a gas, or a solid. There can be no colloidal system consisting of one gas dispersed in another gas, because all mixtures of gases are solutions. But with this exception, the parts of a colloidal system may represent any states of matter.

Since it applies to so many different systems and, under certain conditions, to almost every substance, information concerning the colloidal state is of great value in industry, in agriculture, in medicine and, in fact, wherever materials are used. Living tissue is colloidal, and the various activities in which it is involved in life processes are largely those concerned with the chemistry of the colloidal state. Colloidal chemistry is important in the manufacture of paper, textiles, the tanning of leather, the manufacture of rubber goods, in the production of photographic plates and films, varnishes, glue, inks, plastics, cements, pottery, dairy products (butter, cheese, etc.), salad dressings, food products of all kinds, and in many other industries.

Colloidal systems can be classified rather roughly as follows:

1. Hydrosols: Inorganic (sulfur in water) organic (starch in water)
2. Hydrogels, jellies (gelatin)
3. Organosols and organogels (gelatin in alcohol)
4. Aerosols (smoke or fog)
5. Aerogels (pumice, meerschaum)
6. Emulsions (oil in water)
7. Foams (soap lather)
8. Solid systems (ruby glass, a gold dispersion)
9. Films, fibers, filaments of colloidal dimensions (wool fibers, films of lubricants)
10. Pastes (paints, starch).

4. Lyophilic and Lyophobic Colloidal Systems

Colloidal dispersions in a liquid may be divided into two classes: *lyophilic* and *lyophobic* colloids, or if the liquid is water, *hydrophilic* and *hydrophobic* colloids. The former are substances which naturally form colloidal suspensions when mixed with the liquid without the employment of any special methods of preparation. They include glue, starch, gums, and proteins, such as gelatin and albumen. Lyophobic colloids are, for the most part, elements or compounds of an inorganic character. Special methods (see next section) must be employed to prepare stable suspensions of these substances. Lyophilic colloids react with the liquid in which they are dispersed to form *solvates*, e.g., with water they are hydrated. When these colloids are precipitated, they are converted once more to the colloidal state simply by mixing them with the liquid; and hence, they are said to be *reversible colloids*. Thus, albumen can be precipitated by the addition of a concentrated solution of a salt, but it is redispersed when the precipitate is thoroughly washed and placed in pure water. Lyophobic colloids are not reversible; when

they are precipitated, they are not redispersed when the liquid is again added.

5. The Preparation of Colloidal (Lyophobic) Dispersions

Solids can be dispersed in liquids to form lyophobic suspensions by several methods which are classified as (1) *dispersion* or (2) *condensation* methods. We shall speak only of suspensions in water.

(1) *Dispersion Methods.* These methods of producing colloidal suspensions involve the subdivision of coarse particles of the substance into particles of colloidal dimensions. Grinding or other purely physical operations may be used for this purpose. The *colloid mill* is a machine especially designed to produce the required state of division; it is used in many industries. The dispersion is sometimes effected by adding to the medium a substance that breaks up, or disintegrates, the grains of the material to be dispersed into particles of colloidal dimensions. A substance that acts in this manner is called a *peptizing agent.* Thus, a dilute solution of sodium hydroxide peptizes clay.

Colloidal dispersions of metals below hydrogen in the electrochemical series can be produced in water by the *Bredig arc process.* Two wires of the metal are allowed to dip under water. The outside ends of the wires are attached to an electric circuit. The ends under water are separated slightly, and an electric arc is produced between them. Small particles of the metal are split off of the wire and become dispersed in the liquid. Similar particles may be produced by the condensation of the vapor of the metal which is volatilized at the temperature of the arc and then condensed in the liquid medium to form tiny colloidal particles. The presence of a small amount of sodium hydroxide is desirable, because its hydroxyl ion peptizes the particles of the metal.

(2) *Condensation Methods.* These methods involve the formation of particles of colloidal size by causing smaller particles, molecules for example, to aggregate. They depend upon chemical reactions between the molecules or ions of two substances to form substances that are very slightly soluble in the dispersing medium. These reactions are usually (1) *double decompositions* or (2) *reductions.*

A dark red suspension of ferric hydroxide is formed by mixing a concentrated solution of ferric chloride with hot water. This reaction is a double decomposition (hydrolysis):[1]

$$Fe^{+++} + 3\ Cl^- + 3\ HOH \rightleftharpoons Fe(OH)_3 + 3\ (H^+ + Cl^-).$$

A colloidal suspension of arsenic trisulfide is produced by the reaction occurring in a solution containing hydrogen sulfide and arsenious acid, H_3AsO_3. Small concentrations of As^{+++} and $S^=$ ions in this solution form arsenic trisulfide, As_2S_3, which is very slightly soluble but does not precipitate because it is produced in the form of colloidally dispersed particles. A colloidal gold dispersion can be produced by the reduction of gold (auric) chloride in dilute solutions by tannin, hydroquinone, formaldehyde, or ferrous sulfate.

PROPERTIES OF COLLOIDAL SYSTEMS

6. The Tyndall Effect

When a beam of light enters a darkened room through a small hole in a window shade, small particles of dust that are not visible in a lighted room can be seen. In the darkened room they are observed as tiny flashes of light, and they appear to be moving in all directions in the path of the beam. The same phenomenon can be observed by passing a beam of light through a colloidal suspension (Figure 160). The dispersed particles act in the same manner as dust particles and scatter the light in all directions; and, therefore, if we look at the

[1] The colloidal particles probably are composed of hydrous ferric oxide, $Fe_2O_3.x\ H_2O$, but in the equation this is written as the hydroxide, $Fe(OH)_3$, for convenience.

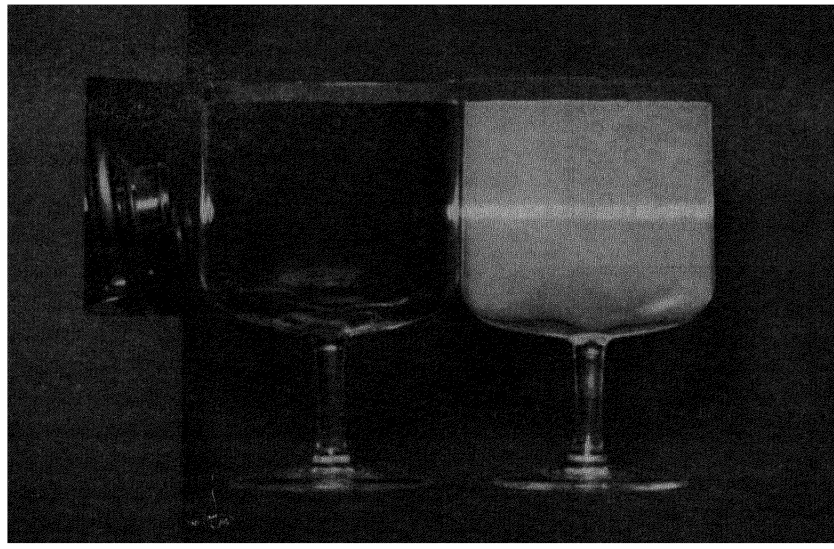


Figure 160. The Tyndall Effect

A beam of light passes through a true solution of potassium dichromate and then through a colloidal suspension of gum mastic.

mixture in a direction that is perpendicular to the beam, some of the scattered light reaches our eyes, and the beam's path through the mixture is made visible to us. The illumination of the beam's path in this manner is called the *Tyndall Effect.* Light passes directly through true solutions without being scattered and it produces, therefore, no visible path. This effect is, then, a method by which a true solution and a colloidal suspension, sometimes called a *colloidal solution*, can be distinguished.

7. The Brownian Movement

If a colloidal suspension is placed against a dark background and illuminated by a beam of light that passes through the suspension from the side, the particles of the colloid, when viewed through a microscope, will be seen to be in constant, random motion (Figures 161–2). This phenomenon is called the Brownian movement. The molecules of the dispersing liquid strike the colloidal particles, driving them first in one direction and then in another. This movement of colloidal particles is one reason why they do not settle out of the medium.

8. Electric Charge

In general, the particles of lyophobic dispersions are electrically charged. The presence of electrical charges can be demonstrated, and the kind of charge can be determined, by placing electrodes, connected to a battery or other source of current, in a colloidal suspension of arsenic trisulfide. The colloidal material, which has a yellow

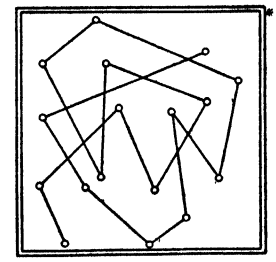


Figure 161. The Brownian Movement

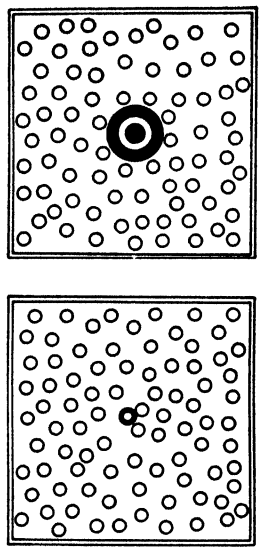


Figure 162. Impacts of Molecules of Solvent with Large Particle (top) and with Small Particle

color, moves toward the anode and is, therefore, negatively charged. At the anode the electric charges of the particles are discharged, and the colloidal dispersion is converted into a precipitate. It appears, therefore, that the electric charges of the particles are necessary, in some way, to the colloidal state of this substance. Since all the particles of one kind carry the same kind of charge, they repel one another, and they cannot coalesce or precipitate until they are discharged. This, then, is one more reason why they remain suspended instead of settling. Most of the sulfides of metals and the metals themselves form negatively charged colloidal dispersions. The hydroxides of the metals, such as ferric hydroxide, have positive charges.

The charges of colloidal particles are probably produced by the adsorption of ions. These ions are frequently hydrogen or hydroxyl ions, but other ions act in a similar manner. Silver bromide, AgBr, is not readily precipitated in an excess of Ag^+ ions, which are adsorbed by particles of AgBr, and which give the particles positive charges that prevent them from coalescing to form a precipitate. If the particles adsorb positive ions more readily than negative ions, they acquire a positive charge and *vice versa.*

9. The Precipitation of Colloidal Suspensions

As a general rule, we may say that colloidal dispersions are likely to be produced in solutions containing low ionic concentrations. When once formed, they are likely to be coagulated by high concentrations of ions which they will adsorb, and which carry charges that are opposite in sign to those that were adsorbed when the colloidal dispersion was formed. A dispersion of negatively charged arsenic trisulfide, for example, is readily coagulated by adding hydrochloric acid. The negative charges of the As_2S_3 particles are produced by the adsorption of hydroxyl ions. The acid removes these ions and converts them into water molecules. In this way the dispersed particles lose their negative charges and can then form larger aggregates.

The effect of ions upon colloidal dispersions is shown when river waters, which contain considerable material in colloidal suspension, flow into the sea. The salts of sea water cause these colloids to be precipitated, and the deposit of this material leads, eventually, to the formation of a delta.

10. The Precipitation of Colloidal Dust Particles

The *Cottrell electrical precipitator* is used to recover substances from smokes or fumes and to prevent smoke from furnaces. The escaping gases are passed between metal plates, between which there is maintained a high voltage. The very small solid particles of the smoke are colloidally dispersed in the air and other gases. Like colloidal dispersions in a liquid, these particles carry electric charges that may be produced by the adsorption of ions, or that may be in-

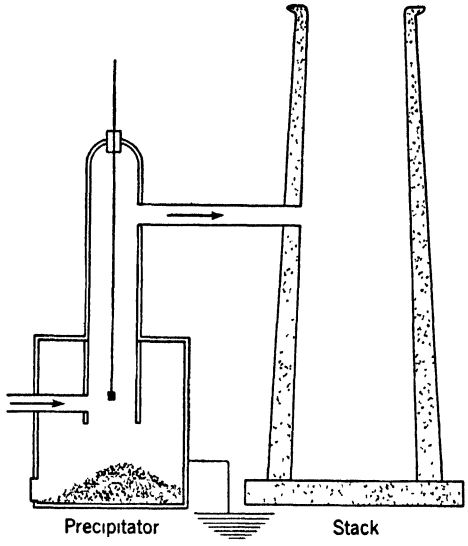


Figure 163. Cottrell Electrical Precipitator

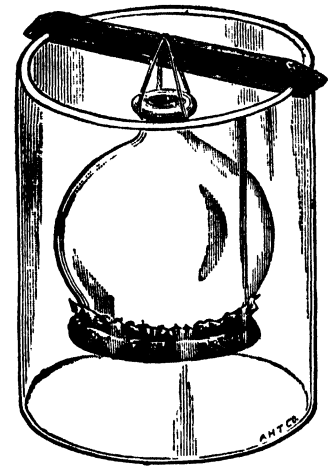


Figure 164. Diagram of Cell Used for Dialysis

The ferric hydroxide dispersion is retained in the bag, while the hydrochloric acid diffuses through the parchment and into the pure water.

duced upon them when they pass through the electric field.

In the Cottrell process the particles are attracted to the highly charged electrodes, where they are discharged and deposited as dust. The process is used to recover valuable products that otherwise would escape from the stacks of smelters, kilns, and furnaces. Potassium salts may thus be recovered from the dust of cement kilns, selenium from the dust of pyrites burners, and valuable metals from the flue dust of smelters and foundries. The Cottrell process is also used to prevent or lessen the "smoke nuisance" in industrial centers. Ordinary smoke is black because it contains unburned particles of carbon and other substances, which can be precipitated in the same manner as other small particles that are colloidally dispersed.

11. Dialysis

Since high concentrations of ions tend to precipitate colloids, these ions must be removed if the colloidal dispersions are to be preserved for any length of time. This can be done by taking advantage of the fact that colloids will not pass through many kinds of membranes that are permeable to water and to the ions of electrolytes dissolved in the water. The separation cannot be made by using ordinary filter paper, but certain kinds of membranes, such as egg skin, parchment paper, and bladder, will hold back the colloidal dispersion, thus permitting it to be separated from substances that are in true solution. This process is called *dialysis* (Figure 164).

12. Protective Colloidal Substances

The coagulation or precipitation of one colloid is prevented sometimes by the presence of another. The second colloid probably forms a *protecting* film or coat around the particles of the first, thus preventing them from coming into direct contact and coagulating to form large particles, which could not be kept in suspension. Gelatin is the most familiar and widely used protective colloid. Its action may be demonstrated by mixing a solution of potassium bromide with a solution of silver nitrate containing about one per cent of gelatin. Naturally, we should expect a precipitate of silver bromide to form, but there is none.

We may assume that the gelatin prevents the formation of a precipitate by forming a protecting film around grains of the silver bromide of colloidal size. The colloidal silver halides on the surface of photographic plates and films are protected by gelatin in this manner. Gelatin also acts as a protective colloid in the manufacture of ice cream, in which it prevents the formation of crystals of ice and sugar. Gum arabic acts in a similar capacity in marshmallows and in inks. Lactalbumen in milk acts in a similar manner to form curds of smaller and more easily digested particles, when the casein of the milk is coagulated in the stomach.

13. Emulsions

An emulsion is a dispersion of very small drops of one liquid in another with which it is not miscible. We may prepare an emulsion of kerosene and water by violently shaking the two liquids together. A milky fluid, consisting of thousands of drops of one liquid in the other is the result. This emulsion, however, is only temporary. The small drops of oil combine to form larger drops, until, finally, the oil separates entirely from the water and forms a distinct layer.

To prepare a stable emulsion, we must employ a third substance called an *emulsifying agent.* The action of this substance may be explained in the following ways: (1) It may decrease the surface tensions of the liquids, a change that lessens the tendency of the drops to combine, forming larger masses of each liquid; (2) it may form protecting layers or films about the drops of one of the liquids.

Soap, for example, is an emulsifying agent for a mixture of kerosene and water. With ordinary soaps, drops of oil are dispersed in water. The cleansing action of soap is explained, in part, by the soap's action as an emulsifying agent in the formation of stable emulsions of water, oils, and grease, which then can be washed off in a stream of water. Milk is an emulsion of drops or globules of butter-fat in water, with casein serving as the emulsifying agent. Mayonnaise is an emulsion of olive oil in dilute vinegar, for which the yolk of eggs acts as the emulsifying agent.

14. Gels and Jellies

When colloidal dispersions of certain lyophilic colloids, or sols, set, they form gels, or jellies. The acidification of a solution of sodium silicate, Na_2SiO_3, produces a gelatinous precipitate, or jelly, of silicic acid, H_4SiO_4.[1] It is thought that the silicic acid forms a mass of highly hydrated material that contains many cell-like structures (Figure 165). The walls of the cells are made up of long, slender filaments or threads composed of strings of united particles. Inside these cells the liquid is held in about the same manner that a sponge holds water. When the jelly is partially dehydrated — to 5 or 7 per cent of water — a porous and very adsorbent product, called *silica gel*, is formed.

The filaments which are largely responsible for the structures of jellies are highly hydrated materials. This is true, for ex-

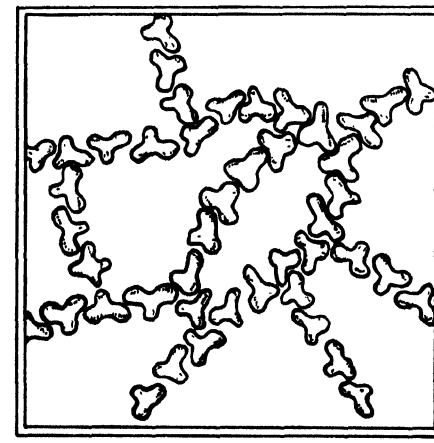


Figure 165. The Structure of a Gel

[1] This substance is frequently represented, for convenience, by this formula, although it is probably hydrated silicon dioxide, $xSiO_2.nH_2O$, the composition of which varies with the conditions under which the substance is formed.

ample, of protein in the tissues of the body which readily hydrate and are present as gels in the body. Excessive hydration of these tissues produces swelling, or oedema. The swelling and bursting of seeds depends upon the hydration of colloidal material.

Fruit jellies are made from the juices of certain acid-containing fruits, sugar, and *pectin*. Only certain fruits, such as apples and grapes, contain pectin. The acid aids in the hydration of the pectin, which is the action that is largely responsible for the formation of the jelly. Soap is a partially dried jelly, or gel, and agate is a dry form of silica gel.

15. Adsorption

Adsorption refers to the tendency of particles (usually molecules or ions) of one substance to adhere to the surface of certain solids or liquids. This term should not be confused with absorption which refers, for example, to the taking up of water by a sponge, or to the penetration of a solid by a liquid or a gas because of the porosity of the solid. Adsorption is a surface phenomenon and, consequently, the capacity for adsorption that a solid or a liquid possesses depends upon the amount of surface that it exposes to the particles of another substance as well as upon its chemical nature. Since colloidal particles are extremely small particles, they possess very large amounts of surface (for a given weight) and, consequently, have extremely great adsorptive powers. Colloidal particles exert a selective action in the adsorption of ions from a solution. Some adsorb positive ions in excess and thus acquire a positive charge, while others adsorb negative ions and become negatively charged (page 228).

16. The Flotation Process of Concentrating the Ores of Metals

Many ores are not used because the cost of working vast quantities of material to ob-

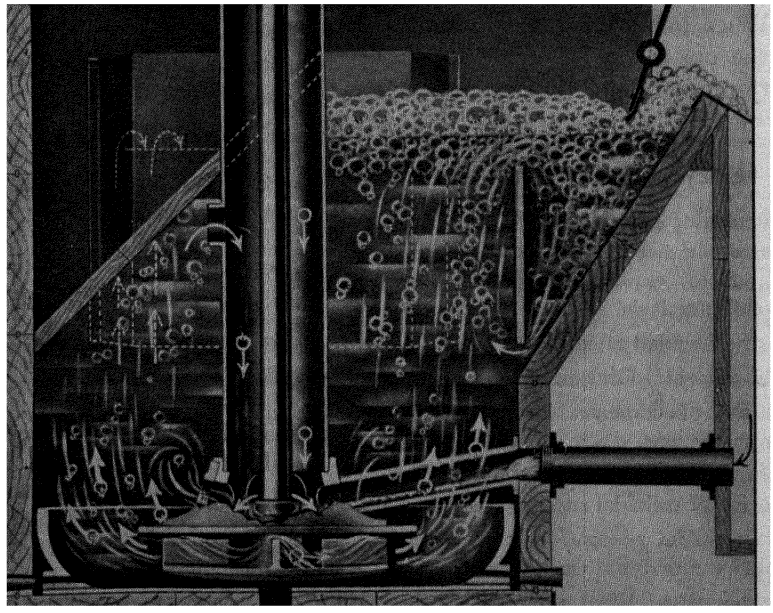


Figure 166. A Flotation Unit in Which Low Grade Ores are Concentrated
(Courtesy of Denver Equipment Company)

tain small yields of the metals is in excess of the price for which the metal can be sold. Therefore, any method of concentrating low grade ores by first removing worthless material that would interfere in metallurgical reactions and operations involved in the extraction of the metals reduces costs and may make possible the utilization of ores that otherwise would have no value. One process employed for this purpose is called *flotation*.

The ore is crushed and thoroughly mixed with water to which about one per cent of some oil or oily material — often creosote — has been added. A froth is produced by adding pine oil and vigorously churning air into the mixture. The particles of the ore that contain the metal are coated by the oil and adhere to the bubbles of air in the froth, which rises to the top and flows over the rim of the vat. Particles of sand and other earthly materials sink, because they are wet more readily by water than by oil. Only the particles that are wet by the oil adhere to the bubbles. For some kinds of ores the worthless material is more readily wetted by the oil and the valuable portions by water. When this is true, the worthless portion of the ore is carried away in the froth, and the metallic portion collects at the bottom of the unit.

REVIEW EXERCISES

1. State the meaning of the following terms and give an example of each: lyophobic colloid; lyophilic colloid; emulsion; hydrosol; protective colloid; dialysis.
2. Describe the Tyndall effect.
3. What is an aerosol? Give an example.
4. Describe the phenomenon known as the Brownian movement.
5. Define adsorption. What part does it play in the formation of colloidal suspensions?
6. Why is a colloidal suspension more stable after it has been dialyzed than before?
7. Define peptization. What are some of the methods by which colloids are peptized?
8. How are colloidal dispersions different from solutions?
9. How does a soap act as a cleansing agent in removing oil and dirt?
10. What is the nature of the dispersing medium and the dispersed substance in fog, foam, whipped cream, and butter?
11. How does dialysis differ from osmosis?
12. What procedure can you suggest as a method of producing a colloidal dispersion of (1) clay, (2) silver, (3) aluminum hydroxide, and (4) the sulfide of arsenic?
13. Why does aresenic trisulfide precipitate instead of forming a colloidal dispersion in the presence of hydrochloric acid?
14. Can you suggest an explanation of the fact that certain soluble salts, like KCl, that are responsible for the fertility of the soil are not dissolved by water and carried away completely?
15. Describe and discuss the principles upon which each of the following is based: (1) The Cottrell precipitator and (2) the flotation method of concentrating ores.
16. What are some of the reasons why a substance in colloidal suspension does not precipitate?
17. What evidence indicates that colloidal particles are electrically charged?
18. Refer to Figure 162. Why is a small particle more likely to show the Brownian movement than a large particle?
19. A colloidal suspension of arsenic trisulfide is precipitated more effectively by aluminum sulfate than by sodium chloride. Can you suggest a possible explanation?

REFERENCES FOR FURTHER READING

Bancroft, W. D., *Applied Colloid Chemistry*, 3d ed. New York: McGraw-Hill Book Company, 1932.

Hartman, R. J., *Colloid Chemistry*. Boston: Houghton Mifflin Company, 1939.

Hawley, Gesmer G., *Small Wonder — The World of Colloids*. New York: Alfred A. Knopf, 1947.

Ind. and Eng. Chem., **15,** 218, 1279 (1923); **17,** 891 (1925); **32,** 652, 1172 (1940).

J. Chem. Ed., **2,** 240, 323, 907 (1925); **3,** 253, 291, 325, 438, 505, 909, 1282 (1926); **6,** 1486, 2115 (1929); **11,** 279 (1934); **17,** 468 (1940); **18,** 590 (1941); **25,** 461 (1948); **26,** 21 (1949).

18

THE ATMOSPHERE

1. Introduction

The term *atmosphere* refers to the mixture of gases that surrounds the earth. Its total weight is estimated as 5.7×10^{15} tons. This mixture is also called air, although the latter term is more often used in referring to a small part of the atmosphere.

The experimental work of Scheele, Priestley, Black, Rutherford, and Lavoisier, during the late eighteenth century, provided the background for Lavoisier's explanation of air as a mixture of oxygen and nitrogen. During the last ten years of the nineteenth century, Lord Rayleigh and Sir William Ramsay discovered argon (1894), and Ramsay (with Travers) discovered neon, krypton, and xenon. Ramsay showed that these inert gases also are constituents of the atmosphere and that traces of helium, the lightest of these gases, are also present. In addition to the elements previously mentioned, the air contains water vapor, carbon dioxide, traces of hydrogen, dust, and other more or less accidental substances, such as hydrogen sulfide, sulfur dioxide, and ammonia. Minute organisms, such as bacteria, yeast cells, and the spores of molds and fungi, are usually present.

The following table represents the average composition of air at sea level:

COMPOSITION OF THE AIR IN PER CENT BY VOLUME

Nitrogen	78
Oxygen	21
Water Vapor	Varies greatly
Argon	0.94
Carbon dioxide	0.03–0.04
Hydrogen	0.01 or less
Neon	0.0012
Helium	0.0003
Krypton	0.00005
Xenon	0.000006

2. Air is a Mixture

We are certain that air is a mixture, and not a compound, for the following reasons:

(1) The composition of the atmosphere is not definite. The variation in composition with altitude is certain proof that air cannot be a compound.

(2) Liquid air does not have a definite boiling point.

(3) The composition of air dissolved in water is not the same as that of ordinary air.

(4) When oxygen and nitrogen are mixed, at ordinary temperatures, there is no change in temperature to indicate a reaction.

(5) If air is a compound, it is totally

unlike any compound of nitrogen and oxygen that has ever been produced.

The proportions of the various components of air are, nevertheless, unusually nearly constant, because of certain changes that balance one another. Carbon dioxide, for example, is thrown off into the air in the respiratory process of animals. Large amounts are also added in the gases produced during the combustion of fuels and in the decay of organic materials. These processes also remove oxygen from the air at the same time that they add carbon dioxide. Plants absorb carbon dioxide and from it synthesize starch, sugar, and cellulose. During these changes, oxygen is released to the air. The life processes of plants, therefore, balance the effects of animal respiration, combustion, and decay upon the composition of the atmosphere.

3. Nitrogen

Most of the nitrogen of the world is in the form of the free element. The atmosphere consists of about 78 per cent of nitrogen by volume, and the weight of the element above every square mile of the earth's surface is about 20,000,000 tons. This nitrogen of the air is extremely valuable to man and to all forms of life. Its presence in such large amounts dilutes the oxygen and slows down oxidation. Life would be different than it now is in an atmosphere of pure oxygen; it would probably be much shorter. The combustion of fuel in stoves and furnaces would be difficult to control; the corrosion of metals would proceed so rapidly that the use of iron and steel would not be practical; and decay would be very rapid. The nitrogen in the air also supplies plants with one of their essentials. Usually, the element is supplied directly by compounds of nitrogen that are present in the soil, but the air is the indirect supply. From this same source during recent years has come more and more of the nitrogen required by industry to produce ammonia, and nitric acid, and the many nitrogenous substances and materials made from them — fertilizers, explosives, dyes, drugs, plastics, lacquers and many others.

4. The Carbon Dioxide of the Atmosphere

Large amounts of carbon dioxide are removed from the air during chemical changes that play an important role in the weathering of different rocks. Thus, a solution of carbon dioxide in water contains carbonic acid, which reacts with limestone and dolomite to form calcium and magnesium bicarbonates,

$$CaCO_3 + H_2O + CO_2 \longrightarrow (Ca^{++} + 2\,HCO_3^-),$$

which are more soluble than the carbonates that are present in the rocks; and, therefore, the rocks gradually wear away.

Water containing carbon dioxide also plays a very important part in the weathering of other kinds of rocks. This is especially true in the decomposition of the *feldspars*, of which *orthoclase* ($KAlSi_3O_8$) is an example. The action of a solution of carbonic acid (H_2CO_3) upon this mineral is shown by the following equation:

$$2\,KAlSi_3O_8 + H_2CO_3 + H_2O \longrightarrow K_2CO_3 + Al_2O_3.2\,SiO_2.2\,H_2O + 4\,SiO_2.$$

(clay) (sand)

Although carbon dioxide is not extremely soluble in water, large quantities must be removed by dissolving in the water that falls through the air as rain. Some also dissolves in the waters of rivers, lakes, and the seas, forming a solution in which the carbon dioxide is in equilibrium with the carbon dioxide in the air. If the concentration of carbon dioxide in the air is increased, more of it must dissolve to establish equilibrium once again.

The quantities of oxygen, carbon dioxide, and nitrogen in the air are so large and the quantities added or removed by plants, animals, and chemical changes of one kind or another are relatively so small, that the total quantities suffer only slight changes.

Changes at one place on the earth's surface may occur to a sufficient extent to become significant, but these are soon destroyed by the winds which mix the air continuously and prevent radical departures from an average composition.

5. The Water Vapor of the Atmosphere: Humidity

At a definite temperature, air can contain a certain maximum quantity of water vapor per unit of volume. This is the quantity of water vapor required to produce equilibrium with the liquid (page 178) at that temperature. When this condition is fulfilled, the air is *saturated* with water vapor, and the *humidity* is 100 per cent. At low temperatures, only a small quantity of water vapor must be present in the space above the liquid to produce a humidity of 100 per cent, but as the temperature rises, the vapor pressure of water increases, and the air must contain more vapor before it becomes saturated.

The *relative humidity* of the air is the ratio (expressed as per cent) of the quantity of water vapor present in a definite volume to the quantity that would have to be present to produce saturation. Since the partial pressure of the water vapor in the atmosphere is directly proportional to the relative amount of that substance (by volume) in a given sample, the relative humidity may be calculated by comparing the partial aqueous vapor pressure in the air to the vapor pressure of water at the same temperature. Thus, the vapor pressure of water at 20° is 17.4 mm. If the partial pressure of the water vapor in the air at 20° is 8.7 mm., the relative humidity is 50 per cent.

6. Precipitation of Moisture

The water vapor of the atmosphere is produced by the evaporation of water from lakes, rivers, seas, oceans, and soil. The air above a large body of water, such as the ocean, may become entirely, or almost, saturated. Winds move this air over the surface of the ocean and finally blow it across the land. If the temperature of the land is higher than that of the ocean, the air is warmed and can absorb more moisture. Hence, the humidity falls to a value less than 100 per cent. But if the saturated air that blows in from the sea is cooled, it will be capable of holding less moisture. The excess may precipitate as rain or, if the temperature is sufficiently low, as snow.

Because water molecules are lighter than molecules of oxygen and nitrogen, moist air is lighter than dry air and tends to rise. At higher elevations, the temperature may be reduced sufficiently to cause the moisture that it contains to exceed the amount required for saturation, and if this happens, precipitation may occur. The dust particles in the atmosphere play an important part in precipitation by acting as nuclei about which drops of water are formed as the vapor condenses.

7. Ventilation and Air-Conditioning

Adequate and efficient ventilating systems are now regarded as essential in every building designed for work or habitation. Ventilation does not mean, merely, the renewal of the air supply. It was once thought that the discomfort experienced by the occupants of closed and poorly ventilated rooms was caused by reduction in the percentage of oxygen and by the poisonous effects of the accumulated carbon dioxide, but this belief has been disproved. This does not mean, however, that such air is just as good to breathe for any considerable length of time as the normal "out-of-doors" air. Certainly the normal air is more invigorating, and our bodies function in it in a more nearly normal manner.

The condition of the air in a house or any other building that determines in large part the comfort and health of the occupants depends upon three factors: humid-

ity, temperature, and circulation. The humidity is important because it controls the evaporation of moisture from the skin. As the humidity becomes higher and approaches the saturation point, evaporation from the skin occurs more and more slowly, and discomfort results. Conditions may be improved by maintaining a fairly low temperature (68° F.) and by keeping the air in motion. If the air is moving, there is no opportunity for the portions immediately surrounding the body to become saturated, thus slowing down evaporation still more.

In winter, cold air containing only small quantities of moisture is brought inside and heated to about 70° F. At this temperature, it can absorb much more moisture than it could possibly contain out-of-doors. Moisture evaporates too rapidly from the skin under these conditions, and the body is chilled. In winter, therefore, provisions should be made to increase the humidity of the air. If this is not done, the skin becomes dry and cracks. Excessively dry air also causes furniture and walls to crack.

Air conditioning provides for regulation of temperature, humidity, and circulation, as well as frequent renewal. For the greatest degree of comfort, the air of buildings should have a relative humidity of 35 to 50 per cent in winter, and 20 to 30 per cent in summer.

8. Liquid Air

The production of liquid air (page 49) has become an important industry, or rather an important part of several industries that use oxygen, nitrogen, argon, and neon. It also finds considerable use in scientific work, whenever extremely low temperatures are desired. It is used to remove moisture from gases by freezing. Charcoal cooled by liquid air will adsorb almost all of the gases remaining in vessels that have been evacuated as completely as possible by vacuum-pumps.

Because of its low boiling point, liquid air cannot be kept in an ordinary container, such as a beaker or a bottle. If it is to be preserved for any length of time, provisions must be made to insulate it from external sources of heat. The *Dewar flask*, designed especially for this purpose, is made of double glass walls, and the space between the walls is evacuated. Heat does not readily pass through a vacuum and, hence, the contents of the flask cannot absorb heat rapidly from the outside. The walls of the flask may be silvered, so that heat from the outside is reflected instead of being absorbed. Thermos bottles are constructed in the same way.

Liquid air is a mixture and, therefore, has no definite boiling or freezing point. It resembles water in appearance, but it has a slightly deeper bluish color, which becomes more intense as the nitrogen escapes and the concentration of oxygen increases. The average density is about 0.9 g. per ml. Its most spectacular property is its effect in cooling familiar, soft materials to an extremely low temperature and causing them to freeze. Flowers, vegetables, fruits, and rubber articles immersed in liquid air become so hard and brittle that they can be pulverized in a mortar.

THE INERT GASES

The air contains almost one per cent

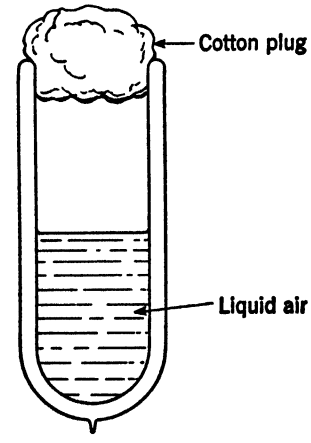


Figure 167. Dewar Flask

(by volume) of argon and much smaller amounts of helium, neon, krypton, and xenon. Because of their chemical inactivity these elements are called the inert gases. The inertness of these elements is explained by the structures of their atoms, each of which contains eight electrons (two in the atom of helium) in its outermost shell. Since their structures are more stable than any other arrangement of electrons would make them, the atoms of these elements do not lose, gain, or share electrons. Because of their lack of chemical activity the inert gases cannot be detected, separated, or identified by means of chemical reactions. Instead, the chemist in studying them must depend very largely upon the spectroscope (page 152).

9. History of the Inert Gases

Cavendish, in 1775, was the first investigator to find evidence of the presence of the inert gases in the atmosphere. He did not realize, however, the significance of his discovery. After causing all the nitrogen in a sample of air to combine with oxygen, under the influence of an electric spark, and after removing the excess of oxygen, the products of the reaction (NO and NO_2), and all other substances known to be in air, Cavendish found that a small part (about 0.008) of the original sample of air remained.

The findings of Cavendish went without explanation for more than one hundred years. In 1892, Lord Rayleigh found that the nitrogen prepared from air had slightly different properties from the pure nitrogen prepared from nitrogen compounds, such as ammonium nitrite. The sample prepared from air was always heavier than an equal volume of the other. In seeking an explanation of this difference, Lord Rayleigh was joined by Sir William Ramsay, who found a small percentage of the nitrogen-fraction of air that would not combine with magnesium to form a nitride. It became necessary, therefore, to recognize this residue as a new element, named *argon* (lazy) because of its chemical inertness. This was in 1894.

Janssen, in 1868, found a line in the spectrum of the sun which could not be identified as belonging to the spectrum of any of the elements. Lockyer assumed that the line belonged in the spectrum of an element not known on the earth and gave it the name *helium* (sun). This element was not discovered on the earth until 1889.

Neon, *krypton*, and *xenon* were discovered by Ramsay and Travers, in 1898. Liquid air was carefully distilled, and fractions were collected at different temperatures. Each of the first fractions was further separated by distillation, and the different samples were studied with the aid of the spectroscope. The spectra revealed lines belonging to three hitherto unknown elements, which were called neon (new), krypton (hidden), and xenon (stranger).

Radon, previously called niton, is also a member of the family of inert gases. It is produced by the radioactive disintegration of radium and is itself radioactive (page 135). Because of its rapid rate of decay (page 135), this gas can never be present anywhere in any considerable quantity.

10. Production and Properties of the Inert Gases

Argon, neon, krypton, and xenon are prepared by the fractional distillation or fractional liquefaction of air (Figure 168). Until World War I, helium was prepared, usually, by heating uranium minerals and was unobtainable in large quantities. Helium is now obtained from the natural gas produced in certain regions of the southwestern portion of the United States; its production is controlled by the government. The gas from some wells contains nitrogen and one to six or seven per cent of helium. The helium is recovered by liquefying the other constituents at a temperature and pressure at which helium

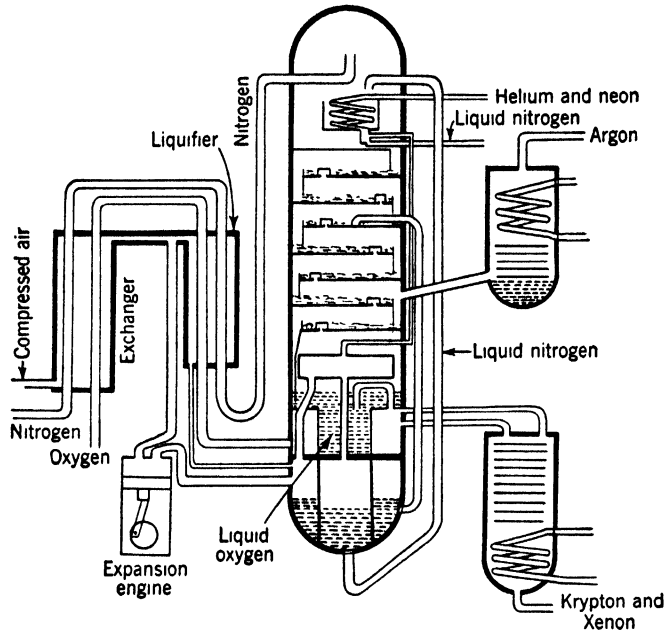


Figure 168. Diagram Showing the Parts of a Plant Designed to Separate the Different Constituents of Air

(Courtesy of Industrial and Engineering Chemistry and Air Reduction Company)

(b.p. — 268.90°) remains in the gaseous state.

The inert gases are composed of monoatomic molecules, and there is little tendency for their molecules to attract one another. Hence, they have very low boiling points. Argon, for example, boils at −185.9° and freezes at −189.3°. Helium boils within 4° of Absolute Zero. They are all colorless, odorless and tasteless. They form a few very unstable compounds of a co-ordinate covalent character. Hydrates of some of them are known.

11. Uses of the Inert Gases

Observation balloons and other lighter than air craft, before World War I, were filled with hydrogen, which is dangerous because of its extremely combustible character. Helium, which is next to hydrogen in lightness and, consequently, in lifting power, is the only gas that meets the requirements of low density and non-combustibility. Its density is 0.178 (grams per liter) and it has a lifting power about 93 per cent as great as hydrogen.

Helium mixed with oxygen is sometimes supplied under high pressures to men who must work in caissons, in diving bells, or in diving suits at considerable depths in water. When air is used, considerable nitrogen dissolves in the blood under the high pressures at which the air is taken into the lungs. When the diver emerges, he is likely to develop a condition called "bends," because the pressure of the air that he breathes is reduced, and the nitrogen that has dissolved in his blood quickly escapes from solution and forms bubbles. If helium, instead of nitrogen, is used to dilute the oxygen which he breathes, the danger is lessened, because helium is less soluble.

By evaporating liquid helium under reduced pressure, a temperature of −272.3°, within 0.7° of absolute zero, has been attained.

Argon is used in electric-light bulbs. An evacuated bulb is undesirable because the heated tungsten filament volatilizes too readily, and the vapor is condensed on the walls of the bulb. The volatilization of the tungsten is greatly reduced by filling the bulb with argon or nitrogen, which will not react with the metal filament. Argon is better suited for this purpose because it is more nearly inert than nitrogen. Argon, mixed with mercury vapor, is used in fluorescent lights. Neon and, sometimes, argon and helium are used in producing the tubes commonly called "neon signs." These tubes find wide use in advertising and in beacons for ships, airplanes, etc. The cost of operation is considerably less than that of the old-fashioned "electric-light" sign, and they give better and farther penetration, particularly through fog. The color of the light emitted by a "neon tube" depends upon the color of the glass of which the tube is made and upon the contents. Different colors are produced by different mixtures of argon, neon, and mercury vapor in tubes made of glass of different colors.

REVIEW EXERCISES

1. What facts show that the air is a mixture and not a compound?
2. What opposing factors cause the composition of air to be almost constant?
3. Explain what is meant by the relative humidity of the air. When is the humidity one hundred per cent?
4. Describe the conditions under which moisture is precipitated from the air.
5. What requirements should be met in providing adequate and efficient ventilation?
6. The density of a sample of liquid air is 0.91 g. per cc. and it contains 24 per cent (by weight) of oxygen. What volume of oxygen under standard conditions can be produced from 10 liters of the liquid, assuming that the oxygen is pure? By what method could this oxygen be separated from other substances in the liquid?
7. A dry 80 ml. sample of oxygen and nitrogen was mixed with 50 ml. of hydrogen and the mixture exploded. After the condensation of the water vapor, the volume of gas remaining was found to be 100 ml. and contained hydrogen and nitrogen. (*a*) What percentage of the original sample was oxygen? (*b*) What percentage of the residue was hydrogen?
8. Why is the lifting power of helium 93 per cent that of hydrogen, although the density of helium is approximately twice that of hydrogen?
9. What components of the atmosphere are likely to vary considerably from day to day in one location?
10. Why is the air in houses during winter weather likely to be drier than in summer?
11. Describe an experiment by which you could prove that the atmosphere has weight.
12. Why does the pressure at one place on the earth's surface vary?
13. How is dust related to the precipitation of moisture from the air?
14. Compare the amounts of water vapor in air that is saturated with vapor at 20° C. and at 0° C.
15. Why is the space between the walls of a Dewar flask evacuated? Why is the outer wall silvered?
16. Which has the greater density, dry air or air almost saturated with water vapor?

REFERENCES FOR FURTHER READING

Cavendish, H., *Experiments on Air*, Alembic Club Reprint, No. 3. Edinburgh: E. and S. Livingstone, 1784.

Harrow, B., *Eminent Chemists of Our Time.*

Ramsay, Sir W. R., *Gases of the Atmosphere.* New York: The Macmillan Company, 1915.

Weeks, M. E., *The Discovery of the Elements.* Also see *J. Chem. Ed.*, **9**, 1413 (1932).

Woodman, A. G., and J. F. Norton, *Air, Water, and Food.*

Air Conditioning: *Ind. and Eng. Chem.*, **31**, 134 (1939); *Chem. and Met. Eng.*, **47**, 285 (1940).

Inert Gases: *Ind. and Eng. Chem.*, **16**, 1200 (1924); **18**, 203 (1926); **21**, 1156 (1929); **27**, 110 (1935); *J. Chem. Ed.*, **3**, 45 (1926); **4**, 1376 (1927); **7**, 2408 (1930); **9**, 1413 (1932).

Origin and Composition of the Atmosphere: *Scientific Monthly*, **24**, 214 (1927).

19

THE ALKALI METALS

1. Introduction

Many of the compounds of the non-metals are also compounds of metals and, frequently, the most important of these are salts of sodium and potassium, two of the metals of the family that we shall now consider. As we study the compounds of the non-metals in the chapters that follow, it will be to our advantage to know something about the metals that so many of their most important compounds contain.

2. General Properties of the Family

The valence number of each element of the family is + 1, because each atom contains a single electron in its outermost, or valence, shell. The ionization potentials of all members of the family are relatively small, and the radii of their atoms and ions are large as compared to those of other elements in the same periods of the Periodic Table. Hence, these elements lose their single valence electron easily to electronegative elements like chlorine, and they are almost always found in ionic compounds, such as Na^+Cl^- or Na^+OH^-. The ionization potential decreases, and the radii of the atoms and ions increase, as the atomic weight and atomic number increase from lithium to cesium; and hence, we find that for cesium the valence electron is farther removed from the nucleus of the atom and is screened from the attraction of the nucleus by a greater number of electrons than the valence electrons in the atoms of any other element in the family. In the lithium atom the valence electron is closer to the nucleus than in any of the others. Hence, cesium is the most active chemically, and the activity decreases as the atomic numbers decrease. If we include element 87 as a member of the family, we would expect it, therefore, to be even more active than cesium.

All the alkali metals are white and have a brilliant luster. They are so soft that they can be cut easily with a knife. Because of their activity they are never found naturally in the free state, and, when prepared, they must be stored under oil or in sealed tubes. In the air they react not only with oxygen but with water and carbon dioxide. Their oxides are the anhydrides of strong bases, and their hydroxides have no tendency to react as acids, e.g., sodium hydroxide always reacts as $(Na^+ + OH^-)$ and never as $(H^+ + NaO^-)$. The members of the family are near the top of the electrochemical series, and cesium is the first element in this series.

Radioactive isotopes of element 87 have been produced by reactions involving atomic nuclei (page 143), and the name *francium*, Fr, has been given this element. It is doubtful that stable isotopes of francium exist in nature.

TABLE 8. PROPERTIES OF THE ALKALI METALS

	Electron Groups	Atomic Number	Atomic Weight	Specific Gravity	Melting Point	Boiling Point	Specific Heat
Lithium	2–1	3	6.94	0.53	186°	1200°	0.837
Sodium.....	2–8–1	11	22.997	0.97	98°	880°	0.297
Potassium ...	2–8–8–1	19	39.096	0.86	62°	760°	0.192
Rubidium....	2–8–18–8–1	37	85.44	1.53	38.5°	700°	0.079
Cesium.....	2–8–18–18–8–1	55	132.81	1.9	26°	670°	0.048

The regular changes in the physical properties of the alkali metals with changes in atomic weight and structure are clearly shown in this table.

SODIUM AND ITS COMPOUNDS

3. History

Metallic sodium and potassium were first prepared by Sir Humphrey Davy in 1807. Previous to that time, the substances which we now recognize as sodium and potassium hydroxides were regarded as elements and were called the "fixed alkalies." Davy prepared the metals by electrolyzing the melted hydroxides. He described the products as "inflammable substances very like metals."

4. Occurrence

The common source of sodium compounds is salt, sodium chloride. Large amounts of sodium are also present in certain silicate-rocks of the earth, such as the sodium feldspar known as *albite* ($NaAlSi_3O_8$). During the weathering of these rocks, sodium compounds are produced and since they are readily soluble in water, most of the sodium is leached out of the soil and finds its way eventually into the sea. Significant deposits of sodium salts can form only in arid regions. Several deposits containing sodium salts and located in desert or semidesert regions are of great importance not as sources of sodium but for other constituents of the compounds found in the deposits. Deposits of *sodium nitrate* are found in Chile; sodium carbonate occurs naturally, as the mineral called *trona*, in Egypt, California, and elsewhere; and *borax* ($Na_2B_4O_7$) is found in the Death Valley region of southern California.

5. Production of Metallic Sodium

Metallic sodium is now prepared by the electrolysis of fused sodium chloride. The Downs cell is shown in Figure 169. The cell is made of iron and lined with fire brick. The metallic sodium is liberated on the surface of the cathode, which is a circular iron or copper band surrounded by an iron gauze, which acts as a diaphragm and separates the sodium from the chlorine liberated at the anode. Fused sodium rises to the surface within the compartments surrounding the cathode and overflows into the receptacle shown at the right in Figure 169, where it is collected under oil. The chlorine liberated at the anode escapes

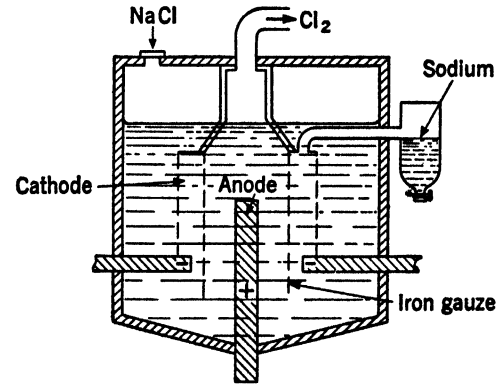


Figure 169

The Downs Cell for the Production of Metallic Sodium by the Electrolysis of Fused Sodium Chloride

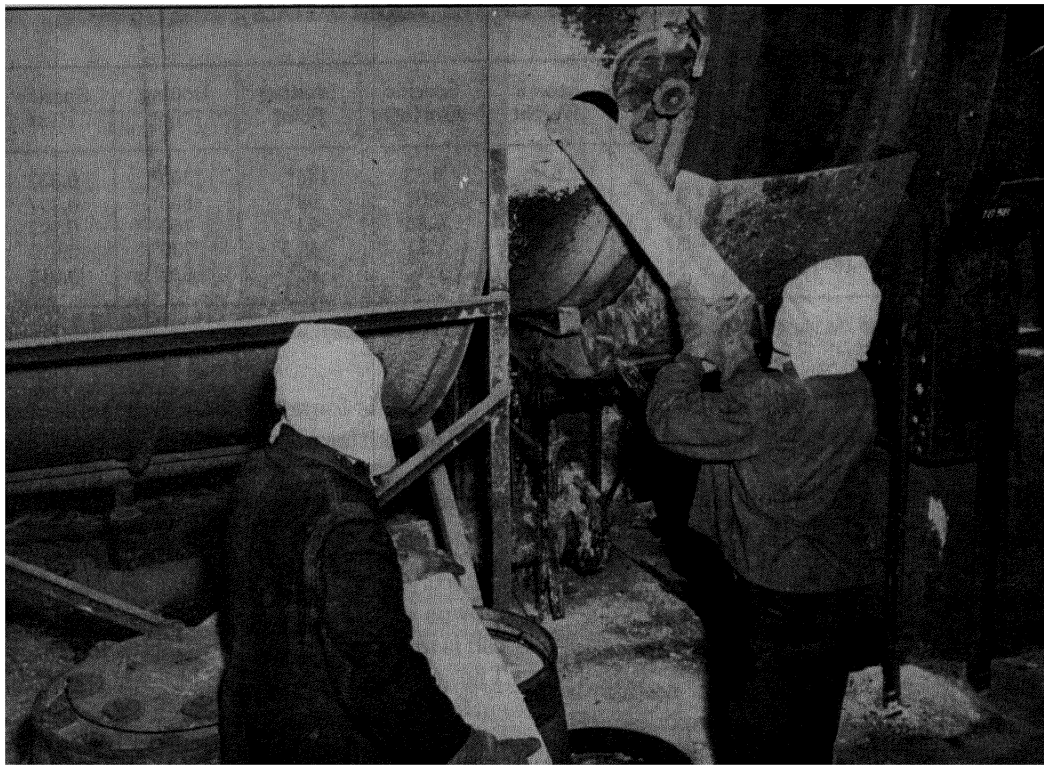


Figure 170. Loading Bricks of Metallic Sodium into a Sodium Monoxide Burner
This is one step in the production of sodium peroxide.
(Courtesy of Du Pont Company)

through an opening in the top of the cell. This is an important commercial source of chlorine.

6. Properties of Metallic Sodium

Sodium is a very soft metal that can be cut easily with a knife and molded into any desired form. It has a brilliant, silver-white appearance when freshly cut. It is slightly lighter than water; its specific gravity is 0.97. It melts at 98° and boils at 880°.

Sodium combines readily with most of the non-metals, such as oxygen, chlorine, sulfur, bromine, and iodine. With oxygen it forms the oxide Na_2O and the peroxide Na_2O_2. When sodium burns, the latter is produced. It displaces hydrogen from most acids, forming the sodium salt of the acid. It vigorously decomposes water, liberating hydrogen and forming sodium hydroxide (page 69). It is a vigorous reducing agent, often acting violently in this respect, e.g. the reduction of the hydrogen in water. It also reduces many of the metals when it reacts with their oxides or chlorides. With several of the metals it forms alloys, such as sodium amalgam (an alloy with mercury), hydrone (an alloy with lead), and the alloy of sodium and potassium, which is a liquid at ordinary temperatures. When heated in a flame, small particles of sodium or certain of its compounds are volatilized and impart a yellow color to the flame.

7. Uses of Metallic Sodium

Metallic sodium is used to prepare com-

pounds of the element which cannot be prepared readily from the chloride. The most important of these are sodium peroxide and sodium cyanide. It is also used to produce compounds of other elements including lead tetraethyl (ethyl gasoline), some dyes (indigo), drugs, and other organic compounds. It is used in some of the processes for manufacturing synthetic rubber. It has limited use as a reducing agent for the reduction of some metals from their oxides or chlorides; for example, before the modern method of producing metallic aluminum was introduced, this metal was made by reducing its chloride with metallic sodium. When a small quantity is placed in an evacuated tube and electricity is discharged through the tube, some of the sodium vaporizes. A tube of this kind containing neon, as well as sodium vapor, is now used as a lamp. Sodium is an excellent conductor of electricity, and, therefore, iron pipes filled with it are used as conductors in some instances for very strong currents. In some types of airplane engines hollow exhaust valves (stems and heads) are filled with sodium to prevent overheating; sodium conducts heat very readily.

Small amounts of sodium are stored under an oil such as kerosene. Large quantities are shipped in sealed tank cars in which air and moisture are excluded. The sodium is removed from the car by melting it by means of hot oil which is circulated through pipes built into the car. The fused metal is then removed by suction in an atmosphere of nitrogen. A tank car may transport as much as 40 tons of sodium.

8. Sodium Chloride

Many deposits of salt occur in different parts of the world. These are, usually, deposits that have been left when the water of lakes or isolated arms of the sea evaporated. There are, for example, enormous deposits of salt in the Stassfurt region of Germany. In this country there is a deposit underlying a vast area in Oklahoma, Texas, and Kansas. Important deposits are also found in New York, Michigan, California, Louisiana, West Virginia, and Ohio. These beds lie beneath the surface, and the salt is removed either by mines or by forcing water down into the deposits to form strong brines, which are then pumped to the surface through wells.

Salt is purified by dissolving the crystals in water, concentrating the solution, and allowing the crystals to form again. Most of the common impurities of salt are more soluble and tend to remain in solution when the salt crystallizes. Salt usually contains a little magnesium chloride, which is hygroscopic and causes the salt to "cake." This prevents salt grains from "pouring" and clogs the openings in the "salt-shaker." To prevent this condition, starch may be added to coat each grain, or sodium bicarbonate may be added to convert the magnesium chloride into the carbonate, which is not hygroscopic.

Sodium chloride is an essential constituent of the food of man and animals. In addition to making our food more palatable, it is the source of chlorine from which the hydrochloric acid found in the gastric juice is produced. Sodium chloride is also found in the blood. A physiological salt solution, containing about 0.8 per cent of sodium chloride is used, sometimes, as an injection in treating persons who have suffered considerable loss of blood. Sodium chloride is also used as a preservative of foods, and in producing freezing mixtures (page 206). The most extensive use of salt, however, is in the manufacture of chlorine, hydrochloric acid, sodium hydroxide, sodium carbonate, and other compounds of sodium and chlorine.

9. Oxides of Sodium

Sodium forms two oxides, the normal oxide, Na_2O, and the peroxide, Na_2O_2.

The former is a vigorous dehydrating agent and reacts with water to form a concentrated solution of sodium hydroxide. Although there is at present considerable interest in its commercial possibilities, it has until recently been of little importance. It can be made by heating the hydroxide with metallic sodium:

$$2NaOH + 2\ Na \longrightarrow 2Na_2O + H_2,$$

or by heating sodium with oxygen under carefully controlled conditions.

The peroxide is formed by the direct combination of sodium and oxygen. Chips of sodium are placed on aluminum trays which are moved slowly through a furnace at 400°. A current of air is passed into the furnace and over the trays from the other end, so that sodium passes one way and air the other. This allows the oxidation to proceed more slowly and under better control than would be possible if sodium were simply heated in the air.

Sodium peroxide is a very vigorous oxidizing agent. It reacts with water and acids to form hydrogen peroxide:

$$(2\ Na^+ + O_2^=) + 2\ H_2O \longrightarrow 2\ (Na^+ + OH^-) + H_2O_2.$$

$$(2\ Na^+ + O_2^=) + (2\ H^+ + SO_4^=) \longrightarrow (2\ Na^+ + SO_4^=) + H_2O_2.$$

The hydrogen peroxide which is formed, particularly when a limited amount of water is used in the first of these reactions, decomposes into oxygen and water at ordinary temperatures.

10. Sodium Carbonate

The most important compound of sodium is sodium carbonate. At one time, it was obtained either from natural deposits of the substance called *trona*, $Na_2CO_3.NaHCO_3.2\ H_2O$, or by leaching the ashes of sea weeds with water. In early times, European countries obtained sodium carbonate from deposits in Egypt. At the present time, practically all of the sodium carbonate used in the world is made from sodium chloride. The United States produces annually more than 3,000,000 tons of which about 3 per cent comes from natural sources.

At the present time, most of the sodium carbonate produced in this country is manufactured by the Solvay process. Ammonia and carbon dioxide are passed into a solution saturated with salt. Ammonia, carbon dioxide, and water react (1) to form ammonium bicarbonate which reacts, in turn, with sodium chloride (2) to form sodium bicarbonate. This substance is only slightly soluble in the salt solution in which it is formed and, consequently, precipitates and is removed by filtration. It may be purified by dissolving it in fresh portions of water and evaporating the water until the bicarbonate, which is the least soluble substance in the solution, crystallizes and can be separated by filtration. By repeating this process several times, a very pure product is obtained. The bicarbonate is changed (3) into the normal carbonate by heating.

After the first separation of sodium bicarbonate crystals, the "mother liquor" is treated (4) with calcium hydroxide to supply hydroxyl ions, OH^-, which react with the ammonium ions to form ammonia and water. The mixture is heated to drive out the ammonia, which is then used again in the first step of the process. The reactions involved in the four steps are shown by the following equations.

(1) $NH_3 + H_2O + CO_2 \rightleftarrows (NH_4^+ + HCO_3^-)$

(2) $(NH_4^+ + HCO_3^-) + (Na^+ + Cl^-) \rightleftarrows NaHCO_3\downarrow + (NH_4^+ + Cl^-)$

(3) $2\ NaHCO_3 \rightleftarrows Na_2CO_3 + H_2O + CO_2$

(4) $2\ (NH_4^+ + Cl^-) + (Ca^{++} + 2\ OH^-) \rightleftarrows 2\ NH_3\uparrow + (Ca^{++} + 2\ Cl^-) + 2\ H_2O.$

Some of the details of the plant which is used to produce sodium bicarbonate by the Solvay process are shown in Figure 171.

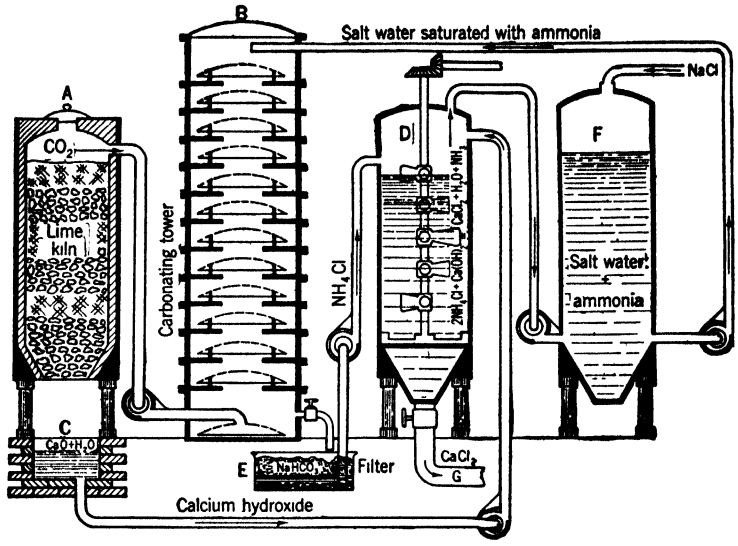


Figure 171. The Solvay Process for the Manufacture of Sodium Bicarbonate

A, lime kiln; B, carbonating tower in which sodium bicarbonate is made; C, hydrator, where "slaked lime" is produced; D, ammonia recovery unit, where the liquor from the filter E is treated with slaked lime from C, thus liberating the ammonia from ammonium chloride; F, tank in which the ammonia recovered in D is passed into brine; the resulting solution is then pumped to B where it is used in making sodium bicarbonate.

The only by-product is calcium chloride, which is not a very valuable substance.

In the electrolytic process, sodium bicarbonate is produced by electrolyzing a solution of sodium chloride saturated with carbon dioxide. Sodium hydroxide is the first product of the electrolysis (page 247), but this substance is converted into the bicarbonate by carbonic acid:

$$(Na^+ + OH^-) + H_2CO_3 \rightleftarrows (Na^+ + HCO_3^-) + H_2O.$$

11. Properties and Uses of Sodium Carbonate

Sodium carbonate crystallizes from solutions at room temperature in the form of large transparent crystals of the decahydrate, $Na_2CO_3.10\,H_2O$. This hydrate has a high dissociation pressure. When it is exposed to a warm, dry atmosphere it loses water, changing into the heptahydrate, $Na_2CO_3.7\,H_2O$, at 32°, to the monohydrate at 35.4°, and at higher temperatures the anhydrous salt, commonly called *soda ash*, is formed.

The decahydrate is called *washing soda* and *sal soda*. As such, it is used in many ways as a cleansing agent. Some of the cheaper soaps contain sodium carbonate as a filler, and some soap powders are made of powdered soap mixed with sodium carbonate. Sodium carbonate shows a pronounced alkaline reaction in aqueous solution. This is the effect of a reaction of sodium carbonate with water:

$$(2\,Na^+ + CO_3^=) + HOH \rightleftarrows (Na^+ + OH^-) + (Na^+ + HCO_3^-)$$

or,
$$CO_3^= + HOH \rightleftarrows HCO_3^- + OH^-.$$

The bicarbonate ion is very slightly ionized ($HCO_3^- \rightleftarrows H^+ + CO_3^=$); and hence, the carbonate ions react with hydrogen ions from water to form HCO_3^- ions, leaving free hydroxyl, OH^-, ions, which give the solution its alkaline character. This reaction is an example of *hydrolysis* (page 188).

More than 50 per cent of the sodium carbonate manufactured in the United States is used in the manufacture of common glass

and sodium hydroxide (Section 14). Other uses include the manufacture of soaps and cleaning mixtures, chemicals, paper, textiles, and petroleum products. It is also used as a water softener. The production in this country during 1949 was about 4,000,000 tons.

12. Sodium Bicarbonate

Sodium bicarbonate is produced directly by the Solvay process; by treating a saturated solution of the normal carbonate with carbon dioxide,

$$CO_3^{=} + H_2O + CO_2 \longrightarrow 2\ HCO_3^{-};$$

or by passing carbon dioxide over crystals of the decahydrate of sodium carbonate:

$$Na_2CO_3 + H_2O + CO_2 \rightleftarrows 2\ NaHCO_3.$$

This reaction is reversible, and when moderately heated, the bicarbonate is readily converted into the carbonate. The aqueous solution of pure sodium bicarbonate is faintly alkaline because of hydrolysis in which some bicarbonate ions react with water to form carbonic acid, H_2CO_3, and to release hydroxyl ions:

$$(Na^+ + HCO_3^-) + HOH \rightleftarrows (Na^+ + OH^-) + H_2CO_3.$$

The acid carbonate is much less hydrolyzed than the normal carbonate, because there is less tendency for HCO_3^- ions to combine with H^+ ions to form molecules of H_2CO_3, than there is for $CO_3^{=}$ ions to combine with H^+ to form HCO_3^-. A solution of sodium bicarbonate is used, sometimes, to neutralize acids:

$$(Na^+ + HCO_3^-) + (H^+ + Cl^-) \rightleftarrows (Na^+ + Cl^-) + H_2CO_3.$$

The carbonic acid decomposes, and the carbon dioxide escapes. Sodium carbonate reacts with acids in a similar manner.

13. Baking Soda and Baking Powder

The principal use of sodium bicarbonate is as an aerating, or leavening, agent in baking. It is sometimes called *baking* soda for this reason. The aerating action depends upon the liberation, within the dough, of carbon dioxide when sodium bicarbonate reacts with an acid. The bubbles of gas formed in the dough make the mixture more porous and less dense. The acid may be supplied by using sour milk, which contains *lactic acid.*

Baking powders contain sodium bicarbonate and some substance which acts as an acid. In aqueous solution, the acid reacts with the sodium bicarbonate to liberate carbon dioxide. The substances used as the acid include *cream of tartar* $KHC_4H_4O_6$, which is the acid potassium salt of tartaric acid ($H_2C_4H_4O_6$), and *monocalcium hydrogen phosphate,* $Ca(H_2PO_4)_2$. Cream of tartar, for example, reacts as follows when the baking powder is mixed with water:

$$(Na^+ + HCO_3^-) + (K^+ + HC_4H_4O_6^-) \longrightarrow H_2O + CO_2\uparrow + (Na^+ + K^+ + C_4H_4O_6^-).$$

Sodium aluminum sulfate is also used:

$$(Na^+ + Al^{+++} + 2\ SO_4^{=}) + 3(Na^+ + HCO_3^-) \longrightarrow 2(2\ Na^+ + SO_4^{=}) + 3\ CO_2\uparrow + Al(OH)_3\downarrow.$$

14. Production of Sodium Hydroxide

Sodium hydroxide is one of the most important compounds of sodium. The annual production in the United States is about 2,250,000 tons. It is often called "caustic soda," and its solution is called "soda lye." It is produced by two methods.

(1) *Reaction of Sodium Carbonate and Calcium Hydroxide.* A suspension of calcium hydroxide in water is mixed with a solution of sodium carbonate:

$$(Ca^{++} + 2\ OH^-) + (2\ Na^+ + CO_3^{=}) \longrightarrow CaCO_3\downarrow + 2\ (Na^+ + OH^-).$$

This is the oldest method of manufacturing sodium hydroxide, and it is still used. The calcium carbonate, which is only slightly

soluble, is removed by filtration. The filtrate is evaporated to dryness, and the residue is fused to remove all the water. The melted sodium hydroxide may be molded in the form of sticks or pellets, or thin sheets of the solid may be broken up to form flakes.

(2) *Electrolysis of an Aqueous Solution of Sodium Chloride.* Sodium hydroxide is also produced by the electrolysis of an aqueous solution of sodium chloride. One of the cells used for this purpose will be described in the chapter on chlorine (page 257).

The sodium hydroxide produced electrolytically contains sodium chloride as an impurity, because the chloride is not completely converted by electrolysis. Since the chloride is much less soluble than the hydroxide, the solution may be evaporated until most of the chloride has separated without losing the hydroxide, which is extremely soluble. After the removal of sodium chloride, the solution is evaporated completely to recover the hydroxide in the solid form. It still contains some chloride. If very pure sodium hydroxide is desired, it may be prepared by dissolving the solid in alcohol, in which sodium chloride and other impurities are only very slightly soluble. The clear solution is separated from the undissolved substances and is evaporated to produce the solid hydroxide. Small amounts of pure sodium hydroxide can be prepared, also, by the action of metallic sodium upon distilled water.

15. Properties of Sodium Hydroxide

Sodium hydroxide is a white crystalline solid. It is extremely deliquescent and is very soluble in water. It acts corrosively, as its common name, "caustic soda," implies; it readily disintegrates most animal and vegetable tissues. In the air, sodium hydroxide absorbs water and carbon dioxide and by the latter is converted into sodium carbonate. When pure sodium hydroxide solutions are desired, it is important that they should be stored under conditions that exclude air. It reacts with some of the metals, especially with those whose hydroxides can function as acids (page 123). Zinc, for example, is attacked by it to form sodium zincate, Na_2ZnO_2, and hydrogen. It reacts with, and its solution dissolves, the oxides of non-metals. For example, a glass vessel in which a solution of sodium hydroxide is stored soon becomes etched because of the reaction of the base with the silica, SiO_2, that glass contains:

$$2\ (Na^+ + OH^-) + SiO_2 \longrightarrow (2\ Na^+ + SiO_3^{=}) + H_2O.$$

Sodium hydroxide is a strong base, and many of its uses in the laboratory and in industry depend upon its capacity of supplying large numbers of hydroxyl ions to neutralize acids and to form other hydroxides, or sodium ions to make sodium salts.

POTASSIUM

16. Potash

The term *potash* refers to any potassium compound used commercially or in fertilizers. The quantity of potash is expressed as the quantity of the oxide, K_2O, that is equivalent in weight to the actual potassium compound or compounds used or produced. Thus, one ton of potassium chloride, KCl, is equivalent to about 0.63 ton of K_2O.

17. Sources of Potassium Compounds

Potassium occurs in several rocks of igneous origin in the form of micas and feldspars. Two of these minerals are *leucite* ($KAlSi_2O_6$) and *orthoclase* ($KAlSi_3O_8$). The decomposition of these rocks leaves at least a portion of the potassium in the soil in the form of various salts, which are essential to plant life. A soil that has borne several crops becomes deficient in potassium, and the salts of this element must be

supplied in the form of fertilizers. These fertilizers may also contain compounds of nitrogen and phosphorus, two elements which are also essential to the soil's fertility.

The German supply of potash comes from the Stassfurt deposits, which are found in the northern and central portions of that country. These salts were probably deposited by the evaporation of water in an isolated arm of the sea. The deposit contains some thirty different mineral substances. The most important of these are:

Sylvite, KCl.
Carnallite, KCl, $MgCl_2.6\ H_2O$.
Kainite, $MgSO_4.KCl.3H_2O$.
Schönite, $K_2SO_4.MgSO_4.6\ H_2O$.
Polyhalite, $MgSO_4.(CaSO_4)_2.K_2SO_4.2\ H_2O$.

The whole deposit is covered with a layer of sandstone, and the different layers of salts are mixed with sedimentary material. The salts are mined, and the potassium is obtained in a more concentrated form by fractional crystallization. The substance placed upon the market is largely potassium chloride or potassium sulfate. From this and a similar deposit in Alsace-Lorraine most of the world's needs for potassium salts were supplied at one time. The United States has now become independent of this supply by developing the potash resources within its own boundaries.

Most of the potash produced in this country comes from Searles Lake in southern California, from deposits near Carlsbad in New Mexico, from the Salduro Marsh in Utah, and from the alcohol and cement industries. At one time, some potash was recovered from wood ashes.

Searles Lake, in the Mohave Desert of southern California, is a bed of salts about 12 square miles in area and containing salt deposits which are about 70 feet thick. The salts are present with a "mother liquor" from which they have crystallized. From this liquor and the crystallized salts, potassium chloride is produced by fractional crystallization. Considerable "potash" is recovered from the ash of wastes remaining after the fermentation of molasses, and from the dust c cement mills and blast furnaces. Potassium salt are also extracted from a deposit containin *sylvite*, *langbeinite* ($K_2SO_4.2\ MgSO_4$), and *poly halite* near Carlsbad in New Mexico. This de posit alone, it is said, can supply all the needs c the United States in the future.

18. Production of Metallic Potassium

Metallic potassium is produced by th electrolysis of fused potassium hydroxid or potassium chloride, usually the former The method is the same, in general, as th method used to produce sodium (page 241) It can also be made by heating potassiun hydroxide with carbon or potassium car bonate with sodium. Sodium compound are much more abundant, and sodium i more easily and more cheaply produce than potassium. Therefore, since there ar few uses for which sodium cannot be mad to serve equally as well, the production o potassium is limited.

19. Properties of Potassium

Potassium resembles sodium. It is a sof metal and can be cut easily. The freshl cut surface has a bright, silvery whit luster, which is soon lost in the air. Th metal reacts even more vigorously witl water than sodium, and sufficient heat i liberated to ignite the liberated hydrogen.

As compared with sodium, potassiun has a smaller ionization potential an larger atomic and ionic radii. Hence, th valence electron of the potassium atom i more easily removed than the valenc electron of the sodium atom, as we shoul expect since the former lies in a grou farther removed from the nucleus than th latter. For the same reason, the potassiun ion is not as easily converted into an aton of the metal as the sodium ion, and, there fore, metallic potassium is more difficult t prepare than metallic sodium.

Metallic potassium melts at 62°, boils a

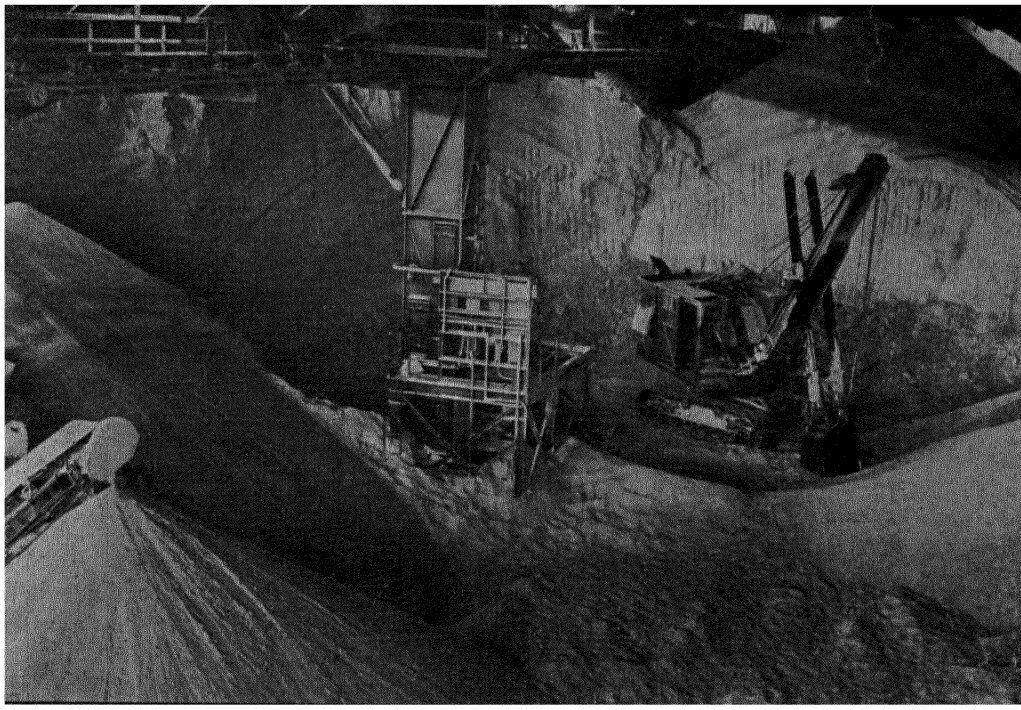


Figure 172. Storage of Potassium Salts (potash) Recovered from Searles Lake
(Courtesy of American Potash and Chemical Company)

774°, and produces a greenish colored vapor. The metal and its compounds impart a violet color to the flame of a Bunsen burner when they are heated in the flame. The color of this flame is observed best through a piece of cobalt (blue) glass, which absorbs all the colors of light from the flame except the blues and violets.

20. Potassium Chloride, Bromide, and Iodide

Almost all potassium compounds are made from potassium chloride. This substance is obtained chiefly from sylvite and carnallite (page 248). It is purified by dissolving these minerals in water and fractionally crystallizing the salts which they contain. In addition to serving as the source of other compounds of potassium, it is used chiefly as a fertilizer.

Potassium bromide and potassium iodide are prepared by adding bromine or iodine to a hot concentrated solution of potassium hydroxide. For iodine the reaction is:

$$6\,(K^+ + OH^-) + 3\,I_2 \longrightarrow 5\,(K^+ + I^-) + (K^+ + IO_3^-) + 3\,H_2O.$$

The solution is evaporated to dryness, and the residue is heated with carbon to reduce potassium iodate to the iodide. After filtration to remove the excess of carbon, the potassium iodide is recovered by crystallization and may be purified by recrystallization.

The iodide and bromide are used in preparing the corresponding silver salts, which are used in making the plates, films, and printing paper used in photography. They also have some use in medicine, the iodide in the treatment of goiter and the bromide as a nerve sedative. **Iodized salt contains a small amount of sodium or potassium iodide as a preventive of goiter.**

21. Potassium Hydroxide

Potassium hydroxide is made by electrolysis in a manner similar to the electrolytic preparation of sodium hydroxide, or it is made by treating potassium carbonate, in solution, with slaked lime. The solution is evaporated, in either case, and impurities, such as the chloride, are removed by crystallization. The hydroxide is then recovered by evaporation to dryness, and the solid is melted and cast into sticks, which usually contain considerable water. Potassium hydroxide is very deliquescent, and since it absorbs water readily, it is used as a dehydrating agent. It is sometimes used to remove water and carbon dioxide simultaneously from air and other gases. It removes carbon dioxide by reacting with it to form potassium carbonate. Its solution is strongly basic in character. It is more expensive than sodium hydroxide, and its use is consequently limited, because the cheaper sodium hydroxide serves almost equally as well for all purposes.

22. Potassium Carbonate (K_2CO_3)

Potassium carbonate cannot be made by the Solvay process. In preparing sodium carbonate, this process can be used because sodium bicarbonate is only slightly soluble in the solution containing brine, ammonia, and carbon dioxide (page 244). Potassium bicarbonate, however, is more soluble and does not precipitate as sodium bicarbonate does. It is produced by the electrolytic method (page 245) from potassium chloride and by passing carbon dioxide into a solution of potassium chloride in which powdered magnesite ($MgCO_3$) is suspended:

$$3\,MgCO_3 + 2\,(K^+ + Cl^-) + H_2CO_3 \longrightarrow 2\,MgKH(CO_3)_2 + (Mg^{++} + 2\,Cl^-).$$

The precipitate of $MgKH(CO_3)_2$ is filtered off and heated, whereupon it decomposes to form $MgCO_3$, K_2CO_3, and carbonic acid ($CO_2 + H_2O$). The residue is then mixed with a saturated solution of potassium chloride, in which the magnesium carbonate is converted into soluble magnesium chloride, and from which potassium carbonate is precipitated:

$$MgCO_3 + 2\,(K^+ + Cl^-) \rightleftarrows (Mg^{++} + 2\,Cl^-) + K_2CO_3\downarrow.$$

The carbonate is used in the manufacture of several salts of potassium. Potassium bicarbonate is produced by saturating a solution of the normal carbonate with carbon dioxide and evaporating the solution.

23. Potassium Nitrate, KNO_3

This substance was widely used by the alchemists, and, since the Battle of Crecy in 1346, it has been used in the manufacture of *black gunpowder*, which is a mixture of potassium nitrate (saltpeter), sulfur (12 per cent), and charcoal (13 per cent). The three components are finely ground and thoroughly mixed to promote extremely rapid combustion of carbon and sulfur for which the potassium nitrate supplies the oxygen. The combustion must be very rapid to produce a large volume of gas almost instantaneously as soon as the mixture is ignited. Until about 1904, black gunpowder was the principal explosive used in warfare, but it has now been replaced by smokeless powders and other explosives.

Potassium nitrate can be produced on a limited scale by fractional crystallization from a mixture of potassium chloride and sodium nitrate (page 200). A more nearly pure product is produced by the action of nitric acid upon potassium chloride or by the reaction of NO_2 upon the chloride:

$$KCl + 2\,NO_2 \rightleftarrows KNO_3 + NOCl.$$

Potassium nitrate forms white, rhombic crystals. Since it is not deliquescent, while sodium nitrate is, it is more desirable than the latter in the manufacture of gunpowder. It is a vigorous oxidizing agent, especially when used as the fused salt. When heated,

it decomposes to form potassium nitrite and oxygen. Because it contains both potassium and nitrogen, it is a very valuable fertilizer. It is still used to manufacture black gunpowder, which is used in fireworks and in blasting. It is also used in medicine and in curing meats.

LITHIUM, RUBIDIUM, AND CESIUM

24. Lithium

The compounds of this element were discovered by Arfvedson, in 1817. Its name signifies "stone." It occurs as *lepidolite*, *amblygonite* and *spodumene* (South Dakota, California, Maine, North Carolina). Lithium compounds are present in small amounts in many igneous rocks and in the soil. Mineral waters containing lithium carbonate, or other salts of this element, are called "lithia waters."

The metal resembles potassium and sodium, both physically and chemically, and it is prepared in the same manner. It is the lightest of the metals; its density is about one half that of water. Some of its most important compounds are: Lithium chloride (LiCl); lithium bromide (LiBr); lithium carbonate (Li_2CO_3); and lithium phosphate (Li_3PO_4). The compounds of lithium find some use in medicine, in compounding artificial mineral waters, in the manufacture of glass and enamel, and for producing red light in fireworks and other forms of pyrotechnical materials.

25. Rubidium

The name of this element signifies "dark red" and refers to the red lines in the spectrum of the element. The element was discovered by Bunsen in 1861. Some rubidium occurs with potassium in carnallite and with lithium in lepidolite. It is also found in small amounts in the soil. The metal may be prepared by reducing the chloride with *misch metal*, which contains several of the rare-earth metals. It resembles potassium and sodium but is considerably more active. Its compounds resemble those of the other elements of the family.

26. Cesium

Cesium was discovered by Bunsen in 1860. Its name means "sky blue" and refers to blue lines in the element's spectrum. Small amounts of it occur in the soil, in plant ashes, in carnallite, and in lepidolite. The most important source, however, is the mineral *pollucite*, which is a cesium aluminum silicate found in New England. Cesium forms compounds which are similar to those of the other alkali metals. It is a liquid at temperatures above 26.5°. In the air it oxidizes with almost explosive violence. Cesium is used in manufacturing an alloy used in radio tubes. Cesium is used in making photoelectric cells, a use that depends upon the emission of electrons by the metal when it is exposed to light.

REVIEW EXERCISES

1. Enumerate the products which are formed and the chemical changes which occur at the electrodes when (1) an aqueous solution of sodium chloride is electrolyzed and (2) when fused sodium chloride is electrolyzed.
2. Why is it not commercially practical to produce sodium hydroxide by the reaction of metallic sodium with water?
3. Why is sodium classified as a metal?
4. Compare the advantages of producing sodium hydroxide electrolytically with those of the process in which sodium carbonate and slaked lime are used.
5. Although usually more expensive, potassium compounds are frequently preferred for use in the laboratory in place of the corresponding sodium compounds. Can you suggest a reason for this choice in situations where either potassium or sodium ion would serve the purpose?
6. Ten liters of normal sodium hydroxide solution are prepared by allowing metallic sodium to react with 1 liter of water and then diluting

the solution to 10 liters. How much sodium must be used?

7. What weight of sodium carbonate must be used with an excess of calcium hydroxide to produce 100 lbs. of sodium hydroxide?
8. What impurities are usually present in the sodium hydroxide produced by the electrolytic process? What impurities are present in sodium hydroxide which has been exposed to the air?
9. What volume of half normal $\left(\frac{N}{2}\right)$ sulfuric acid solution is required to neutralize 10 liters of normal sodium hydroxide solution?
10. How would you proceed to secure a very nearly pure sample of sodium chloride from sea water?
11. What is the original source of the salt in the sea? What is the explanation of the origin of the deposits of sodium chloride that are found in various regions of the world?
12. Why does potassium chloride cost more than sodium chloride?
13. Starting with 100 lbs. of salt what weight of sodium carbonate can be produced?
14. Identify the following substances or materials, which have been described in this chapter: Sal soda, francium, albite, orthoclase, lepidolite, pollucite, sylvite, carnallite, potash, caustic soda, baking soda, gunpowder, lye.
15. What other substances would you use and how would you proceed to prepare KNO_3 from KCl, K_2S from K_2SO_4, K_2SO_4 from KCl, and K_2CO_3 from KCl?
16. Which of the alkali metals should francium resemble most closely?
17. What is the common structural feature possessed by the atoms of all alkali metals?
18. Which of the elements of this group most readily forms positive ions? Which is least active in this respect? Account for the difference.
19. What are the sources of potassium compounds in the United States?
20. Compare the members of this family of elements with respect to the properties listed below: Activity; formulas of oxides, chlorides, and sulfates; colors which they impart to a flame; density, melting point, and boiling point; physical state at ordinary temperature; solubility of salts; etc. Supplement data from text with data from handbooks and other sources.
21. What weights of ammonia, carbon dioxide, and salt are required to produce a ton of sodium carbonate by the Solvay process? Although an excess of some of these raw materials is used in practice, base your calculations upon the minimum quantities required.
22. Why is sodium carbonate preferable to sodium chloride in the preparation of sodium compounds, such as sodium bromide from HBr?
23. Why do the alkali metals seldom form covalent or coordinate covalent compounds with other elements?
24. Why is a saturated sodium chloride solution used in the Solvay process?
25. Why is a solution of sodium carbonate alkaline?
26. What are the limitations in the choice of an acidic substance that can be used in baking powders?
27. According to the analysis stated on the tag of a 100 pound bag of fertilizer, it contains 5 per cent of potash. If the potassium compound in the fertilizer is KCl, what weight of that substance does the bag contain?
28. True or false?
    (*a*) Rubidium stands above sodium in the activity, or electro-chemical, series.
    (*b*) Cesium has a higher ionization potential than potassium.
    (*c*) Each of the alkali metals has one valence electron per atom.
    (*d*) The ionic radius of cesium is larger than that of potassium.
29. True or false?
    (*a*) Sodium can be prepared by the electrolysis of an aqueous solution of sodium chloride.
    (*b*) Sodium bicarbonate can be prepared by saturating a solution of sodium carbonate with carbon dioxide and crystallizing the bicarbonate from the solution.
    (*c*) Sodium bicarbonate can also be prepared by heating sodium carbonate.
    (*d*) Potassium bicarbonate can be made by

the Solvay process if potassium chloride is used in place of sodium chloride.

(*e*) Sodium bicarbonate produced by the Solvay process is likely to contain sodium chloride.

REFERENCES FOR FURTHER READING

Davy, Sir H., *The Decomposition of the Fixed Alkalies*, Alembic Club Reprint, No. 6. Edinburgh: E. and S. Livingstone, 1808.

Hou, T. P., *Manufacture of Soda*, Am. Chem. Soc. Monograph, No. 65. New York: Reinhold Publishing Company, 1941.

Minerals Yearbook, U.S. Dept. of Interior, published annually. Washington, D.C.

Turrentine, J. W., *Potash in North America*. New York: Reinhold Publishing Corporation, 1943.

Baking Powders: *J. Chem. Ed.*, **3,** 492 (1925); **9,** 1340 (1932).

Potash: *J. Chem. Ed.*, **3,** 749, 1109 (1926); **4,** 230 (1927); **7,** 737 (1930); *Ind. and Eng. Chem.*, **9,** 688 (1917); **10,** 832 (1918); **11,** 864 (1919); **13,** 249 (1921); **14,** 542 (1922); **23,** 78, 84 (1931); **26,** 493 (1934); **28,** 956 (1936); **29,** 333, 475 (1937); **30,** 854, 865, 878 (1938); **32,** 1171 (1940); *Chem. and Met. Eng.*, **36,** 268 (1929); **37,** 728 (1930); **38,** 666 (1931); **40,** 172 (1933); **42,** 128, 691 (1935); **45,** 484 (1938); **48,** 77 (1941).

Salt: *J. Chem. Ed.*, **9,** 407 (1932); **12,** 203 (1935); *Chem. and Met. Eng.*, **24,** 201 (1921); **30,** 426 (1924); **39,** 338 (1932); **42,** 124 (1935); *Ind. and Eng. Chem.*, **23,** 336 (1931); **27,** 1274, 1411 (1935).

Sodium Carbonate (Soda): *Chem. and Met. Eng.*, **26,** 1202 (1922); **40,** 126 (1933); **41,** 253, 408, 410 (1934); **45,** 144 (1938); **49,** 2 (1942); *Ind. and Eng. Chem.*, **14,** 1156 (1922); **23,** 478 (1931); **27,** 627 (1935).

20

THE HALOGENS

1. Introduction

The next *family* of elements that we shall study consists of four members — fluorine, chlorine, bromine, and iodine — which are located in group seven of the periodic table. This family has been given the name of *halogens*, which is derived from Greek words meaning "formers of sea salt" and refers to the occurrence of salts of chlorine, bromine, and iodine and of at least traces of salts of fluorine in sea water.

Element 85 belongs to this family. It has not been found in nature, but radioactive isotopes of atomic number 85 have been produced by means of reactions involving atomic nuclei. The element has been given the name *astatine*, At.

2. General Characteristics of the Family

Each halogen comes just before one of the inert gases in the Periodic Table and, therefore, the atoms of each element have one electron less than the number required for a stable group of eight in the valence shell. Therefore, the negative oxidation number of each element is one, and the maximum positive oxidation number is seven. The elements have positive oxidation numbers in certain ions and in compounds such as $HClO_4$. All the elements are active oxidizing agents, the order of activity being fluorine, chlorine, bromine, and iodine.

Differences in the chemical behavior of the four elements can be explained by con-

TABLE 9. PROPERTIES OF THE HALOGENS

Element	Atomic weight	Melting point	Boiling point	Color and physical state	Boiling point of hydrogen compound	Ionization potential (volts)	Atomic radii *	Ionic radii * X^-
Fluorine	19	−223°	−187°	Light yellow gas	19°	16.9	0.68	1.36
Chlorine	35.46	−102°	−35°	Greenish-yellow gas	−83°	13	0.97	1.81
Bromine	79.92	−7.3°	59°	Reddish-brown liquid	−67°	11.6	1.13	1.91
Iodine	126.92	114°	184°	Purple-black crystalline plates	−34°	8	1.35	2.16

* Angstrom units.

sidering their ionization potentials and atomic and ionic radii. The high ionization potentials indicate, of course, the strong attraction that atoms of the elements have for electrons and explain their failure to form positively charged ions. The change in ionizing potentials from fluorine to iodine is in keeping with the oxidizing actions of the elements. The fluorine atom is smallest and attracts electrons most strongly, because even the farthest removed electrons of its atoms lie relatively near the nucleus. The iodine atom is the largest, and its valence electrons are farthest removed, and are most effectively screened by the electrons of other shells from the nucleus. Consequently, the iodine atom holds these electrons less firmly and has less attraction for an eighth electron than the atoms of any of the other halogens. It is also easier to separate the electron which the iodine atom acquires, when it becomes an iodide ion, than it is to separate the extra electron from any other halide ion. For this reason hydrogen iodide is a better reducing agent than the other hydro-halogen compounds.

There is some evidence that atoms of iodine may sometimes form positive ions. Thus, the compound ICl behaves as the ionic compound, I^+Cl^-, when dissolved in a solvent such as sulfur dioxide; this solution is a conductor and can be electrolysed, liberating iodine at the cathode.

CHLORINE

3. History

Chlorine was probably first prepared (1774) by Scheele from the substance that we now call hydrogen chloride, but which was then called "marine-acid air." He treated this substance with manganese dioxide (MnO_2), and found that a heavy, greenish-yellow gas was produced. Scheele called the new substance "dephlogisticated marine-acid air." By others, it was thought to be an oxide of "marine-acid." It was Davy who finally showed that the substance is an element, and he gave it the name *chlorine*, because of its green color.

4. Occurrence

Because of its very great activity, chlorine is never found in the free state. In the form of the chlorides of different metals, however, it is one of the moderately abundant elements of the earth's crust. Of these compounds, sodium chloride is by far the most abundant. Rock salt is a mineral form of sodium chloride. Potassium, calcium, sodium, and magnesium chlorides, together with calcium sulfate, magnesium sulfate, and other substances, are found in deposits formed by the evaporation of sea water or lakes.

Hydrogen chloride is present in the gastric juice as a solution of hydrochloric acid, which aids in the digestion of certain foods. In man, the normal percentage is about 0.3. Sodium chloride is also present in the blood and in various other fluids of the body.

5. Production of Chlorine by the Oxidation of Hydrogen Chloride

Hydrogen chloride and oxygen react very slowly to produce chlorine and water, unless the reaction is catalyzed and is carried out at 400° or higher. The *Deacon process*, once used to produce chlorine for commercial purposes, was based upon this reaction and used pumice impregnated with the sulfate or chloride of copper as a catalyst.

Chlorine can be produced in the laboratory by the action of many oxidizing agents upon hydrogen chloride or upon a solution of it in water, called hydrochloric acid. Manganese dioxide, MnO_2, is most often used as the oxidizing agent. It is placed in a flask fitted with a thistle tube, or dropping funnel, through which concentrated hydrochloric acid is added, and with a delivery tube for the escape of the chlorine. The mixture is heated slightly to increase the rate at which chlorine is

evolved, and the gas is collected by allowing it to displace the air in an upright bottle or cylinder. It does this readily, because it is heavier than air. The reaction is

$$MnO_2 + 4\,(H^+ + Cl^-) \longrightarrow (Mn^{++} + 2\,Cl^-) + 2\,H_2O + Cl_2.$$

Sometimes, chlorine is prepared by adding concentrated sulfuric acid to a mixture of manganese dioxide and solid sodium chloride. All the reactions involved can be summarized as

$$2\,NaCl + 2\,H_2SO_4 + MnO_2 \longrightarrow Cl_2 + Na_2SO_4 + MnSO_4 + 2\,H_2O.$$

Other oxidizing agents can be used in place of manganese dioxide. Thus, a *solution* of potassium permanganate, $KMnO_4$, reacts with hydrochloric acid to liberate chlorine:

$$2(K^+ + MnO_4^-) + 16(H^+ + Cl^-) \longrightarrow 2(K^+ + Cl^-) + 2(Mn^{++} + 2\,Cl^-) + 5\,Cl_2 + 8\,H_2O.$$

Potassium dichromate, $K_2Cr_2O_7$, lead dioxide, PbO_2, potassium chlorate, $KClO_3$, and nitric acid, HNO_3 may also be used as oxidizing agents in the preparation of chlorine from hydrogen chloride.

6. Production of Chlorine by Electrolysis

Chlorine is prepared for commercial use by the electrolysis of fused sodium chloride or of a concentrated aqueous solution (brine) of the same compound. The changes that occur during the electrolysis of the solution are explained with the help of Figure 173. Sodium chloride is composed of sodium and chloride ions. From a consideration of the behavior of water, we are led to the conclusion that it produces a relatively small number of ions, H_3O^+, or H^+, and OH^-, by a reaction involving two molecules of water:

$$H:\ddot{O}:H + H:\ddot{O}:H \longrightarrow H:\underset{\displaystyle H}{\ddot{O}}:H^+ + :\ddot{O}:H^-.$$

An aqueous solution of sodium chloride contains, therefore, molecules of water and

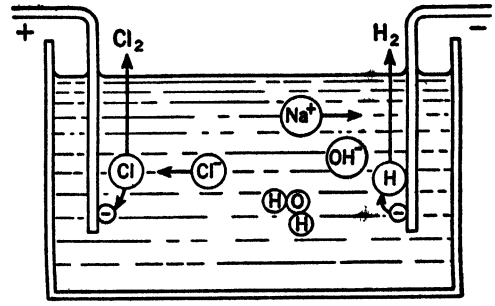


Figure 173. The Electrolysis of a Solution of Sodium Chloride

sodium, chloride, hydrogen, and hydroxyl ions.

The positively charged ions of sodium and hydrogen move toward the cathode; the negatively charged chloride and hydroxyl ions move toward the anode. Hydrogen is liberated at the cathode as a result of a reaction in which each hydrogen ion or proton (from water) removes one electron from the cathode and becomes an atom of free hydrogen. The hydroxyl ions remain in the solution and, therefore, we may write the reaction for the over-all change at the cathode as follows:

$$2\,H_2O + 2\,e \longrightarrow 2\,OH^- + H_2.$$

Why is hydrogen but not sodium liberated at the cathode? Sodium atoms are more readily converted into positive ions, and, conversely, sodium ions are converted into neutral atoms less readily than hydrogen ions. A greater voltage is required to discharge sodium ions than is required to liberate hydrogen. To state the matter in a slightly different manner, there must be a relatively greater accumulation of electrons on the cathode before the sodium ion will remove one of them, while the hydrogen ion, which has stronger attraction for electrons, will remove one when the accumulation of electrons is considerably less. Hence, *hydrogen is liberated at the cathode when the voltage is not sufficient to liberate sodium.*

As hydrogen is discharged, there is a greater and greater accumulation of hydroxyl ions at the cathode or in its vicinity. These ions with those of sodium give a solution of sodium hydroxide.

At the anode the *chloride ions are discharged, by the transfer of electrons to the*

anode, and become neutral atoms. Two of these atoms then combine to make the molecule Cl_2. Since chlorine is not very soluble in the solution, most of it escapes. The hydroxyl ion is not discharged at the anode unless the concentration of chloride ion becomes very small, because it is more difficult to separate the extra electron, which is responsible for the negative charge, from the hydroxyl ion than it is to separate an electron from the chloride ion.

7. An Electrolytic Cell for the Production of Chlorine

The chlorine discharged at the anode dissolves to some extent and reacts readily with sodium hydroxide to form sodium hypochlorite, NaClO, and sodium chloride:

$$2\,(Na^+ + OH^-) + Cl_2 \longrightarrow (Na^+ + Cl^-) + (Na^+ + ClO^-) + H_2O.$$

This reaction interferes with the production of both chlorine and sodium hydroxide and must be prevented by keeping the two substances separated. The anode and cathode compartments of the cell are separated by a porous diaphragm or partition. The *Nelson electrolytic cell* (Figure 174) solves this problem by using a perforated iron cathode and an asbestos diaphragm.

The Nelson cell consists of inner and outer compartments, and the outside walls of the cell are made of slate. The anode is made of graphite and is suspended in the inner compartment from the cover of the slate box. The inner compartment is an iron vessel which contains the solution of sodium chloride and acts as the cathode. Its walls are perforated and covered on the inside with an asbestos diaphragm. During electrolysis, chlorine is liberated at the anode and escapes through an outlet tube in the slate box. (The anode is made of graphite and the box of slate, because chlorine does not attack these materials.) The sodium chloride solution seeps through the asbestos lining of the inner compartment

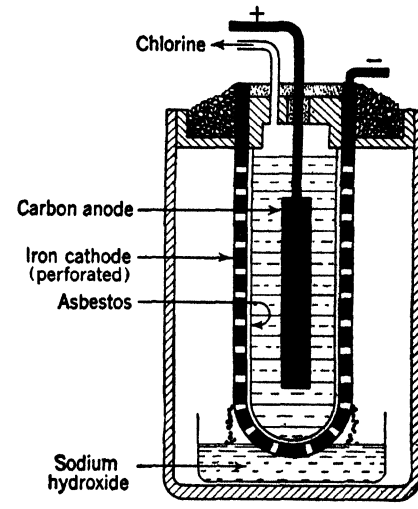


Figure 174. Diagram Showing the Cross-Section of the Nelson Electrolytic Cell

and comes into contact with the perforated iron cathode. Here, hydrogen is discharged and escapes from the outer compartment through an outlet tube in the top of the tank. The solution that passes through the perforations in the cathode and collects in the container at the bottom of the cell contains both sodium hydroxide and sodium chloride.

A large cell of the Nelson type consists of a long cathode vessel in which are placed from 10 to 14 graphite anodes. Hydrogen and chlorine outlets deliver the gases that are produced in a single cell to the main line, through which they are led to compressors by which they are forced under high pressure into steel cylinders for storage and transportation. Chlorine may be compressed and shipped as a liquid in steel tank cars.

8. Physical Properties of Chlorine

Chlorine is a greenish yellow gas and has a sharp, disagreeable, and irritating odor. At 0° C. and 760 mm., 1.46 g. of chlorine dissolve in 100 g. of water. The solution, often called *chlorine water*, possesses the color and odor of the element. When

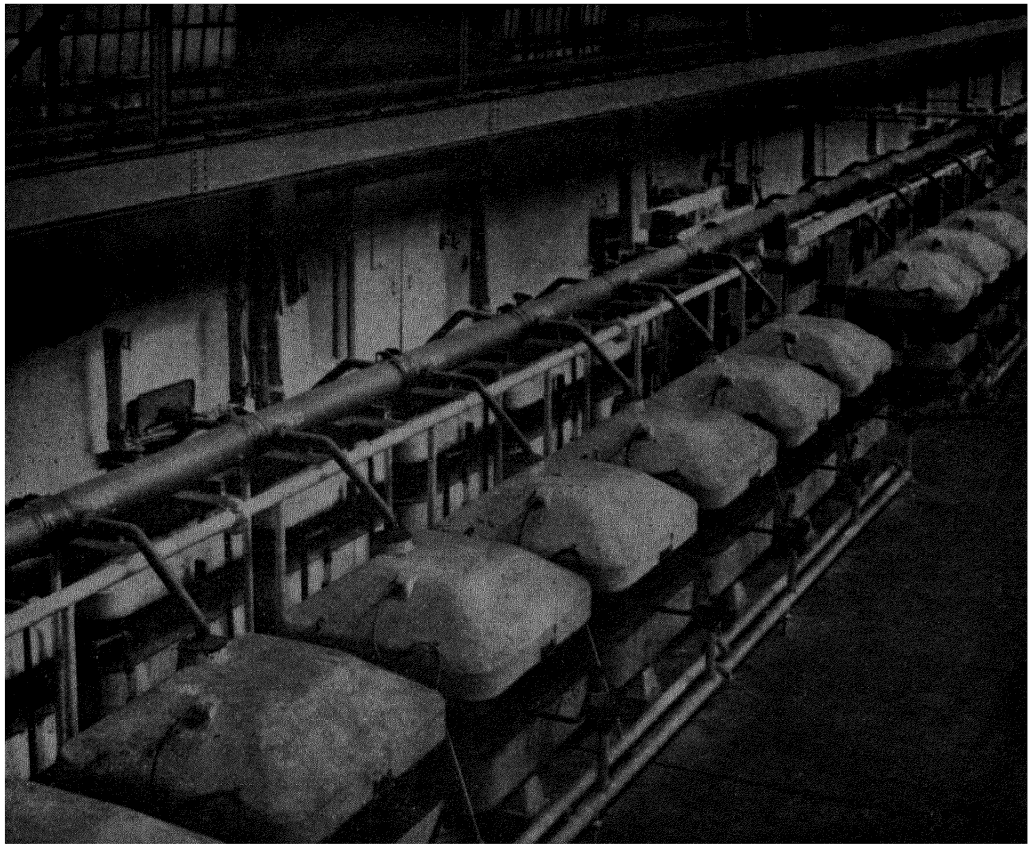


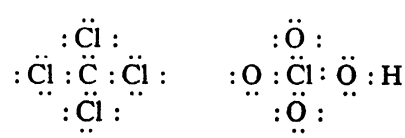
Figure 175. Electrolytic Cells Used in the Production of Chlorine
(Courtesy of Hooker Electrochemical Company)

cooled to a temperature of $-34.7°$ C., at one atmosphere of pressure, the gas changes to a greenish-yellow liquid, which freezes at $-102°$. The molecule consists of two atoms, which share a pair of electrons.

In concentrations of about 0.00002 g. per liter of air, chlorine causes inflammation and congestion of the lungs and other parts of the respiratory system. Inhaling chlorine in larger quantities may result fatally.

9. Chemical Properties of Chlorine

The chemical properties of chlorine may be described briefly as those of (1) a typical non-metal and (2) a very active oxidizing agent. It resembles oxygen in some respects but differs in showing greater activity in its reactions with the metals. Oxygen, on the other hand, combines more actively with non-metals than chlorine. The most characteristic activity of chlorine is displayed when it acquires a single electron per atom, thus forming the chloride ion, Cl^-. As this ion, chlorine is found in all the chlorides of the metals. It also forms covalent linkages with several kinds of atoms, with which it shares one, two, three, and four pairs of electrons. Typical covalent compounds of chlorine are *carbon tetrachloride* and *perchloric acid:*



10. Reactions of Chlorine with Metals

The reaction of chlorine with gold and platinum is slow, but a thin foil of copper (if warm) and finely divided antimony (even when cold) oxidize so rapidly that combustion results. The more active metals react very vigorously in an atmosphere of chlorine. In all these reactions, chlorides of the metals are formed:

$$2\,Au + 3\,Cl_2 \longrightarrow 2\,AuCl_3$$
$$Cu + Cl_2 \longrightarrow CuCl_2$$
$$2\,Sb + 3\,Cl_2 \longrightarrow 2\,SbCl_3$$
$$2\,Na + Cl_2 \longrightarrow 2\,NaCl.$$

If chlorine is carefully dried, it has almost no tendency to react with metals. In fact, it is so nearly inactive that liquid chlorine is shipped in steel tank cars.

11. Reaction of Chlorine with Non-Metallic Elements

Chlorine reacts with many of the non-metals. Carbon, nitrogen, oxygen, and fluorine are exceptions, although compounds with the first three of these are known and can be prepared indirectly. Three oxides of chlorine, Cl_2O, ClO_2, and Cl_2O , can be produced from certain compounds that contain both elements but not by the direct combination of chlorine and oxygen. Phosphorus burns in an atmosphere of chlorine, forming phosphorus trichloride (PCl_3) or, in an excess of chlorine, phosphorus pentachloride, (PCl_5). Chlorine reacts directly with fused sulfur to form sulfur monochloride (S_2Cl_2).

12. Reaction of Chlorine and Hydrogen

The reaction between hydrogen and chlorine is too slow in the dark to be detected. In ordinary light, the reaction takes place slowly, but if the mixture is exposed to direct sunlight, to a source of ultra-violet light, or to the light produced by burning

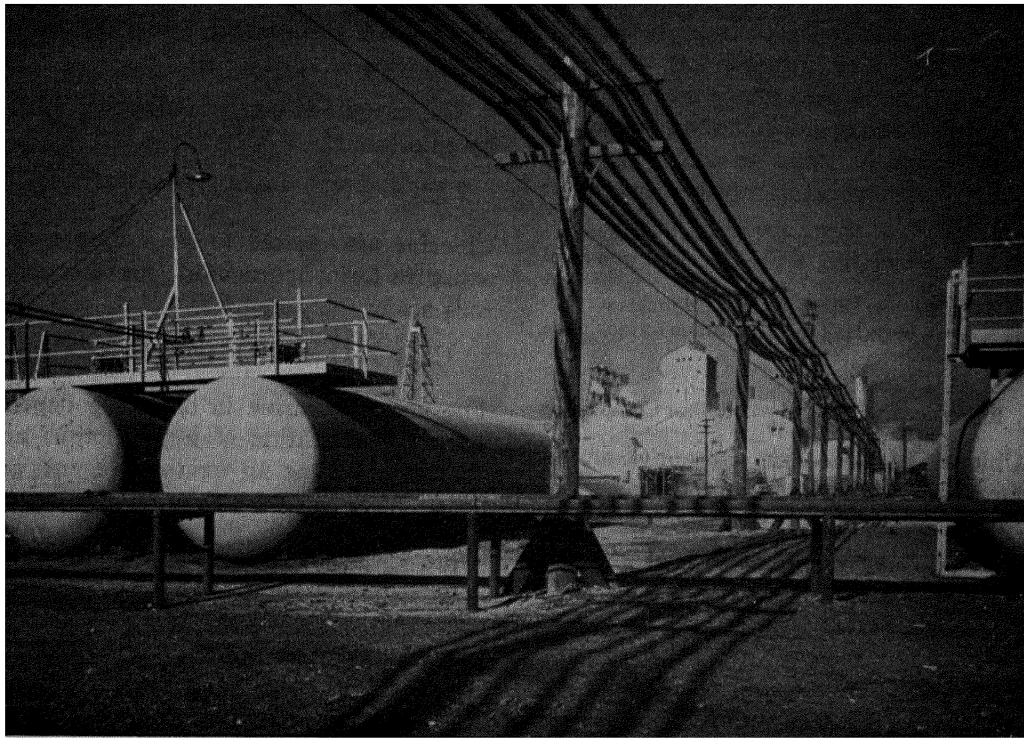


Figure 176. Storage Tanks for Liquid Chlorine
(Courtesy of Columbia Chemical Division, Pittsburgh Plate Glass Company)

magnesium, the reaction occurs explosively. If a stream of hydrogen is first ignited, it burns in an atmosphere of chlorine to form hydrogen chloride, just as it does in oxygen to form water.

13. Reaction of Chlorine with Compounds Containing Hydrogen

Natural gas, which is composed largely of methane (CH_4), continues to burn when a lighted jet of it is introduced into a cylinder filled with chlorine. Hydrogen chloride and free carbon are produced:

$$CH_4 + 2\,Cl_2 \longrightarrow C + 4\,HCl.$$

A strip of filter paper saturated with turpentine ignites spontaneously when lowered into a cylinder filled with chlorine. The reaction is similar to the reaction between methane and chlorine:

$$C_{10}H_{16} + 8\,Cl_2 \longrightarrow 16\,HCl + 10\,C.$$

The black smoke which is produced consists of particles of carbon (soot).

In bright sunlight, a mixture of methane and chlorine reacts more slowly, and the reaction occurs in steps in which chlorine both combines with and replaces hydrogen:

$CH_4 + Cl_2 \longrightarrow HCl + CH_3Cl$, methyl chloride
$CH_3Cl + Cl_2 \longrightarrow HCl + CH_2Cl_2$, methylene chloride
$CH_2Cl_2 + Cl_2 \longrightarrow HCl + CHCl_3$, chloroform
$CHCl_3 + Cl_2 \longrightarrow HCl + CCl_4$, carbon tetrachloride

14. Reactions of Chlorine with Other Compounds

Chlorine displaces less active non-metals from their compounds. In these reactions chlorine acts as an oxidizing agent:

$$Cl_2 + H_2S \longrightarrow 2\,HCl + S$$
$$Cl_2 + 2(Na^+ + Br^-) \longrightarrow 2(Na^+ + Cl^-) + Br_2$$
$$Cl_2 + 2(Na^+ + I^-) \longrightarrow 2(Na^+ + Cl^-) + I_2.$$

Chlorine itself is displaced by fluorine, and bromine will displace iodine. Hence, the order of activity of the halogens is fluorine, chlorine, bromine, iodine.

Chlorine combines directly with certain compounds. With carbon monoxide it forms *phosgene*, $COCl_2$, one of the most widely used poisonous gases of the first World War. When ice-cold water is saturated with chlorine, yellowish-green crystals of the hydrate, $Cl_2.8\,H_2O$ are formed. Chlorine also reacts with certain chlorides in much the same manner that oxygen reacts with certain oxides. Thus, cuprous chloride, CuCl, is oxidized to cupric chloride, $CuCl_2$, by chlorine:

$$2\,CuCl + Cl_2 \longrightarrow 2\,CuCl_2.$$

With ammonia, chlorine reacts under suitable conditions to liberate nitrogen:

$$8\,NH_3 + 3\,Cl_2 \longrightarrow 6\,(NH_4^+ + Cl^-) + N_2,$$

or, in a slightly acid solution, to form nitrogen trichloride:

$$NH_3 + 3\,Cl_2 \longrightarrow NCl_3 + 3\,(H^+ + Cl^-).$$

15. Action of Chlorine upon Water and Hydroxide-Bases

The oxygen of water is slowly displaced by chlorine:

$$2\,Cl_2 + 2\,H_2O \longrightarrow 4\,(H^+ + Cl^-) + O_2.$$

Chlorine also reacts to some extent with water to form hydrochloric and hypochlorous acids:

$$Cl_2 + H_2O \longrightarrow (H^+ + Cl^-) + HClO.$$

The use of chlorine in bleaching depends upon the formation of hypochlorous acid and its action as an oxidizing agent; and hence, bleaching with chlorine requires the presence of water.

If a base is added, chlorine is completely converted into chloride and hypochlorite ions. Thus, sodium hydroxide, when added to a solution of chlorine, forms sodium chloride and sodium hypochlorite (NaClO):

$$2\,(Na^+ + OH^-) + Cl_2 \longrightarrow (Na^+ + Cl^-) + (Na^+ + ClO^-) + H_2O.$$

16. Tests for Chlorine

Free chlorine can be detected by employing the reaction in which it displaces iodine from an iodide, followed by tests to detect the presence of the iodine that is liberated (page 56). A strip of filter paper is moistened with a solution of sodium or potassium iodide which contains a suspension of starch (iodostarch paper). When this paper is brought into contact with free chlorine, iodine is liberated and produces a dark blue coloration of the starch. Since iodine is also liberated by other substances, including bromine and ozone, this is not a specific test for chlorine. These substances must be eliminated or proved absent before this reaction is used to detect chlorine.

17. Uses of Chlorine

About 1,750,000 short tons of chlorine are used in this country each year.

(*a*) The most extensive use of chlorine is in bleaching certain textiles and in the preparation of materials, such as wood pulp, from which paper is made. Water is necessary, since the substance directly responsible for the bleaching action is hypochlorous acid.

(*b*) Chlorine is used to purify water for drinking purposes and for use in swimming pools. Liquid chlorine in steel cylinders is supplied for this purpose. All dangerous micro-organisms can be destroyed by as little as 0.3 to 1.5 parts of chlorine in 1,000,000 parts of water, although an excess, which may be removed later, is sometimes added.

(*c*) Chlorine is used in the preparation of germicidal solutions which contain, usually sodium hypochlorite. One of the best known of these is Dakin's solution, which is made by treating a solution of sodium carbonate (Na_2CO_3) with chlorine. The product is a solution containing sodium hypochlorite and sodium chloride.

(*d*) Chlorine is used in the manufacture of many dyes, drugs, explosives, disinfectants, and the chlorides of sulfur, arsenic, aluminum, tin, antimony, carbon, silicon, and phosphorus.

(*e*) Gold may be extracted from its ores by chlorine, which reacts with the metal to form auric chloride, $AuCl_3$. Tin may be recovered from "tin" cans by treating them with chlorine, which converts the coating of tin on the surface of the iron sheet into stannic chloride, $SnCl_4$.

(*f*) Chlorine is used in the manufacture of *bleaching powder*, $CaOCl_2$. Before liquid chlorine was as readily available and as widely used as it is today, bleaching powder was used to purify water, in bleaching, and for many other purposes. It is still used, especially in bleaching operations.

(*g*) Chlorine was the first poisonous gas used during the first World War, but gases that were more poisonous largely replaced it before that war ended. For the most part, these compounds were liquid compounds of chlorine having high vapor pressures at ordinary temperatures. Two of the most widely used poisonous substances were phosgene and *mustard gas* $(C_2H_4Cl)_2S$, which is called in chemistry *dichlorodiethyl sulfide*.

BROMINE

18. History

The liquid remaining after salt has been separated by crystallization from sea water contains bromide, iodide, and several metallic ions. Balard first prepared bromine, in 1826, by treating such a solution with chlorine and, also, by evaporating the solution remaining after the extraction of salt from sea water and then treating the residue with manganese dioxide and concentrated sulfuric acid. He observed that two different substances were produced, and he successfully separated them by distilling one of them from the mixture. He showed that this product was a new element, for which he suggested the name bromine, a name referring to the odor or *stench* of the

substance. He did not establish the nature of the other substance, but this was later shown to be iodine.

19. Occurrence

Bromine usually occurs as sodium, potassium, or magnesium bromide along with sodium chloride in salt deposits. When sea water, or the more concentrated solution of sodium chloride that is obtained from salt wells, is evaporated, the chlorides are less soluble and are, therefore, deposited first, leaving a *mother liquor*, so-called because it is the solution from which crystals of salt are produced, that is rich in bromide. From this solution bromine is recovered by methods similar to those used by Balard in discovering the element.

20. Laboratory Production

The methods used to produce chlorine by the oxidation of its compounds can also be used to produce bromine. For example, bromine is liberated by the action of manganese dioxide and sulfuric acid upon crystals of sodium bromide:

$$2\ NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HBr$$
$$4\ HBr + MnO_2 \longrightarrow MnBr_2 + Br_2 + 2\ H_2O.$$

Bromine is also liberated from bromides by the action of chlorine as an oxidizing agent:

$$2\ (Na^+ + Br^-) + Cl_2 \longrightarrow 2\ (Na^+ + Cl^-) + Br_2.$$

The bromine produced by any of these reactions is purified by distillation. Since it is liquid under ordinary conditions, bromine can be collected in a receiver that is cooled by immersion in cold water.

21. The Production of Bromine for Commercial Uses

Until about 1934, most of the bromine produced in this country was recovered from brines pumped from salt wells in Michigan and a few places in the Ohio Valley. In recent years, sea water has become an important source of supply. The concentration of bromide ion in the water of the oceans is very small — about 67 parts per million — but the total quantity in the water of all the oceans can be measured in billions of tons.

The location of a plant for the extraction of bromine from sea water is very important. Preferably, it should be located on an arm of land that extends for some distance into the ocean, so that ocean water can be withdrawn for use on one side and the water, after use, can be discharged on the other. In this manner, the water to be used is not allowed to mix with water from which the bromine has been removed. The water is first pumped into ponds, where it is heated by the sun until its temperature has risen several degrees.

When ready to be treated for the extraction of bromine, the water is acidified slightly with sulfuric acid; the bromine is then liberated in a tower into which the water is sprayed and through which chlorine is passed. The bromine is removed from the water that collects at the base of the tower by air into which the bromine vaporizes (page 199). The air with its load of bromine vapor is then passed into a second tower, where it comes into contact with a solution of sodium carbonate that flows from the top of the tower over tile or stone. Here, the bromine reacts to form bromide and bromate ions:

$$3\ Br_2 + 3\ (2\ Na^+ + CO_3^-) \longrightarrow 5\ (Na^+ + Br^-) + (Na^+ + BrO_3^-) + 3\ CO_2.$$

The mixture of sodium bromide and sodium bromate is then treated with sulfuric acid; bromine is liberated,

$$5(Na^+ + Br^-) + (Na^+ + BrO_3^-) + 3(2H^+ + SO_4^=) \longrightarrow 3\ (2\ Na^+ + SO_4^=) + 3\ Br_2 + 3\ H_2O,$$

and finally recovered by distillation. This reaction may also be written in the following form, which shows only the ions actually involved:

$$5\ Br^- + BrO_3^- + 6\ H^+ \longrightarrow 3\ Br_2 + 3\ H_2O.$$

Bromine is recovered from the brines pumped from salt wells by similar reactions.

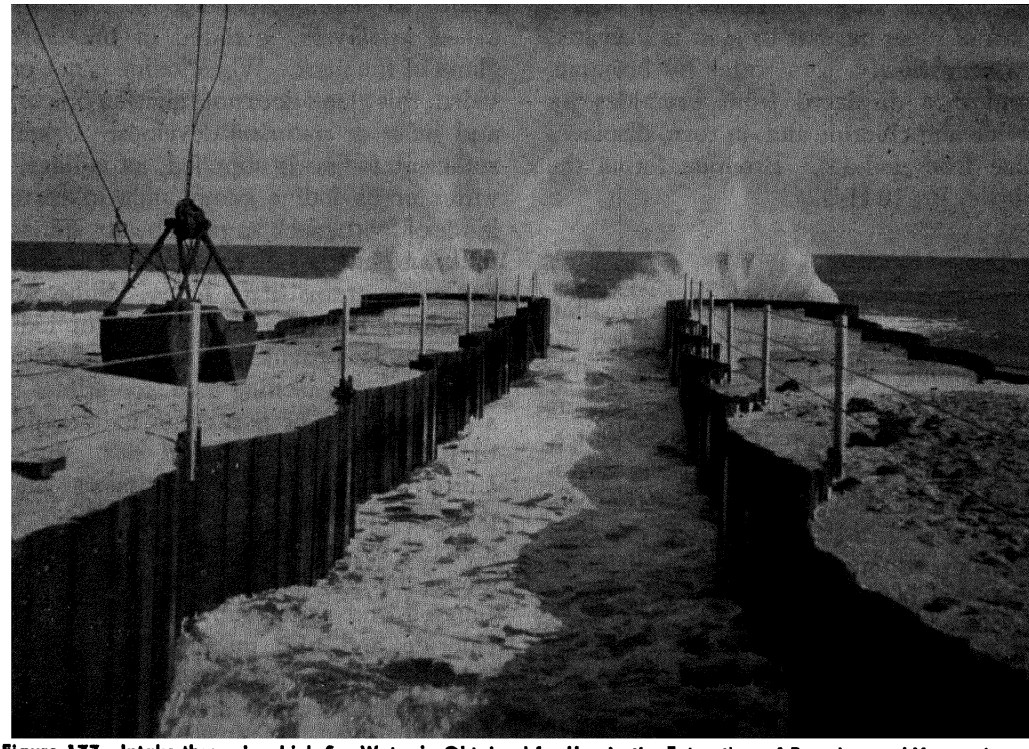


Figure 177. Intake through which Sea Water is Obtained for Use in the Extraction of Bromine and Magnesium

22. Physical Properties

Under ordinary conditions, bromine is a dark reddish-brown liquid, which evolves a dense brown vapor. Its boiling point is 59° C., as compared with − 34.6° for chlorine. Its freezing point is − 7.2° as compared with − 102° for chlorine. Its density at 0° is about 3.2 g. per ml. It is more soluble in water than chlorine; at 0° and 760 mm., 4.22 g. dissolve in 100 g. of water. The aqueous solution is called *bromine water*. Carbon disulfide, carbon tetrachloride, ether, and chloroform dissolve it readily, and form solutions that are straw to dark reddish-brown in color, depending upon the concentration of bromine.

Bromine has a very disagreeable and irritating odor. The vapor is very irritating to the eyes and, when breathed, produces serious inflammation of the respiratory tract. Bromine must be handled at all times with extreme caution. When the liquid is spilled on the flesh it produces very serious burns, which are extremely slow in healing.

23. Chemical Properties

In its chemical behavior, bromine resembles chlorine very closely, but it is considerably less active. It does not combine with the least active metals, such as platinum and gold, but it does form mercuric bromide ($HgBr_2$) with mercury. The more active metals are attacked readily. Bromine also combines with certain non-metals forming compounds such as PBr_3, PBr_5, S_2Br_2, IBr, and Br_2F_3. It does not combine with oxygen, carbon, chlorine, or nitrogen. With hydrogen, bromine reacts very slowly at low temperatures but more rapidly at high temperatures, particularly in bright light or in the presence of platinum. Its

reaction with water corresponds to the reaction of chlorine, but oxygen is liberated only very slowly from water by bromine. Bromine is displaced from bromides by fluorine and chlorine and, in turn, displaces iodine from iodides. Bromine forms the hydrate, $Br_2.10\ H_2O$.

24. Uses of Bromine

The uses of bromine are less extensive than those of chlorine. From it is prepared silver bromide, which is a light-sensitive material that is suspended in the gelatine coating of photographic films and plates. It is also used in making ethylene dibromide, which, in turn, is used in the production of "anti-knock" (ethyl) gasoline. Potassium bromide is used in medicine as a sedative for the nerves and in treating cases of epilepsy and "lockjaw." Bromine, itself, is used in the manufacture of metallic bromides and several organic compounds, among which are certain important dye-stuffs. The annual production in the United States is about 50,000 tons.

IODINE

25. History

Because of our acquaintance with *tincture of iodine* as a household antiseptic, most of us are more familiar with this element than we are with the other halogens. The tincture is an alcoholic solution of iodine. The element, itself, is a solid.

Shortly after the discovery of chlorine, Courtois produced a new substance that evolved violet colored vapor by heating the ashes of certain sea weeds with concentrated sulfuric acid. Gay-Lussac, in 1814, showed that the substance produced by Courtois was an element, to which he gave the name of iodine, a word derived from the Greek word signifying *violet.*

26. Occurrence

Iodine appears to be essential to the health of man. A compound of iodine, called *iodothyrin*, is found in the *thyroid* gland of the neck. When iodine is not provided, this gland does not function properly, and *goiter* or *cretinism* develops. Usually, sufficient iodine is supplied, as iodides, in water or as iodine compounds in certain kinds of foods, such as green beans, spinach, milk, and butter. In some places, however, the soil contains little, or no, iodine, and, therefore, the necessary supply of iodine may not be provided in foods and water. Salt, used in seasoning food, sometimes has a little sodium or potassium iodide added to it and is called *iodized salt.* In the United States more than 17 times as many persons (per thousand inhabitants) are afflicted by goiter in the inland states as along the sea coasts. Near the oceans, the soil and water supplies contain more chloride and also more iodide, and the average diet usually contains more sea foods, most of which are relatively rich in iodine.

Iodides occur with bromides in the liquor remaining after sodium chloride is recovered by crystallization from sea water. It also occurs in sponges and sea weeds. Much of the world's supply of iodine comes, however, from the sodium nitrate beds of Chile. Here it occurs as sodium iodate, $NaIO_3$, with $NaNO_3$ (Chile saltpeter). Among the elements iodine ranks twenty eighth in abundance.

27. Production

Brines from certain oil wells contain iodides. These are converted into free iodine by the action of sulfuric acid and sodium nitrite $NaNO_2$, and the iodine is removed by adsorption on charcoal. It is then converted into NaI and $NaIO_3$ by the action of NaOH. Finally, free iodine is again produced from these compounds by the use of chromic acid. It is produced from iodides in the ashes of kelp by oxidation with MnO_2 and H_2SO_4 or by Cl_2. Iodine is re-

covered from the sodium iodate, which is first separated from Chile saltpeter, by reduction with sodium bisulfite, $NaHSO_3$.

$$2\,(Na^+ + IO_3^-) + 5\,(Na^+ + HSO_3^-) \longrightarrow$$
$$2\,(2\,Na^+ + SO_4^{=}) + 3\,(Na^+ + HSO_4^-) + H_2O + I_2.$$

If the solution in which this reaction occurs is evaporated to dryness, the iodine may be separated from the other solid substances by sublimation.

28. Properties

At ordinary temperatures, iodine exists as dark gray or black, and slightly lustrous, crystalline plates. Its melting point is 113° and its boiling point is 184°. When heated, the gray solid changes into violet-colored vapor without melting. It may therefore be *sublimed*. In the gaseous state and in solution, molecules of iodine appear to have the formula I_2. Iodine dissolves in water and in ethyl alcohol to form brown-colored solutions. The solubility in water at 25° C. is about 0.2 g. per liter. It dissolves readily in certain organic solvents, such as carbon tetrachloride, benzene, and chloroform, in which it forms violet-colored solutions.

Chemically, its behavior is much like that of the other halogens. It is the least active member of the family. The oxides I_2O_4 and I_2O_5, the fluoride IF_3, the bromide IBr, the chloride ICl, and phosphorus tri-iodide, PI_3, are representative of its compounds with the non-metals. With hydrogen, iodine reacts very slowly at ordinary temperatures to form hydrogen iodide, HI. It combines with all the active, and with some of the less active, metals. It is displaced from the iodides by oxygen and by the other halogens; and hence, it is a less vigorous oxidizing agent than these elements. Thus, iodine oxidizes iron to ferrous ion (Fe^{++}) only, whereas both bromine and chlorine form ferric ion (Fe^{+++}). Solutions containing the iodide ion dissolve much more iodine than the pure solvent because of the formation of the tri-iodide:

$$(K^+ + I^-) + I_2 \rightleftarrows (K^+ + I_3^-).$$

Somewhat similar compounds are $KICl_4$, potassium tetrachloroiodide, and KIF_6, potassium hexafluoroiodide.

29. Uses

Iodine's best known use is as an antiseptic. Silver iodide is used in photography in the same manner as silver bromide. Iodine is used in the synthesis of many organic compounds, of which some of the dyes are most important. The use of iodides in the prevention and treatment of goiter has been mentioned previously. The element is also used to produce the iodides of the metals, of which sodium and potassium iodides are most important.

FLUORINE

30. Occurrence

Fluorine is a fairly abundant element in the earth's crust, but it is never found free because of its extreme activity. Its most widely distributed compound is *fluorspar*, CaF_2, but it occurs also in *cryolite*, Na_3AlF_6, and *fluor-apatite*, $CaF_2.(Ca_3(PO_4)_2)_3$. Very small traces of fluorides are present in sea water. It is also present in the enamel of teeth.

31. Preparation

Hydrofluoric acid and several other compounds of fluorine were known long before the element was prepared in the free state. Fluorine was first isolated, in 1886, by Moissan, who prepared it by electrolyzing a solution of potassium fluoride in pure hydrofluoric acid at a temperature of about − 23°. The U-shaped cell (Figure 178) was made of an alloy of platinum and iridium. The electrodes were made of the same material and were suspended in the arms of the cell through fluorspar stoppers. Flu-

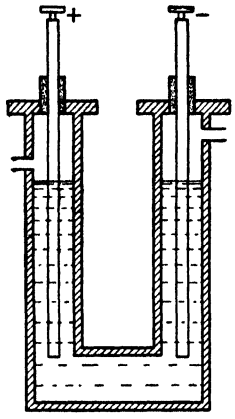


Figure 178. Electrolytic Cell for the Production of Fluorine

orine is now prepared in a copper cell, which acts as the cathode, with a graphite rod serving as the anode. A magnesium vessel and graphite electrodes are also used. Both copper and magnesium are attacked by fluorine, but they are protected from extensive action by the formation of a coat of copper or magnesium fluoride upon their surfaces. The electrolyte is melted potassium acid fluoride (KHF_2).

Fluorine cannot be produced by the oxidation of hydrogen fluoride, as chlorine is produced from hydrogen chloride, because there is no oxidizing agent that will liberate it.

32. Properties

Fluorine is a pale greenish-yellow gas. It is slightly heavier than air and has been condensed to a liquid at − 188° and to a solid at − 223°. It is very poisonous.

Fluorine does not dissolve in water. Instead, it reacts vigorously to form hydrogen fluoride and oxygen:

$$2\,H_2O + 2\,F_2 \longrightarrow 4\,HF + O_2.$$

Fluorine reacts very vigorously with almost all other elements. It combines explosively with hydrogen in the dark and at temperatures as low as − 250°. With oxygen, however, fluorine shows less tendency to form compounds than chlorine. The very unstable compound, OF_2, and possibly also O_2F_2, have been prepared. Fluorine replaces all other halogens, and in fact all other non-metals, from their compounds with hydrogen or the metals.

33. Uses

The difficulty of preparing, storing, transporting, and using fluorine has prevented the development of uses of the element. The fluoride of calcium plays an important part in the building up of bones and the enamel of the teeth. Fluorides are also present, in very small traces, in the blood and have been suggested as related in some way to clotting. Fluorspar is used as a flux to combine with certain substances that cannot be melted readily, thus forming easily fused substances. Ammonium fluoride is used as a disinfectant, and sodium fluoride as an insecticide, as a flux, and in treating wood to prevent the growth of fungi. Fused cryolite, Na_3AlF_6, is used as the bath in the preparation of metallic aluminum by the electrolysis of bauxite, an oxide of aluminum. Fluorine organic compounds are also used as refrigerants.

REVIEW EXERCISES

1. In what respects is chlorine like oxygen and in what respects do the two elements differ?
2. What volume of chlorine can be produced from 10 liters (standard conditions) of hydrogen chloride by the Deacon process if 75 per cent of the chloride is oxidized?
3. Assuming that there is no loss in the process, what weight of sodium chloride would be required to produce by electrolysis 140,000 tons of chlorine?
4. What weight of chlorine can be produced by oxidizing HCl (in excess) by one gram-molecular weight each of MnO_2, $KMnO_4$, and $K_2Cr_2O_7$ (reduced to $CrCl_3$)? What weight of chlorine can be prepared by the same reactions using 1000 grams of each of these oxidizing agents?

5. What weight of sodium chloride must be used with an excess of H_2SO_4 and MnO_2 to form one gram-molecular weight of chlorine?
6. What volume of hydrogen chloride (calculated for standard conditions) could be produced from the combination of the hydrogen and chlorine resulting from the electrolysis of 100 grams of sodium chloride? Assume that there are no losses.
7. For what reasons is the production of chlorine by the electrolysis of sodium chloride solutions more satisfactory than the Deacon process?
8. Although chlorine reacts with water, it can still be said that chlorine forms a solution in water. How is this possible?
9. Summarize the chemical behavior of chlorine by writing equations to show how it reacts with: Metals, phosphorus, sulfur, hydrogen, water, sodium bromide, sodium iodide, hydrogen sulfide, methane, and carbon monoxide.
10. Why is water necessary when chlorine acts as a bleaching agent?
11. Describe the production of chlorine by the electrolysis of a solution of sodium chloride. What other products are formed? What changes occur at the electrodes?
12. Describe the Nelson Cell and explain the function of each part of the cell.
13. What are the most important uses of chlorine? Upon what property of the element does each of these uses depend?
14. Describe the variations in the properties of the halogens with increasing atomic weight and atomic number.
15. Element 85 is a member of the halogen family. What should be its properties? Consider: Color and physical state; melting and boiling points; vigor of its reaction with hydrogen; oxidizing power; the attraction of its atoms for electrons; its atomic structure; the ease with which the hydrogen compound can be oxidized; valence numbers; and formulas of typical compounds.
16. What evidence indicates that chlorine is a better oxidizing agent than iodine but a poorer one than fluorine? Account for these differences on the basis of the atomic structures of the elements.
17. Assuming that Chile saltpeter contains 0.1 per cent of $NaIO_3$, what weight of the saltpeter is required to produce 100 grams of iodine? Assume that there are no losses.
18. How would you proceed to separate bromine and chlorine from a mixture of the gaseous states of the two substances so that fairly pure samples of each are obtained?
19. How is iodine most easily purified?
20. What weight of chlorine would be required to liberate all the iodine contained in one liter of a molar solution of sodium iodide, if an excess of 10 per cent of chlorine is used? How would you proceed to obtain the released iodine in a fairly pure state?
21. What volume of chlorine at 22° C. and 738 mm. will be required to replace completely the bromine in 250 ml. of a 0.2 normal solution of sodium bromide?
22. One ml. of liquid bromine weighs 3.18 times as much as 1 ml. of water. What volume of liquid bromine would be required, if it were completely converted into HBr, to produce one liter of a solution of the same concentration as could be produced by dissolving 44.8 liters (standard) of hydrogen chloride in a liter of water?
23. Using the structures of their atoms as a basis, explain (1) why fluorine is a stronger oxidizing agent than iodine, and (2) why iodide ion is more easily oxidized to free iodine than fluoride ion.
24. What are the names of $COCl_2$, MnO_2, $KMnO_4$, $CHCl_3$, HClO, $NaIO_3$, KI_3, CaF_2, KHF_2.
25. Which of the halogens is most difficult to produce in the free state? Why?
26. Why should Scheele (page 255) have decided that the substance which he produced by treating "marine acid air" with manganese dioxide was an oxide?
27. In what way do you believe that molecules of water are attached to Cl_2 molecules in the hydrate of chlorine, $Cl_2.8\ H_2O$?

REFERENCES FOR FURTHER READING

Davy, H., *Elementary Nature of Chlorine*, Alembic Club Reprint, No. 9. Edinburgh: E. and S. Livingstone.

Bromine: *Chem. and Met. Eng.*, **40,** 234, 437 (1933); **41,** 402 (1934); *J. Chem. Ed.*, **3,** 382 (1926); **14,** 187, 394 (1937); *Ind. and Eng. Chem.*, **21,** 434 (1929); **26,** 361 (1934); *Chem. and Met. Eng.*, **42,** 477, 599 (1935); **46,** 77 (1939); *Chem. and Eng. News*, **21,** 846 (1943).

Chlorine: *J. Chem. Ed.*, **4,** 313, 454, 596 (1927); **6,** 2147 (1929); **7,** 294 (1930); **9,** 407 (1932); *Chem. and Met. Eng.*, **19,** 667 (1918); **33,** 274 (1926); **35,** 158 (1928); **45,** 354 (1938); **47,** 166, 396 (1940); *Ind. and Eng. Chem.*, **17,** 107 (1925); **33,** 741, 1472 (1941).

Fluorine: *J. Chem. Ed.*, **6,** 1281 (1929); **10,** 330 (1933); **24,** 314 (1947); *Ind. and Eng. Chem.*, **7,** 56 (1915); **23,** 996 (1931); **24,** 637 (1932); **26,** 849 (1934); **28,** 947 (1936); **30,** 160, 1011 (1938); **33,** 1046 (1941); *Chem. and Met. Eng.*, **28,** 129 (1923); **34,** 660 (1927); **43,** 366 (1936); **47,** 542 (1940).

Iodine: *Ind. and Eng. Chem.*, **18,** 808 (1926); **26,** 376 (1934); *Chem. and Met. Eng.*, **39,** 422 (1932); **41,** 568 (1934); **42,** 434 (1935); *J. Chem. Ed.*, **7,** 2590 (1930); **8,** 391 (1931); **10,** 649 (1933); **14,** 215 (1937); *Science*, **89,** 162 (1939).

War Gases: *J. Chem. Ed.*, **20,** 339, 351, 439 (1943); **21,** 92, 219 (1944).

21

OXIDATION AND REDUCTION

1. Introduction

Oxidation and reduction have been explained in Chapter 5. In this chapter we are to study the methods used to balance equations representing chemical changes of this kind. An understanding of this subject is of special importance in the study of the oxy-halogen compounds discussed in the next chapter.

EQUATIONS FOR OXIDATION-REDUCTION REACTIONS

2. The Reaction of Antimony and Chlorine

Balancing an equation for the reaction that occurs between an oxidizing and a reducing agent calls essentially for a balance of the decrease in oxidation number of one element against the increase in the oxidation number of the other. The oxidation number of one is reduced as much as that of the other is increased.

Let us consider a simple example of oxidation and reduction: Antimony, Sb, reacts with chlorine, Cl_2, to form antimony trichloride, $SbCl_3$:

$$Sb + Cl_2 \longrightarrow Sb^{+++} + 3\ Cl^-.$$

Element oxidized, Sb. Change in oxidation number from 0 to + 3, a gain of 3.

Element reduced, Cl. Change in oxidation number from 0 to − 1, a loss of 1 per atom.

Since each atom of antimony undergoes a change of + 3 in oxidation number, and each atom of chlorine a change of − 1, it is evident that three atoms of chlorine must be used in order that chlorine will show as much decrease as one atom of antimony increases or, in other words, three atoms of chlorine must be used to remove three electrons from one atom of antimony. Hence, we could write our equation as

$$Sb + 3\ Cl \longrightarrow (Sb^{+++} + 3\ Cl^-),$$

but chlorine exists as molecules of Cl_2 and not as single atoms. Therefore, in order that the equation will show this fact, we must double the quantity of each substance:

$$2\ Sb + 3\ Cl_2 \longrightarrow 2\ (Sb^{+++} + 3\ Cl^-).$$

3. The Oxidation Numbers of Elements in Covalent Compounds and Ions

In reactions like that of antimony and chlorine oxidation numbers are equal to the number of electrons that an atom loses or gains, and are positive if electrons are lost and negative if they are gained. For covalent compounds, and especially for ions in which atoms share electrons, the oxidation numbers of elements are somewhat more difficult to determine.

The oxidation number of an element that is combined with oxygen in an ion such as $SO_4^=$, $Cr_2O_7^=$, ClO^-, etc. can be calculated as follows. The four atoms of oxygen in

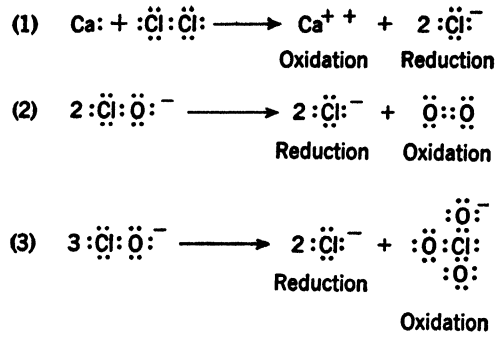


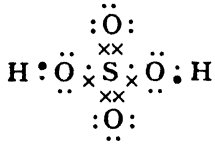
Figure 179. Oxidation and Reduction

In (1) calcium is oxidized from 0 to +2, and chlorine is reduced from 0 to −1. In (2) chlorine is reduced from +1 to −1, and oxygen is oxidized from −2 to 0. In (3) two chlorine atoms are reduced from +1 to −1, and one atom, in ClO_3^- is oxidized from +1 to 5.

the $SO_4^=$ ion have a total oxidation number of − 8. Since the ion $SO_4^=$ has the number − 2, this then leaves − 6 as the oxidation number of the four oxygen atoms (total − 8) which must be balanced by + 6 for the one atom of sulfur. In $Cr_2O_7^=$ the oxidation number of chromium is + 6, because the seven atoms of oxygen have an oxidation number, combined, of − 14, and the valence of the ion is − 2. Hence, the two atoms of chromium must have a combined oxidation number of + 12, or each has an oxidation number of + 6.

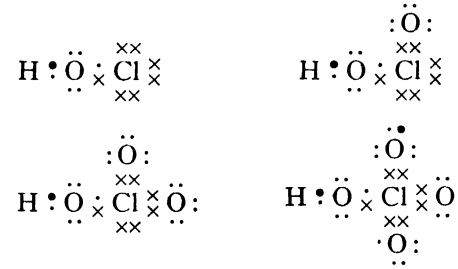
4. An Explanation of the Oxidation Numbers of Elements in Covalent Compounds

The oxidation number of an element in a covalent compound depends upon the number of electrons that an atom of the element *uses* in sharing electrons with other atoms. The non-metallic elements in acids that contain oxygen, for example sulfur in sulfuric acid, are linked with oxygen by shared pairs of electrons:

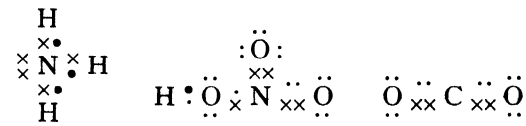


The sulfur atom uses all six of its valence electrons — indicated by x — in forming the bonds with oxygen. Since the oxygen atoms have only 6 valence electrons each, and since two of these oxygen atoms use one electron (·) each in forming bonds with hydrogen (·), it is apparent that the sulfur atom must provide six of the eight electrons by which it is bound to oxygen. Therefore, we may say that the oxidation number of sulfur is + 6. The oxidation numbers of hydrogen and oxygen are + 1 and − 2, respectively.

Similarly, the oxidation numbers of chlorine in the acids indicated below are 1, 3, 5, and 7, respectively, because the chlorine atom uses 1, 3, 5, and 7 of its electrons in forming bonds with oxygen.



The oxidation number of nitrogen is 3 in ammonia and five in nitric acid. Carbon's oxidation number is four in carbon dioxide.



The procedure discussed above for the calculation of oxidation numbers in covalent compounds can be applied to most of the compounds of this kind, but there are some to which it cannot strictly be applied because of somewhat peculiar features of their molecular structures.

5. What Substances are Produced?

One cannot write any equation unless one knows the substances produced, and if more than one oxidation state of any of the ele-

ments involved are possible, one must also know which of these are represented in the original substances and in the products. It is not enough to know that iron is oxidized by chlorine. Before we can write the equation, we must know whether the iron ion produced is Fe^{++} or Fe^{+++}.

Sometimes, the products of a reaction can be predicted almost, if not completely, with certainty from a knowledge of the chemical properties of the substances involved. Calcium in its compounds always has an oxidation number of + 2; and hence, when metallic calcium is oxidized it can form only Ca^{++} ion, and when this ion is reduced, it can form only metallic calcium. It is also helpful to remember that hydrogen always has an oxidation number of + 1, except in a few hydrides of metals like LiH, in which it's oxidation number is − 1; that oxygen's number is − 2; and that chlorine in compounds with the metals or hydrogen always has a number of − 1.

For elements like iron that have two or more oxidation states the chemist must sometimes rely upon laboratory tests to determine what substance is produced in a reaction. If one oxidizes iron by means of chlorine, bromine, iodine, or some other oxidizing agent, either Fe^{++} or Fe^{+++} is produced, and it is not always the same ion. The chemist can easily decide which ion is produced by a simple test that gives one result if the ion is Fe^{++} and another if it is Fe^{+++}. Upon adding potassium ferrocyanide, $K_4Fe(CN)_6$, to a solution containing iron ions and hydrochloric acid, a dark blue precipitate of $Fe_4[Fe(CN)_6]_3$ is formed if Fe^{+++} is present; a white precipitate of $Fe_2Fe(CN)_6$ forms if Fe^{++}, but no Fe^{+++}, is present. A similar dark blue precipitate of $Fe_3[Fe(CN)_6]_2$ is produced by adding potassium ferricyanide, $K_3Fe(CN)_6$, if Fe^{++} instead of Fe^{+++} has been formed.

We may mention other simple facts that one may well keep in mind in writing equations for reactions in which changes in oxidation states occur:

(1) We should not expect an active metal to be produced by the reduction of its ions in the presence of water. Sodium, for example, reacts with water to form sodium hydroxide and cannot, therefore, be reduced from Na^+ to Na in an aqueous solution.

(2) We should not expect the oxide of a metal to be produced in a reaction if an acid is present. Thus, the oxidation of copper by sulfuric acid does not produce cupric oxide, CuO, because this oxide will react with the acid to produce cupric sulfate, $Cu^{++}SO_4^{=}$, and water. Similarly, the oxide of a non-metal will not be produced in the presence of a hydroxide-base, such as NaOH. If chloride ion, Cl^-, for example, is oxidized in the presence of OH^- ion, it should not be expected to form free chlorine or an oxide of chlorine. Free chlorine will not be formed because it reacts (page 260) with hydroxyl ion:

$$Cl_2 + 2\,OH^- \longrightarrow Cl^- + ClO^- + H_2O.$$

The oxide should not be expected because, since it is the anhydride of an acid, it will react with hydroxyl ion to form a salt, or the ions of a salt:

$$Cl_2O + 2\,OH^- \longrightarrow 2\,ClO^- + H_2O.$$

Likewise, sulfur when oxidized in the presence of OH^-, or even in water, to an oxidation number of + 6, forms not the oxide, SO_3, but the sulfate, $SO_4^{=}$, ion, because SO_3 is the anhydride of sulfuric acid.

6. The Oxidation of Copper by Sulfuric Acid

The products of this reaction are Cu^{++}; sulfur dioxide, SO_2; and water. Let us first write a tentative equation, and under the elements that are oxidized and reduced let us write their oxidation numbers before and after the change occurs:

$$\underset{0}{Cu} + H_2\underset{6}{S}O_4 \longrightarrow \underset{2}{Cu^{++}} + \underset{4}{S}O_2 + H_2O$$

Oxygen and hydrogen do not undergo any change involving their oxidation numbers. The changes for copper and sulfur are:

	Copper	Sulfur
Change in oxidation number per atom	0 to + 2 gain of 2	+ 6 to + 4. loss of 2

Since each sulfur atom loses as much in oxidation number as each copper atom gains, the equation is balanced by using one atom of each, and, therefore, may be allowed to remain in the tentative form that we first wrote. If, however, we wish to indicate a sulfate ion, $SO_4^{=}$, which will go along in the solution with the Cu^{++} ion to make a complete set of the ions of cupric sulfate, one more molecule of sulfuric acid must be added on the left to supply this ion. If we do this, the equation becomes

$$Cu + 2\,H_2SO_4 \longrightarrow (Cu^{++} + SO_4^{=}) + SO_2 + 2\,H_2O.$$

7. Oxidation of Hydrochloric Acid by Potassium Permanganate

Let us next turn to a reaction that has been used (page 256) to produce chlorine, namely the oxidation of hydrochloric acid by potassium permanganate. To balance this equation we must know that manganese is reduced to Mn^{++} and that chlorine is oxidized to Cl_2. It is actually only the permanganate, MnO_4^-, ion that is involved, and we may, for the time being at least, omit the potassium ion and, for the same reason, the hydrogen ion of the hydrochloric acid.

	MnO_4^-	+ Cl^- ⟶	Mn^{++}	+ Cl_2
Oxidation number	+ 7	− 1	+ 2	0
Change per atom	− 5	+ 1		
Atoms required to balance	1	5		

Therefore, we may write the equation as

$$MnO_4^- + 5\,Cl^- \longrightarrow Mn^{++} + 5\,Cl \text{ or } 2\tfrac{1}{2}\,Cl_2,$$

or, to show a whole number of *molecules* of chlorine, as

$$2\,MnO_4^- + 10\,Cl^- \longrightarrow 2\,Mn^{++} + 5\,Cl_2.$$

The equation is not yet complete, however, because we have not shown what becomes of the oxygen in the two MnO_4^- ions. Manganese, after the reaction, cannot appear as the oxide, MnO, because this is a basic oxide, and the solution contains an acid, HCl. The hydrogen ions of this acid are the only substances in the entire mixture that can react with the oxygen of MnO_4^- and, therefore, we must add on the left a sufficient number of H^+ ions to react with all the oxygen in two MnO_4^- ions. To determine the number of H^+ ions that must be added one can proceed in either of two ways. First, consider the difference in the charges on the left and on the right. On the right the total charge is $2 \times (+ 2)$ or + 4, and on the left it is $(- 2) + (- 10)$ or − 12. To equalize these we must add 16 + charges on the left, and since each hydrogen ion has a charge of + 1, 16 H^+ ions are required. We can arrive at the same conclusion by noting that the 8 atoms of oxygen in the two MnO_4^- ions require 16 atoms of hydrogen and will form 8 molecules of water.

Our equation now becomes

$$2\,MnO_4^- + 10\,Cl^- + 16\,H^+ \longrightarrow 2\,Mn^{++} + 5\,Cl_2 + 8\,H_2O.$$

If we wish to fill in the equation with missing ions to make complete sets with Mn^{++}, MnO_4^-, Cl^-, and H^+ ions we may write

$$2\,(K^+ + MnO_4^-) + 16\,(H^+ + Cl^-) \longrightarrow 2(Mn^{++} + 2\,Cl^-) + 2\,(K^+ + Cl^-) + 5\,Cl_2 + 8\,H_2O.$$

All that has been done in this final step is to add 6 Cl^- ions (2 for the potassium, K^+, ions and 2 each for the two Mn^{++} ions) on the right-hand side of the equation and the same number of Cl^- ions on the left.

8. Oxidation of Ferrous Sulfate by Sodium Dichromate

Let us next consider the oxidation of ferrous ion, Fe^{++}, to ferric ion, Fe^{+++}, by the dichromate ion, $Cr_2O_7^{=}$. As reagents we may use $FeSO_4$ and $Na_2Cr_2O_7$. The dichromate ion is converted by this reaction

into chromic ion, Cr^{+++}, which is about the only change that can occur for chromium, which has only two important oxidation numbers, + 3 and + 6; in a few rare compounds it has a number of + 2.

Using the same procedure to balance the equation as in the preceding examples, we write first

$$Fe^{++} + Cr_2O_7^{=} \longrightarrow Fe^{+++} + Cr^{+++}$$

Oxidation number per atom	+ 2	+ 6	+ 3	+ 3
Change in oxidation number per atom	+ 1	− 3		
Atoms required to balance	3	1		

Since there are two atoms of chromium in each $Cr_2O_7^{=}$ ion, it is obvious that 6 atoms of iron, or 6 Fe^{++}, must be indicated on the left and 2 Cr^{+++} ions on the right. Hence,

$$6\ Fe^{++} + Cr_2O_7^{=} \longrightarrow 6\ Fe^{+++} + 2\ Cr^{+++}$$

Electrical charges	(6 × 2) + (−2) = + 10	(6 × 3) + (2 × 3) = + 24
Number of H^+ to be added	14	

Therefore,

$$6\ Fe^{++} + Cr_2O_7^{=} + 14\ H^+ \longrightarrow 6\ Fe^{+++} + 2\ Cr^{+++} + 7\ H_2O.$$

If we now add to the equation the 2 Na^+ ions for $Cr_2O_7^{=}$, 6 $SO_4^{=}$ ions for 6 Fe^{++}, and 7 $SO_4^{=}$ ions for 14 H^+ on the left, and 9 $SO_4^{=}$ ions for 6 Fe^{+++}, 3 $SO_4^{=}$ ions for 2 Cr^{+++}, and (2 Na^+ + $SO_4^{=}$) on the right we show all the ions as complete sets:

$$6\ (Fe^{++} + SO_4^{=}) + (2\ Na^+ + Cr_2O_7^{=}) + 7\ (2\ H^+ + SO_4^{=}) \longrightarrow 3\ (2\ Fe^{+++} + 3\ SO_4^{=}) + (2\ Cr^{+++} + 3\ SO_4^{=}) + (2\ Na^+ + SO_4^{=}) + 7\ H_2O.$$

9. Oxidation in an Alkaline Solution

Sodium chromite, $NaCrO_2$, is oxidized by sodium hypochlorite, NaClO, to sodium chromate, Na_2CrO_4, but only in an alkaline solution. The hypochlorite ion, ClO^-, is reduced at the same time to Cl^- ion. Free chlorine should not be expected as the product of the reaction, because (page 271) chlorine reacts with hydroxyl ion to form Cl^- and ClO^- ions.

$$CrO_2^- + ClO^- \longrightarrow CrO_4^{=} + Cl^-$$

Oxidation number per atom	+3	+1	+6	−1
Change in oxidation number per atom	+3	−2		
Atoms required to balance	2	3		

$$2\ CrO_2^- + 3\ ClO^- \longrightarrow 2\ CrO_4^{=} + 3\ Cl^-$$

Electrical charges	−5	−7
Negative charges to be added	2	

The negative charges required on the left are supplied by adding 2 OH^- ions:

$$2\ CrO_2^- + 3\ ClO^- + 2\ OH^- \longrightarrow 2\ CrO_4^{=} + 3\ Cl^- + H_2O.$$

or, $2(Na^+ + CrO_2^-) + 3\ (Na^+ + ClO^-) + 2(Na^+ + OH^-) \longrightarrow 2\ (2\ Na^+ + CrO_4^{=}) + 3\ (Na^+ + Cl^-) + H_2O.$

10. A Reaction in which the Same Element is both Oxidized and Reduced

When it reacts with hydroxyl ion, chlorine is reduced to chloride ion, Cl^-, and it is also oxidized to hypochlorite ion, ClO^-, in which its oxidation number is + 1. However, we shall consider a somewhat more complicated example of a similar change, namely the conversion of sodium hypochlorite, when it is heated, into sodium chloride and sodium chlorate. Let us consider only the ions containing chlorine:

$$ClO^- \longrightarrow ClO_3^- + Cl^-$$

Oxidation number	+ 1	+ 5	− 1
Changes in oxidation number	$ClO^- \longrightarrow ClO_3^-$,	+ 4	
	$ClO^- \longrightarrow Cl^-$.	− 2	

The loss and the gain in oxidation number are equalized only when 2 ClO^- ions are reduced to Cl^-; and hence, it is evident that for each ClO^- ion converted into ClO_3^- two ClO^- ions must be converted into Cl^- ions. Hence,

$$3\ ClO^- \longrightarrow ClO_3^- + 2\ Cl^-$$

or, $3\ (Na^+ + ClO^-) \longrightarrow (Na^+ + ClO_3^-) + 2\ (Na^+ + Cl^-).$

11. The Ion-Electron Method of Balancing Equations for Oxidation-Reduction Reactions

This method of balancing equations gives the same results as the method already described and is preferred by some. It depends essentially upon the determination of the number of *electrons transferred* from the reducing agent to the oxidizing agent in the reaction. Let us consider the reaction of dichromate ion with ferrous ion:

$$Cr_2O_7^{=} + Fe^{++} \longrightarrow 2\ Cr^{+++} + Fe^{+++}$$

Let us look separately at the oxidation and reduction. The reduction is shown by $Cr_2O_7^{=} \longrightarrow 2\ Cr^{+++}$, and the oxidation by $Fe^{++} \longrightarrow Fe^{+++}$. Now when $Cr_2O_7^{=}$ is reduced, 14 H^+ must be added to react with the 7 atoms of oxygen to form water: $Cr_2O_7^{=} + 14\ H^+ \longrightarrow 2\ Cr^{+++} + 7\ H_2O$. The net charges are + 12 on the left and + 6 on the right. To balance these we must add 6 electrons, indicated by 6 e, on the left. Hence, for this portion of the equation we have

$$Cr_2O_7^{=} + 14\ H^+ + 6\ e \longrightarrow 2\ Cr^{+++} + 7\ H_2O.$$

Now for the other part of the equation one electron must be added on the right to balance the charges:

$$Fe^{++} \longrightarrow Fe^{+++} + 1\ e.$$

The two portions of the equation now show that the first half must obtain 6 electrons from the second half, which as written gives up only one. Therefore, the quantities in the second half must be multiplied by 6:

$$6\ Fe^{++} \longrightarrow 6\ Fe^{+++} + 6\ e.$$

If we now add the two halves of the equation and cancel out 6 e, which occur on both sides, we obtain:

$$6\ Fe^{++} + Cr_2O_7^{=} + 14\ H^+ \longrightarrow 2\ Cr^{+++} + 6\ Fe^{+++} + 7\ H_2O.$$

Let us balance by the same method the equation (page 273) for the oxidation of CrO_2^- to $CrO_4^{=}$ by ClO^- in the presence of OH^-.

Oxidation: $CrO_2^- \longrightarrow CrO_4^{=}$.

Two oxygen atoms are required to form $CrO_4^{=}$, since CrO_2^- contains but two, and 2 OH^- will be required to provide them. However, we need some oxygen left over to form water with the hydrogen of the OH^- ions; hence, we must use more than 2 OH^-. Three OH^- ions will not do, because this would give three atoms of hydrogen and only one of oxygen. Four OH^- ions must be used, because they will provide oxygen atoms to change CrO_2^- to $CrO_4^{=}$ and also two to form water with the four atoms of hydrogen. Hence,

$$CrO_2^- + 4\ OH^- \longrightarrow CrO_4^{=} + 2\ H_2O + 3\ e$$
Charges, − 5 − 2

Three electrons must be added on the right to balance the charges.

Reduction: $ClO^- \longrightarrow Cl^-$.

The oxygen atom of the ClO^- ion must be taken care of in some way, and the only way in which this can be done in an alkaline solution is by means of a molecule of water with which it will form 2 OH^- ions. Hence, for this half of the equation we may write

$$ClO^- + H_2O + 2\ e \longrightarrow Cl^- + 2\ OH^-.$$

Two electrons are required to balance the charges. This half of the equation requires two electrons and the first half provides three. Hence, to balance one half against the other, we multiply the second half by three and the other half by 2, add, and cancel out the electrons:

$$\begin{array}{r} 2\ CrO_2^- + 8\ OH^- \longrightarrow 2\ CrO_4^{=} + 4\ H_2O + 6\ e \\ 3\ ClO^- + 3\ H_2O + 6\ e \longrightarrow 3\ Cl^- + 6\ OH^- \\ \hline 2\ CrO_2^- + 2\ OH^- + 3\ ClO^- \longrightarrow 2\ CrO_4 + 3\ Cl^- + H_2O. \end{array}$$

OXIDIZING AND REDUCING AGENTS

12. The Relative Oxidizing and Reducing Powers of Different Substances

On several occasions in early chapters we have referred to the different degrees of attraction that atoms of different elements have for electrons. The large atoms of the

alkali metals — large as compared to atoms of other elements in the same periods as themselves — possess relatively weak attraction for their valence electron and, therefore, they are readily converted into positive ions, i.e., they are very active reducing agents. Atoms of the halogens, on the other hand, have strong attraction for electrons and, therefore, acting as oxidizing agents they remove electrons from other atoms and become negative ions. Since oxidation and reduction involve losses of electrons by some atoms and acquisitions by others, it should be possible to arrange the elements in a table according to their relative attraction for electrons and, therefore, according to their oxidizing and reducing powers. Such a table can be determined by more accurate methods, but at least a satisfactory comparison can be made by determining other elements that each element will replace from their compounds. For example, iron will replace copper from a solution containing Cu^{++} ions; and hence, copper must have more attraction for electrons than iron, because an atom of copper removes two electrons in this reaction from each atom of iron:

$$Fe + Cu^{++} \longrightarrow Cu + Fe^{++}.$$

Therefore, when copper and iron are listed in the order of their powers or strengths as reducing agents, iron should be placed above copper, and when listed as oxidizing agents cupric ion comes before ferrous iron.

Chlorine replaces iodine from solutions containing I^- ions; and hence, chlorine atoms must possess stronger attraction for electrons than iodine. Therefore, in a list of oxidizing agents chlorine is placed above iodine. By similar comparisons, and by studying the effects of different oxidizing agents upon the same reducing agents, we can compile a list in which many substances in addition to the metals, the nonmetals, and their ions are arranged in the order of their oxidizing and reducing powers. Table 10 includes many of the common oxidizing and reducing agents arranged in this manner.

TABLE 10. SOME OF THE COMMON OXIDIZING AGENTS ARRANGED IN THE ORDER OF THEIR STRENGTHS *

Fluorine
Ozone
Cobaltic chloride, $CoCl_3$
Hypochlorous acid, $HClO$
Potassium chlorate, $KClO_3$
Lead dioxide, PbO_2
Potassium permanganate, $KMnO_4$
Potassium dichromate, $K_2Cr_2O_7$
Nitric acid, concentrated
Chlorine
Sulfuric acid, concentrated and hot
Oxygen
Sodium iodate, $NaIO_3$
Bromine
Silver ion, Ag^+
Ferric chloride, $FeCl_3$, and other ferric salts
Iodine
Sulfur
Stannic chloride, $SnCl_4$

* This list is not complete, nor are the positions of the different substances very definite. Changes in concentration, temperature, and other conditions sometimes cause changes in the relative oxidizing actions of different substances and, therefore, changes in the order of the positions in this list. The concentration of acid that is present in a mixture in which the oxidizing agent reacts is very often an important factor in determining the oxidizing strength of a substance and, also, in determining the extent to which the same substance is reduced. The effect of the acid is particularly noticeable in the action of lead dioxide, nitric acid, potassium permanganate, and potassium dichromate.

REVIEW EXERCISES

1. Using the method that is illustrated on pages 271–273, balance the following equations:

   a. $Sn + Cl_2 \longrightarrow SnCl_4$.
   b. $H_2S + O_2 \longrightarrow H_2O + S$.
   c. $AlCl_3 + Na \longrightarrow NaCl + Al$.
   d. $(Fe^{+++} + 3\ Cl^-) + H_2S \longrightarrow (Fe^{++} + 2\ Cl^-) + (H^+ + Cl^-) + S$.
   e. $(K^+ + MnO_4^-) + H_2S + (2\ H^+ + SO_4^{=}) \longrightarrow (2\ K^+ + SO_4^{=}) + (Mn^{++} + SO_4^{=}) + S + H_2O$.
   f. $(2\ K^+ + Cr_2O_7^{=}) + (H^+ + Cl^-) \longrightarrow (K^+ + Cl^-) + (Cr^{+++} + 3\ Cl^-) + Cl_2 + H_2O$.

2. In each of the reactions of (1) name the oxidizing agent and the reducing agent.

3. What weight of chlorine is required to liberate 10 g. of iodine from sodium iodide?
4. Chlorine can be produced by the action of hydrogen chloride upon potassium permanganate. What is the maximum quantity of chlorine that can be produced from 13 g. of potassium permanganate by this reaction?
5. In the following reactions what elements are oxidized and what substances act as the oxidizing agents:

   a. $Br_2 + H_2O \longrightarrow (H^+ + Br^-) + HBrO.$
   b. $Cl_2 + (Ni^{++} + 2\ Br^-) \longrightarrow (Ni^{++} + 2\ Cl^-) + Br_2.$
   c. $2\ (Fe^{+++} + 3\ Cl^-) + 3\ H_2S \longrightarrow 2\ FeS + S + 6\ (H^+ + Cl^-).$
   d. $Zn + 2\ (Na^+ + OH^-) \longrightarrow (2\ Na^+ + ZnO_2^{=}) + H_2.$
   e. $2\ (H^+ + NO_3^-) + 6\ (H^+ + Cl^-) \longrightarrow 3\ Cl_2 + 2\ NO + 4\ H_2O.$

6. What changes in oxidation numbers occur in each of the equations of (5)?
7. What are the oxidation numbers of the underlined elements in $\underline{CO_3}^{=}$, $\underline{PO_4}^{\equiv}$, $\underline{SiO_3}^{=}$, $\underline{CrO_2}^-$, $\underline{NO_3}^-$, $\underline{BO_3}^{\equiv}$, $\underline{AsO_4}^{\equiv}$, and $\underline{MnO_4}^-$?
8. Balance the following equations:

   a. $Cr_2O_3 + Al \longrightarrow Cr + Al_2O_3.$
   b. $(K^+ + IO_3^-) + (K^+ + I^-) + (H^+ + Cl^-) \longrightarrow (K^+ + Cl^-) + I_2 + H_2O.$
   c. $(Cu^{++} + SO_4^{=}) + (K^+ + I^-) \longrightarrow CuI\downarrow + (2\ K^+ + SO_4^{=}) + I_2.$
   d. $(Ba^{++} + 2\ BrO_3^-) + H_3AsO_3 \longrightarrow (Ba^{++} + 2\ Br^-) + H_3AsO_4.$
   e. $(H^+ + NO_3^-) + Cu \longrightarrow (Cu^{++} + 2\ NO_3^-) + NO + H_2O.$
   f. $(H^+ + Cl^-) + (H^+ + NO_3) \longrightarrow HClO + NO + H_2O.$
   g. $HNO_3 + I_2 \longrightarrow 2\ HIO_3 + NO_2 + H_2O.$
   h. $Na_2Cr_2O_7 + S \longrightarrow Cr_2O_3 + Na_2SO_4.$
   i. $P + HNO_3 + H_2O \longrightarrow H_3PO_4 + NO.$

REFERENCES FOR FURTHER READING

Balancing Oxidation-Reduction Equations: *J. Chem. Ed.*, **3**, 1305 (1926); **4**, 1021, 1159 (1927); **6**, 1136 (1929); **11**, 125 (1934); **12**, 189 (1935); **15**, 538 (1938); *Sch. Sci. and Math.*, **41**, 419 (1941).

22

THE COMPOUNDS OF THE HALOGENS

THE HYDROGEN HALIDES

1. Introduction

Only the aqueous solutions of the hydrogen compounds of the halogens are usually called hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids. According to present views concerning acids, however, it is not necessary for a substance to be dissolved in water to have the properties of an acid; it may act as an acid, for example, when it is dissolved in a non-aqueous solution. Nevertheless, there are so many differences between the pure substances and the aqueous solutions of the hydrogen halides that this distinction is frequently convenient and desirable.

2. Production by the Direct Combination of the Elements

Compounds of hydrogen and the halogens can be prepared by the direct combination of the elements. The vigor of the reaction varies, however, from a combination with explosive violence in the case of fluorine to the reaction of hydrogen and iodine, which is very slow and incomplete regardless of conditions. Considerable hydrochloric acid is now prepared by the direct combination of hydrogen and chlorine. This reaction may be carried out at fairly low temperatures, if a catalyst, usually charcoal, is used to increase the reaction's speed.

3. Production by the Action of Sulfuric Acid upon Salts of the Acids

Hydrofluoric and hydrochloric acids can be made by the action of concentrated sulfuric acid upon salts of these acids. Sulfuric acid is used because it is a strong, nonvolatile acid and because it does not oxidize the chloride to free chlorine.

Because of their relative abundance, *fluorspar* is used to make hydrofluoric, and *salt* is used to produce hydrochloric acid:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF$$
$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl.$$

At higher temperatures and in the presence of an excess of salt, the second reaction goes one step farther:

$$NaHSO_4 + NaCl \longrightarrow HCl + Na_2SO_4.$$

Hydrogen chloride and hydrogen fluoride, which are gases, are collected by dissolving them in water in which they are very soluble. Hydrofluoric acid must be prepared in lead or platinum vessels, which are not readily attacked by the acid, and the aqueous solution of hydrogen fluoride is usually stored in wax containers.

4. Action of Sulfuric Acid upon Hydrogen Bromide and Hydrogen Iodide

When concentrated sulfuric acid reacts with solid sodium bromide, the gas evolved contains considerable quantities of hydro-

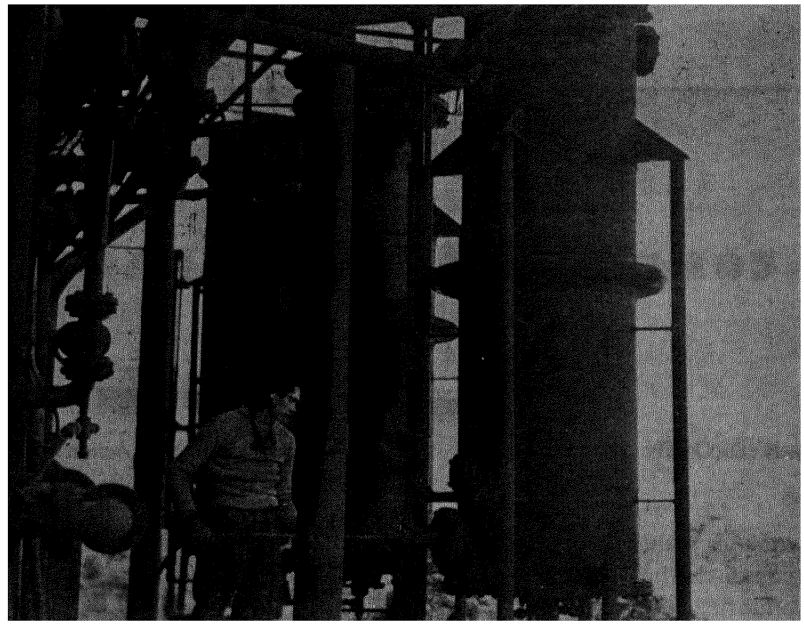


Figure 180. Manufacture of Hydrochloric Acid

Anhydrous hydrogen chloride is synthesized from chlorine gas and hydrogen gas in these burners, one of which is being lighted by an operator.

(Courtesy of Hooker Electrochemical Company)

gen bromide, but it also contains free bromine and sulfur dioxide, SO_2. In the reaction of the iodide with sulfuric acid, some hydrogen iodide is present in the gases evolved, but free iodine, sulfur dioxide, and even hydrogen sulfide, H_2S, are also present. Therefore, the acid must act as an oxidizing agent upon the bromide and the iodide instead of reacting, as it does with a chloride, to form the hydrogen compound of the halogen.

$$H_2SO_4 + 2\,HBr \longrightarrow Br_2 + H_2SO_3 + H_2O,$$
$$H_2SO_3 \longrightarrow H_2O + SO_2.$$
$$H_2SO_4 + 8\,HI \longrightarrow H_2S + 4\,I_2 + 4\,H_2O.$$

We must conclude, therefore, that pure hydrobromic and hydriodic acids cannot be prepared by the action of sulfuric acid upon bromides and iodides.

5. Preparation of Hydrogen Bromide and Hydrogen Iodide

Pure hydrobromic and hydriodic acids are usually prepared from phosphorus tribromide and phosphorus tri-iodide, which are first produced by the direct combination of phosphorus with the halogens. These compounds then react with water, by double decomposition, as follows:

$$(1)\quad PBr_3 + 3\,HOH \longrightarrow 3\,HBr + H_3PO_3$$
$$(2)\quad PI_3 + 3\,HOH \longrightarrow 3\,HI + H_3PO_3.$$

These reactions are additional examples of hydrolysis (page 188). The compound $P(OH)_3$ is *phosphorous acid*, and, therefore, its formula is usually written as H_3PO_3.

The hydrogen bromide and iodide escape, when the mixtures are heated slightly, and are collected by dissolving them in water.

6. Production of Hydrochloric Acid for Commercial Use

The commercial grade of hydrochloric acid contains about 40 per cent of hydrogen chloride. It contains many impurities and

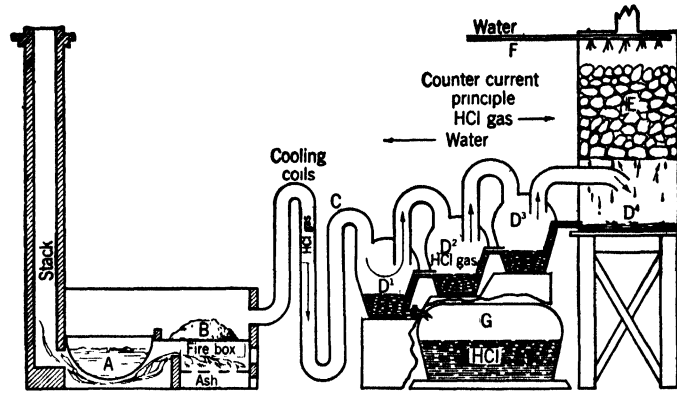


Figure 181. Diagram of a Plant Producing Hydrochloric Acid

A is the retort containing the charge of sulfuric acid and salt; here the salt is converted into sodium acid sulfate. The second reaction is then carried out at B by heating the mass, which is raked from the retort, directly above the firebox at B. Here sodium acid sulfate is converted into sodium sulfate. The hydrogen chloride is dissolved in the water contained in the jars (D) and in the washing tower (D_4). The solution of acid is collected in the receiver G.

usually has a yellow color, chiefly because it contains ferric chloride. It is often called *muriatic acid*. Chemically pure, C.P., acid contains about 36 per cent of hydrogen chloride and has a specific gravity of 1.19.

For commercial uses hydrogen chloride, or hydrochloric acid, is produced by the reaction of salt with sulfuric acid (page 277 and Figure 181); by the direct combination of hydrogen and chlorine; and as a by-product of the production of chlorine derivatives of the hydrocarbons (page 260), especially, in the production of *chlorobenzene*, C_6H_5Cl, which is made by treating benzene, C_6H_6, with chlorine.

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl.$$

7. The Properties of Hydrogen Chloride

Pure hydrogen chloride is colorless and has a very sharp and irritating odor. Under standard conditions, a liter weighs 1.6392 g. The liquid is practically a non-conductor of the electric current in sharp contrast to the solution, which is an excellent conductor.

Hydrogen chloride is extremely soluble in water. Its solubility can be demonstrated rather spectacularly by the experiment shown in Figure 182. The upper flask is filled with hydrogen chloride. The gas dissolves slowly at first, because of the small surface of water exposed to the gas. As the gas dissolves, the water rises in the tube and finally overflows into the upper flask containing hydrogen chloride. The gas dissolves completely and at once, leaving almost a complete vacuum in the upper flask, into which the water is forced by the pressure of the atmosphere. One milliliter of water at 0° dissolves slightly more than 500 ml. of (gaseous) hydrogen chloride, and about 455 ml. at 15°.

Hydrogen chloride can be liquefied at temperatures below its critical temperature, 52°, by increases of pressure. The liquid boils at − 85° at one atmosphere of pressure and freezes at − 114°.

8. Chemical Properties of Hydrochloric Acid

The chemical properties of hydrochloric acid are those of a typical strong acid. Like the solutions of all common acids it has a sour taste, turns blue-litmus red and a red (alkaline) solution of phenolphthalein colorless, is a conductor of the electric current, and neutralizes hydroxide-bases to form salts and water. The properties discussed below are those of many acids and are not specific characteristics of hydrochloric acid.

(*a*) *Action upon Metals.* All the metals above hydrogen in the electrochemical

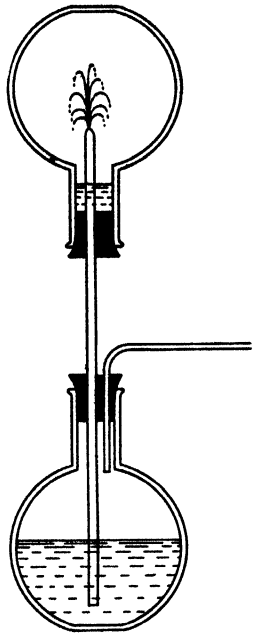


Figure 182. A Method by Which the Solubility of Hydrogen Chloride in Water can be Demonstrated

series react with hydrochloric acid to liberate hydrogen and to form chlorides of the metals.

(*b*) *Action upon Oxides and Hydroxides of the Metals.* Acids react with the oxides and hydroxides of the metals to form water and salts. When the acid is hydrochloric, the salts are chlorides.

(*c*) *Action upon Salts.* Hydrochloric acid reacts with salts, such as the carbonates and sulfites, that form volatile acids or acids that decompose to give volatile substances, such as carbon dioxide.

$$2\,(H^+ + Cl^-) + (2\,Na^+ + CO_3^=) \longrightarrow 2\,(Na^+ + Cl^-) + H_2CO_3$$

$$H_2CO_3 \longrightarrow H_2O + CO_2 \uparrow .$$

9. Properties of Hydrochloric Acid Which are Independent of Its Acid Character

(*a*) *Action as a Reducing Agent.* In discussing the methods of preparing chlorine (page 256), the effects of different oxidizing agents upon hydrochloric acid were considered.

(*b*) *Action as a Soluble Chloride.* Silver chloride and mercurous chloride are only slightly soluble and may be precipitated by adding hydrochloric acid, or any soluble chloride, to a solution of the nitrates of the two metals. Lead chloride is also precipitated in the same manner, but precipitation is never complete because lead chloride is fairly soluble. It is easily separated from the chlorides of silver and mercury by dissolving it in hot water. All other chlorides of the common metals are readily soluble in water.

10. Test for Chloride Ion

The reaction with silver nitrate is often used as a means of detecting chloride ion. This test is regarded as positive when the addition of silver nitrate to a solution causes the formation of a white, curdy precipitate of silver chloride that turns dark upon exposure to light because of the decomposition of this compound and the formation of free silver. Nitric acid may be added to dissolve certain other silver compounds that precipitate in an alkaline or neutral solution. This test is not very satisfactory if bromide or iodide ion is present, because silver bromide and silver iodide are also only slightly soluble even in the presence of nitric acid. These salts are both slightly colored, however, while silver chloride is white. Certain other ions also interfere by forming slightly soluble silver compounds.

11. Uses of Hydrochloric Acid

Hydrochloric acid ranks along with sulfuric and nitric acids in its importance to industry. It is one of the strongest acids. It is considerably stronger than sulfuric acid, but in certain reactions it is less desirable because it is volatile, and because it acts as a reducing agent. Industrially, hydrochloric acid is used in making "pickling" baths for iron that is to be coated with tin or zinc. The acid cleans the surface of the metal by dissolving the coat of oxide. It is also used as a catalyst in the produc-

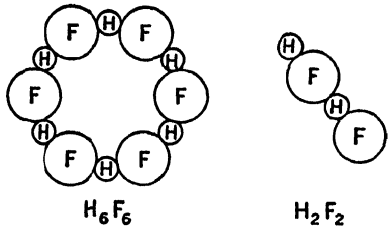


Figure 183. Molecular Structure of Hydrogen Fluoride

tion of syrup from cornstarch; in preparing glue from various animal tissues such as cartilage; in the manufacture of dyes and drugs; in dissolving the calcium phosphate in bone charcoal; in the manufacture of textiles; and to produce the chlorides of many metals from their oxides, hydroxides, or carbonates.

12. Hydrofluoric Acid

The formula of hydrogen fluoride is still somewhat in doubt. At temperatures above 90°, the density of the gas corresponds to the formula HF. At lower temperatures the density is greater and indicates that several types of molecules represented by the general formula $(HF)_x$ may be present. It has also been suggested that the gas, at temperatures below 90°, consists of HF molecules joined together in short, kinked chains in which the negative end of one molecule (F) lies next to the positive end (H) of another, HF⟨HF⟩HF. The existence of salts, such as potassium acid fluoride, KHF_2, has led to the use of the formula H_2F_2 to represent the acid in solution, but it appears somewhat more likely that the HF_2^- ion is composed of two fluorine atoms with a hydrogen atom between them: $[F—H—F]^-$. We shall, therefore, use the simplest formula, HF, to represent the acid.

Hydrofluoric acid is a relatively weak acid. As compared with hydrochloric acid, it reacts more slowly and less vigorously upon metals and their oxides and hydroxides, and its solution is a poorer conductor of electricity. It reacts with silica (SiO_2) and with silicates, such as calcium silicate, $CaSiO_3$:

$$SiO_2 + 4\,HF \longrightarrow SiF_4\uparrow + 2\,H_2O$$
$$CaSiO_3 + 6\,HF \longrightarrow SiF_4\uparrow + CaF_2 + 3\,H_2O.$$

Glass, porcelain, and clay-wares contain silicates of different metals. Hydrofluoric acid, therefore, attacks these materials and cannot be stored or used in vessels made of them. Its containers are made of lead, platinum, hard rubber, Bakelite, or wax.

It is used to etch graduations and scales on glass in making thermometers, cylinders, burettes, and flasks. The glass article is coated with paraffin, and the portion to be etched is exposed by cutting through or scraping away the wax. The article is then exposed to a solution of hydrofluoric acid or to gaseous hydrogen fluoride. Glass is frosted by a mixture of hydrofluoric acid and ammonium fluoride. The solution of the acid is used in analytical chemistry to dissolve silicates or materials containing silicates.

The acid, the gas, and all soluble fluorides are very poisonous. Solutions of hydrofluoric acid produce serious, deep, slowly healing burns. Extreme care should be taken not to spill the acid upon the flesh or clothing.

13. Hydrobromic and Hydriodic Acids and Their Salts

The hydrogen compounds of bromine and iodine are relatively unimportant. Their solutions act as strong acids, but are seldom used, since hydrochloric is just as strong and is cheaper and more stable. Hydrogen bromide and iodide (especially the latter) are easily decomposed into the elements, and free bromine and iodine are usually present in the solutions of the acids. They are much more readily oxidized than hydrochloric acid (page 278).

TABLE 11. PROPERTIES OF THE HYDROGEN HALIDES

Property	HF	HCl	HBr	HI
Solubility in 1 cc. of water at 0°	264 cc. (10°)	506 cc.	610 cc.	425 cc. (10°)
Temperature of constant boiling solution (760 mm.)	120°	110°	126°	127°
Composition of constant boiling solution	35%	20.2%	47.8%	57%
Boiling point of pure substance	19°	−85°	−67°	−36°
Stability — Per cent dissociated at 325°	0	1.5×10^{-6}	3.5×10^{-3}	19
Heat of formation (cal. per mole)	38,000	22,000	8,600	−6,000
Strength of the acid	weak	very strong	very strong	very strong
Action as reducing agent	none	fair	strong	very strong
Silver salt	white, soluble	white, slightly soluble	light yellow or tan, slightly soluble	yellow, slightly soluble

Silver bromide and iodide are used in photography, and the sodium and potassium salts are used in medicine.

14. Properties of the Hydrogen Halides

Some of the important properties of the hydrogen compounds of the halogens are shown in Table 11.

15. Tests for the Bromide, Iodide, and Fluoride Ions

The addition of silver nitrate to a solution containing bromide ion forms a light yellow precipitate of AgBr, and in a solution containing iodide ion, yellowish-green AgI is precipitated. Both precipitates are insoluble in nitric acid and much less soluble in ammonium hydroxide than silver chloride. Silver fluoride is very soluble in water, but calcium fluoride, unlike the calcium compounds of the other halogens, is very slightly soluble.

If an unknown substance in solution forms a precipitate with silver nitrate which indicates that bromide ion may be present, a fresh portion of the solution is treated with a few drops of chlorine water, and then it is shaken with a few milliliters of carbon disulfide. Chlorine liberates free bromine, which then dissolves in the carbon disulfide to which it gives a straw to reddish brown color, depending upon the concentration of the bromine. If only the iodide ion is present, the same procedure forms a pink to violet colored solution in the carbon disulfide, the color depending upon the concentration. If both bromide and iodide are present, the first addition of chlorine liberates free iodine. By the addition of more chlorine, iodine is converted into a colorless compound, iodic acid, and still more chlorine will then liberate the bromine.

Fluorides are detected by adding concentrated sulfuric acid to the solid in a lead or platinum dish or crucible, which is then covered by a glass plate that is coated, except for a small part of its surface, with wax. The hydrogen fluoride that is evolved etches the exposed surface of the glass plate.

OXYGEN COMPOUNDS

16. Introduction

Oxygen compounds of all four halogens are known. In addition to their oxides chlorine, bromine, and iodine, and possibly fluorine form oxygen acids, such as HClO and $HClO_3$, at least in aqueous solutions, and salts of these acids, e.g., potassium chlorate, $KClO_3$.

The oxides of chlorine are Cl_2O, and ClO_2, and Cl_2O_7 (Cl_2O_6 has also been reported); of bromine, Br_3O_8, Br_2O, and BrO_2 have all been reported in the literature but their existence is questionable; of iodine, I_2O_4 and I_2O_5 (I_2O_8 also has been reported); and of fluorine, OF_2 (O_2F_2 also has been reported).

TABLE 12. THE OXYGEN ACIDS OF THE HALOGENS *

Formula	Name	Anhydride	Name
$HClO$	Hypochlorous acid	Cl_2O	Chlorine monoxide
$HClO_2$	Chlorous acid	(Cl_2O_3)	Chlorine trioxide
$HClO_3$	Chloric acid	(Cl_2O_5)	Chlorine pentoxide
$HClO_4$	Perchloric acid	Cl_2O_7	Chlorine heptoxide
$HBrO$	Hypobromous acid	(Br_2O)	Bromine monoxide
$HBrO_3$	Bromic acid	(Br_2O_5)	Bromine pentoxide
HIO	Hypoiodous acid	(I_2O)	Iodine monoxide
HIO_3	Iodic acid	I_2O_5	Iodine pentoxide
HIO_4 / H_5IO_6	Periodic acid	(I_2O_7)	Iodine heptoxide
$(HFO?)$	Hypofluorous acid	OF_2	Oxygen fluoride

* The compounds enclosed in parentheses are hypothetical or of uncertain existence only.

17. The Oxides of the Halogens

Chlorine monoxide, Cl_2O, is a yellow gas, which explodes violently, condenses to a liquid at about 4°, and reacts with water to form hypochlorous acid. It can be made by passing chlorine over mercuric oxide:

$$2\ Cl_2 + 2\ HgO \longrightarrow (HgO,\ HgCl_2) + Cl_2O.$$

Chlorine dioxide, ClO_2, is also a yellow gas; it decomposes with explosive violence, condenses to a liquid at about 10°, and reacts with water to form both chlorous and chloric acids. It is used to bleach cotton. It is produced when a solid chlorate is treated with sulfuric acid:

$$6\ KClO_3 + 3\ H_2SO_4 \longrightarrow 3\ K_2SO_4 + 2\ HClO_4 + 4\ ClO_2 + 2\ H_2O,$$

or from chlorine and sodium chlorite:

$$Cl_2 + 2\ NaClO_2 \longrightarrow 2\ NaCl + 2\ ClO_2.$$

Chlorine heptoxide, Cl_2O_7, is a colorless, oily liquid which explodes violently when heated or when jarred roughly. It is prepared by removing water from perchloric acid by means of phosphorus pentoxide:

$$4\ HClO_4 + P_4O_{10} \longrightarrow 4\ HPO_3 + 2\ Cl_2O_7.$$

Oxygen fluoride, OF_2, is produced by the reaction of fluorine upon water. It boils at − 147° and freezes at − 224°. The most clearly established oxide of bromine is Br_3O_8, which, it is claimed, has been made by the reaction of bromine and ozone at low temperatures. It is described as a white solid, which explodes at room temperature. The best known oxide of iodine is the pentoxide, I_2O_5, which can be produced by the action of concentrated nitric acid upon iodine to form iodic acid, which, when heated to about 175°, loses water and forms the oxide:

$$2\ HIO_3 \longrightarrow H_2O + I_2O_5.$$

It is a solid and is a fairly stable substance. When heated to about 300°, it decomposes, without exploding, into iodine and oxygen.

18. Hypochlorous Acid

Chlorine reacts with water to form both hydrochloric acid and hypochlorous acid:

$$Cl_2 + H_2O \longrightarrow (H^+ + Cl^-) + HClO.^1$$

If calcium carbonate or sodium bicarbonate is added to this solution, the hydrochloric acid can be neutralized, but unless an excess of sodium bicarbonate is added, hypochlorous acid does not react. Therefore, if the solution is distilled, a dilute solution of this acid is obtained as the distillate. Such a solution can also be obtained by distilling a mixture of dilute sulfuric acid and sodium hypochlorite, $NaClO$:

[1] In this equation we have shown hydrochloric acid as $H^+ + Cl^-$, because it is a strong acid and, therefore, in solution it is almost completely ionized. Hypochlorous acid, on the other hand, is a weak acid and exists in solution for the most part as molecules of $HClO$, which, therefore, we have shown in the equation.

$$(Na^+ + ClO^-) + 2\ H^+ + SO_4^{=}) \longrightarrow Na^+ + HSO_4^- + HClO.$$

Pure, dry hypochlorous acid has not been prepared, because it is extremely unstable. It is known only in solution.

19. Sodium Hypochlorite

A solution containing sodium chloride and sodium hypochlorite can be prepared by passing chlorine into a cold solution of sodium hydroxide:

$$2\ (Na^+ + OH^-) + Cl_2 \longrightarrow (Na^+ + Cl^-) + (Na^+ + ClO^-) + H_2O$$

or, $$2\ OH^- + Cl_2 \longrightarrow Cl^- + ClO^- + H_2O.$$

A solution containing sodium chloride and sodium hypochlorite can be prepared, also, by *electrolyzing* a cold solution of sodium chloride under conditions that allow the chlorine liberated at the anode to react with sodium hydroxide, which collects around the cathode. As the solution is electrolyzed, it is stirred to mix the two substances, thus allowing them to form NaCl and NaClO.

When a strong acid, such as sulfuric, is added to a solution containing chloride and hypochlorite ions, the hydrogen ions of the acid do not combine with chloride ions, because hydrochloric acid, HCl, is very highly ionized, but they do combine with hypochlorite ions to form molecules of HClO. Upon standing for some time, especially if in the sunlight, or if in contact with a substance that is readily oxidized, hypochlorous acid liberates oxygen:

$$2\ HClO \longrightarrow 2\ (H^+ + Cl^-) + O_2.$$

Oxygen is liberated in the atomic form and, although it can exist only momentarily as single atoms, it is a much more vigorous oxidizing agent when liberated in this form than ordinary oxygen.

20. Uses of Sodium Hypochlorite

The most extensive use of sodium hypochlorite is in bleaching certain kinds of cloth. The bleaching process is shown in Figure 184. The cloth to be bleached is first passed over rollers and through a solution of sodium hydroxide or lime water (calcium hydroxide). The cloth then passes, continuously, into a tank containing a dilute solution of an acid, which neutralizes the excess of the base, and next into a solution of sodium hypochlorite or a suspension of *bleaching powder*, which is, in part, calcium hypochlorite. The acid on the cloth reacts with the hypochlorite to liberate hypochlorous acid, which is the substance responsible for bleaching. The excess of chlorine and hypochlorous acid must be removed to prevent them from weakening the cloth. Therefore, the cloth is next passed through a tank containing an *antichlor*, such as sodium thiosulfate or sodium sulfite, which converts chlorine into sodium chloride. The cloth is then washed with water and passed through a drying chamber in which heated air is circulated.

A solution containing sodium hypochlorite and some sodium chloride is sold

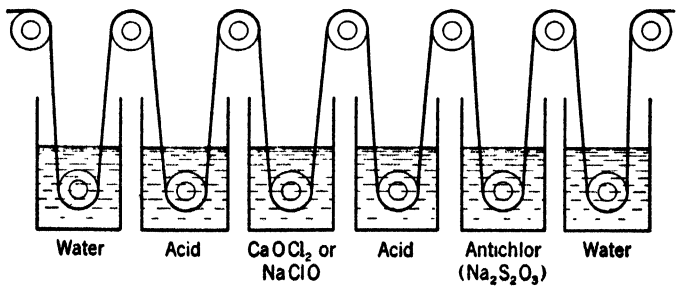


Figure 184. The Bleaching of Cloth by Means of a Solution of Sodium Hypochlorite or Bleaching Powder

under different trade names for use as a bleaching agent in the laundry. It should not be used in laundering wool and silk fabrics, which are rapidly weakened and soon destroyed by chlorine or hypochlorite.

Solutions of hypochlorites, usually a solution of sodium chloride and sodium hypochlorite, are produced and sold under several different trade names for use as antiseptics. *Carrel-Dakin* solution is an antiseptic of this kind.

21. Bleaching Powder

Before the extensive use of liquid chlorine for the purification of water supplies and of sodium hypochlorite in bleaching, the substance $CaOCl_2$, called bleaching powder, was widely used for these purposes. If chlorine is passed over calcium hydroxide, the dry powder which is produced appears to be, not a definite compound, but a mixture containing calcium chloride and calcium hypochlorite, $Ca(ClO)_2$. Some calcium hydroxide is usually also present. Chlorine probably reacts with traces of moisture present in the calcium hydroxide (slaked lime) to form hydrochloric and hypochlorous acids, as already explained. Calcium hydroxide then neutralizes the two acids:

$$2\,(Ca^{++} + 2\,OH^-) + 2\,(H^+ + Cl^-) + 2\,HClO \longrightarrow 4\,H_2O + (Ca^{++} + 2\,Cl^-) + (Ca^{++} + 2\,ClO^-).$$

When bleaching powder is mixed with water and the mixture is acidified with a strong acid, such as sulfuric, the ions of hydrochloric acid and molecules — with a few ions — of hypochlorous acid are produced in the solutions:

$$(Ca^{++} + 2\,Cl^-) + (Ca^{++} + 2\,ClO^-) + 2\,(2\,H^+ + SO_4^=) \longrightarrow 2\,CaSO_4\downarrow + 2\,(H^+ + Cl^-) + 2\,HClO.$$

The two acids then react to some extent to produce chlorine:

$$(H^+ + Cl^-) + HClO \rightleftharpoons Cl_2 + H_2O.$$

This is the reverse of the reaction of chlorine and water (page 283). Hence, the properties of an acidified mixture of bleaching powder and water should be the same, as regards bleaching for example, as a mixture of chlorine and water.

A solution of sodium hypochlorite, containing, also, sodium chloride, can be prepared by treating a suspension of bleaching powder in water with sodium carbonate:

$$(Ca^{++} + Cl^- + ClO^-) + (2\,Na^+ + CO_3^=) \longrightarrow CaCO_3\downarrow + (Na^+ + Cl^-) + (Na^+ + ClO^-)$$

The calcium carbonate is only slightly soluble and can be removed by filtration leaving a fairly pure solution of the two sodium salts. This reaction is sometimes used to prepare the hypochlorite used in laundries and as an antiseptic.

Bleaching powder is made from cheap materials, is easily manufactured, can be transported readily, and its chlorine can be liberated easily whenever required. It usually contains about 36 per cent of available chlorine. It must be transported and stored in air-tight containers to prevent its reaction with the carbon dioxide and moisture of the air. A different bleaching powder that contains a much larger per cent of available chlorine is also used. This is essentially calcium hypochlorite, $Ca(ClO)_2$, and is called *High Test Hyperchlorite*, or H.T.H. It usually contains some slaked lime.

22. Chlorous Acid and Sodium Chlorite

Chlorous acid, $HClO_2$, is a stronger acid than hypochlorous. Sodium chlorite $NaClO_2$, is produced with sodium chlorate when ClO_2 is dissolved in a solution of sodium hydroxide. It does not act so vigorously as an oxidizing agent as the hypochlorite and for this reason is somewhat more satisfactory as a bleaching agent.

23. Chloric Acid

Chloric acid is produced when a solution of barium chlorate is mixed with dilute sulfuric acid.

$$(Ba^{++} + 2\ ClO_3^-) + (2\ H^+ + SO_4^=) \longrightarrow BaSO_4 \downarrow + 2\ (H^+ + ClO_3^-).$$

Sulfuric acid is added in the exact amount required to react with the barium chlorate. The barium sulfate is only slightly soluble and can be removed by filtration. The dilute solution of chloric acid thus produced can be concentrated to 40 per cent, if the solution is evaporated at a temperature below 40° C., under very low pressure, or in a vacuum desiccator over concentrated sulfuric acid.

Chloric acid is a colorless liquid. It is more stable than hypochlorous acid, but when it is slightly heated it decomposes violently to form chlorine dioxide. It is a strong acid and a very active oxidizing agent; a piece of paper ignites spontaneously when dipped into the 40 per cent solution.

24. Potassium Chlorate

Potassium chlorate is the most important salt of chloric acid. It is made by passing chlorine into a hot concentrated solution of potassium hydroxide. In accordance with the reactions already discussed (page 283), chlorine reacts with water to form HCl and HClO; these acids are then neutralized by the base to form the salts, KCl and KClO. Potassium hypochlorite is converted into potassium chloride and potassium chlorate in the hot solution:

$$3\ (K^+ + ClO^-) \longrightarrow (K^+ + ClO_3^-) + 2\ (K^+ + Cl^-).$$

When the solution is partially evaporated and allowed to cool, crystals of potassium chlorate form and can be separated by filtering or by *decantation* (pouring off the clear solution from the crystals). Unless the evaporation is carried too far, the more soluble potassium chloride remains in the solution. The potassium chlorate is purified by recrystallization.

Potassium chlorate is also produced (1) by the electrolysis of a hot aqueous solution of potassium chloride and (2) from calcium chlorate. The latter is first prepared by passing chlorine into a moderately hot suspension of calcium hydroxide in water:

$$6\ Ca(OH)_2 + 6\ Cl_2 \longrightarrow (Ca^{++} + 2\ ClO_3^-) + 5\ (Ca^{++} + 2\ Cl^-) + 6\ H_2O.$$

Potassium chloride is then added and reacts with the calcium chlorate to form calcium chloride and potassium chlorate:

$$(Ca^{++} + 2\ ClO_3^-) + 2\ (K^+ + Cl^-) \longrightarrow (Ca^{++} + 2\ Cl^-) + 2\ (K^+ + ClO_3^-).$$

Potassium chlorate is recovered by crystallization, and the calcium chloride, which is very soluble, remains in the solution.

Potassium chlorate is an active oxidizing agent. If it is mixed with an easily oxidized substance, such as charcoal-dust, and ground to a powder in a mortar, the mixture will explode violently. (Do not attempt this experiment.) A splinter of wood or a bit of sawdust dropped into melted potassium chlorate burns very vigorously. When it is heated at moderate temperatures, slightly above its melting point, potassium chlorate decomposes into potassium chloride and oxygen (page 51). If it is heated at lower temperatures and if the evolution of oxygen is avoided, potassium chlorate may be changed into potassium perchlorate:

$$4\ KClO_3 \longrightarrow 3\ KClO_4 + KCl.$$

Potassium chlorate is used in the manufacture of matches, fireworks, and *cheddite*, an explosive. In chemical manufacturing, potassium chlorate is used as an oxidizing agent.

25. Perchloric Acid and the Perchlorates

The anhydride of perchloric acid ($HClO_4$) is Cl_2O_7. A solution of the acid is prepared by mixing solutions of barium perchlorate and sulfuric acid, and filtering off the insoluble barium sulfate.

$$(Ba^{++} + 2\ ClO_4^-) + (2\ H^+ + SO_4^=) \longrightarrow BaSO_4 \downarrow + 2\ (H^+ + ClO_4^-).$$

A more concentrated solution of perchloric acid may be obtained by evaporating the dilute solution under reduced pressure. Even the anhydrous acid may be prepared, since it is fairly stable at temperatures below 90°. The 60 or 70 per cent solution instead of the pure acid is used in the laboratory. It is a less vigorous oxidizing agent than any other oxygen acid of chlorine.

A solution of perchloric acid is used in analytical chemistry to detect and to determine the quantity of potassium in samples of materials. This use of perchloric acid is based upon the slight solubility of potassium perchlorate, as compared with the solubilities of other perchlorates and other potassium salts. Perchloric acid is one of the strongest of all acids, comparing favorably in this respect with hydrochloric and nitric acids.

Potassium perchlorate is the most important of the salts of perchloric acid. It is prepared by carefully heating potassium chlorate (page 286). It can also be prepared by the prolonged electrolysis of a hot solution of potassium chloride. When heated strongly, potassium perchlorate decomposes:

$$KClO_4 \longrightarrow KCl + 2\ O_2.$$

The perchlorates are more stable and less active oxidizing agents than the chlorates. Potassium perchlorate is used in the manufacture of matches, fireworks, and explosives. Anhydrous barium perchlorate and magnesium perchlorate are used as dehydrating agents, because they form stable hydrates.

26. The Oxygen Acids of Bromine and Iodine

Bromine and iodine show less tendency to react with water than chlorine does, but in the presence of an hydroxide-base (NaOH or KOH) the reaction is almost complete. *Sodium hypobromite*, or *hypoiodite*, and sodium bromide, or iodide, are formed. *Hypobromous acid* and *bromic acid* are prepared in the same way as hypochlorous and chloric acids, which they resemble in general properties.

Iodic acid is prepared by heating iodine, suspended in water, with chlorine. The latter reacts with the water to form hypochlorous acid, which then oxidizes iodine to iodic acid:

$$5\ HClO + H_2O + I_2 \longrightarrow 2\ (H^+ + IO_3^-) + 5\ (H^+ + Cl^-).$$

When the solution is evaporated, crystals of iodic acid separate. In aqueous solution, iodic acid is a somewhat less active oxidizing agent than chloric and bromic acids. *Sodium iodate* is the most important salt of iodic acid. It is found in the deposits of sodium nitrate in South America (page 241). It may be prepared by the action of sodium chlorate upon iodine:

$$2\ (Na^+ + ClO_3^-) + I_2 \longrightarrow 2\ (Na^+ + IO_3^-) + Cl_2.$$

The iodates and iodic acid have limited uses as reagents in the chemical laboratory, and the former have some slight use in medicine.

There are several acids to which the name *periodic* may be applied. All of these have the same anhydride, I_2O_7. The best-known salts are derivatives of H_5IO_6 and HIO_4.

$$I_2O_7 + 5\ H_2O \longrightarrow 2\ H_5IO_6.$$
$$I_2O_7 + H_2O \longrightarrow 2\ HIO_4.$$

In acidified solutions the periodates — e.g., sodium periodate, $NaIO_4$ or Na_5IO_6 — are vigorous oxidizing agents.

REVIEW EXERCISES

1. Compare and contrast the properties of pure hydrogen chloride with the properties of its aqueous solution.
2. How would you prepare a constant boiling solution of hydrochloric acid? How do we

know that this is not a compound of water and HCl?

3. Suggest a procedure by which the silver iodide used in the manufacture of photographic plates and films might be produced.
4. How would you test a solution to determine which acid is present if the solution is known to contain HBr or HI?
5. Write the equation for the hydrolysis of phosphorus tribromide.
6. Compare the reactions of sulfuric acid with (1) chlorides and (2) bromides and iodides.
7. How many liters of 1 N HCl solution can be prepared from the HCl obtained by treating 100 g. of $BaCl_2$ with concentrated sulfuric acid? Assume that there are no losses.
8. Write equations, using whatever other substances are necessary to show how you would prepare NaCl from NaBr; Na_2SO_4 from $NaHSO_4$; HI from H_2S; SiF_4 from SiO_2; HF from CaF_2; HClO from H_2O.
9. Calculate the volume of 1 M potassium permanganate solution which would be required to liberate the iodine in one liter of 1 N hydriodic acid solution.
10. Complete the following equations and underline all products which would precipitate when aqueous solutions of moderate concentration and containing the reagents indicated are mixed?
    (*a*) Silver nitrate and potassium iodide.
    (*b*) Lead nitrate and sodium bromide.
    (*c*) Mercurous nitrate and sodium iodide.
    (*d*) Ferric chloride and mercurous nitrate.
11. What is the weight of one liter of hydrogen iodide (gas) calculated for 0° and 760 mm.?
12. Write an equation to show the reaction of hydrogen fluoride upon silica.
13. What are the names of the following compounds? $CaCl_2$, $Ca(ClO)_2$, $Ca(ClO_2)_2$ $CaOCl_2$, $Ca(ClO_3)_2$, $Ca(ClO_4)_2$. What is the oxidation number of chlorine in each of these?
14. How does the stability of the oxygen-acids of chlorine, and their salts, vary with the number of atoms of oxygen in the molecule?
15. Why is it less expensive to prepare potassium perchlorate by electrolyzing a solution of potassium chloride, under the proper conditions, than it is to prepare it by heating potassium chlorate?
16. What impurity would you expect to find in potassium chlorate prepared by treating a warm solution of pure potassium hydroxide with pure chlorine?
17. How is chlorine liberated when bleaching powder is treated with a dilute solution of sulfuric acid?
18. Write a balanced equation to show the oxidation of iodine to iodic acid, HIO_3, by hypochlorous acid if HCl is the other product.
19. Write equations for all of the reactions which occur when a hot solution of sodium hydroxide is treated with bromine.
20. Write a balanced equation which shows the oxidation of iodine to iodic acid by nitric acid, if the nitrogen appears at the end of the reaction as nitric oxide (NO).
21. How would you prepare the barium chlorate which is used in making a fairly pure solution of chloric acid (page 286)?
22. Write a balanced equation to show the reaction of chloric acid with iodine, if the products of the reaction are iodic acid and free chlorine.
23. What are some of the indications, as revealed by the properties of their compounds, that chlorine is more electronegative than iodine?
24. What is the oxidation number of iodine in the acid H_5IO_6? Account for the fact that the oxidation number of the periodate (IO_6) ion is -5.
25. Solutions of hydriodic acid become discolored when they are allowed to stand in the light. What happens?
26. Show by an equation how potassium chlorate is changed into potassium perchlorate.
27. Write the formulas for potassium iodate, sodium bromate, calcium periodate, the anhydride of perchloric acid, and magnesium hypobromite.
28. What weight of potassium chlorate could be produced by the action of an excess of chlorine upon one liter of 10 N potassium hydroxide solution? Assume that the product recovered amounts to 90 per cent of the theoretical yield.
29. How can potassium perchlorate be obtained in a fairly pure condition from a mixture which contains potassium perchlorate and potassium chloride?

30. A compound contains 31.9 per cent of potassium, 39.2 per cent of oxygen, and 28.9 per cent of chlorine. What is the formula of the compound?
31. In what ways do the properties of hydrogen fluoride differ from those of the other hydrogen halides?
32. Write equations to show the formation of sodium chloride and sodium hypochlorite from chlorine and sodium carbonate.
33. Balance the following equations:

$$HI + HClO \longrightarrow I_2 + H_2O + Cl_2.$$
$$HClO + H_2O + I_2 \longrightarrow HIO_3 + HCl.$$
$$HClO_2 \longrightarrow ClO_2 + HClO_3 + HCl + H_2O.$$

REFERENCES FOR FURTHER READING

Calcium Hypochlorite: *Chem. and Met. Eng.*, **36,** 295 (1929).

Chlorates: *Chem. and Met. Eng.*, **44,** 302 (1937); **45,** 692 (1938); **47,** 468 (1940).

Chlorine Compounds: *Chem. and Met. Eng.*, **33,** 274 (1926); *J. Chem. Ed.*, **4,** 596 (1927).

Chlorites: *Chem. and Met. Eng.*, **47,** 630 (1940); *Ind. and Eng. Chem.*, **32,** 899 (1940); **34,** 782 (1942).

Perchloric Acid: *Chem. and Met. Eng.*, **25,** 1093 (1921).

Sodium Hypochlorite: *Ind. and Eng. Chem.*, **15,** 845 (1923).

23

CARBON

1. Occurrence

Carbon is found in nature as the free element and in many of its compounds. It constitutes only about 0.03 per cent of the earth's crust, but this relatively small amount of the element is of vast importance as shown by the fact that 400,000 or more of its compounds have been produced either from natural sources or by synthesis.

Carbon, or carbon compounds, furnish us with practically all of our food, fuel, and clothing. We depend upon carbon and its compounds also to provide a very large part of the energy used in our industrial activities, and it is also used in many industrial processes, such as the reduction of metals from their ores. It is to be ranked along with oxygen and hydrogen as one of the three or four elements most important to man.

Carbon dioxide is the most familiar of the gaseous compounds of carbon. It is produced by oxidation in the body and is removed through the lungs. Large quantities of it are also thrown into the atmosphere by household and industrial furnaces in which wood, coal, coke, oil, or gas is burned. Petroleum is composed almost entirely of hydrocarbons, compounds of carbon and hydrogen, and the products of the petroleum refining industry — gasoline, kerosene, fuel oil, motor oil, petrolatum, paraffin — are mixtures of these compounds. Natural gas, also, contains hydrocarbons, particularly methane, CH_4. The carbonates are important sources of some of the metals, and two of them, calcium and magnesium carbonate, form vast deposits of sedimentary rocks, called limestones and dolomites. Calcium carbonate is also the principal constituent of coral, and the shells and skeletons of many aquatic forms of life.

FORMS OF CARBON

Diamond and graphite, two allotropic forms of carbon, are both crystalline but differ in their crystal-lattice patterns. Coke, charcoal, lampblack and similar materials are usually classified as *amorphous carbon*.

2. Diamond: Occurrence

The earliest diamonds of which we have any record were found in India. In the early part of the eighteenth century, mines were opened in Brazil. But both of these sources were overshadowed in importance when, in 1867, diamonds were found in South Africa, and a few years later, the famous mines at Kimberley were opened. Here, diamonds occur in the *blue ground* that fills very deep vertical *pipes*, which are probably the necks of old volcanoes. The mass of material removed from the pipes is crushed and treated with flowing water to remove the lighter portions of earth from the *concentrate*, in which the

diamonds are collected. From this concentrate the diamonds are completely separated by carrying off the worthless materials in a stream of water that flows over plates covered with grease. Diamonds are caught and held by the grease, which has more attraction for them than water has.

The value of a diamond depends upon its weight and freedom from flaws and impurities. Its weight is expressed in carats. A *carat* is 0.2 g. Although uniformity of color is of great importance, coloring may enhance rather than decrease the value. The Florentine diamond is yellow, and the Hope diamond is blue.

Some famous diamonds are: the Kohinor (106 carats); the Jubilee (240 carats); the Victoria (180 carats); the Regent (410 carats), now in the Louvre; the Orloff (193 carats), which was among the Russian crown jewels until the time of the revolution; and the Nizam (277 carats). The Cullinan, weighing 3026 carats, was found in the Transvaal in 1905. The Jonker, found in South Africa in 1935, weighs 726 carats.

3. Artificial Diamonds

Small diamonds of inferior value and badly colored can be produced artifically. Moissan was the first to produce them. In 1893, he dissolved carbon in melted iron and poured the liquid into water. A crust of solid iron formed, inclosing a mass of still liquid material. As the iron crystallized, some of the carbon separated and formed tiny diamonds under the influence of the high pressure inside the mass of iron. The iron was removed, finally, by the addition of hydrochloric acid, in which diamond does not dissolve while iron does.

4. Properties

In 1914, Davy proved that the diamond is a form of pure carbon by converting a sample completely into carbon dioxide. Its density is 3.5 g. per cc. It is very brittle and in hardness ranks above all other natural substances. Some of the carbides (binary carbon compounds) are also extremely hard. Even the diamond may be scratched by the carbide of boron, and tungsten carbide has been used in the place of diamond in the teeth of stone-saws. Diamond is very inert and resists the action of most substances. It begins to burn in air, however, at about 900° and in pure oxygen at about 700°.

5. Uses

Black diamonds, many of which are obtained in Brazil, are called *carbonado*. These and other badly colored stones are set in the teeth of saws and in the bits of drills, which are used to cut stone. They are also used in grinding and polishing hard materials. Diamond dust is used to polish diamonds and other precious stones.

Rough diamonds are usually not very lustrous. The cutting of a rough stone consists of producing facets which are so arranged that light that enters the crystal will be reflected back and forth from one facet to another. Because of its high index of refraction and great dispersing power, diamond breaks up white light into different colors.

6. Graphite: Occurrence

The second crystalline allotropic form of carbon, now called graphite, was once thought to be a compound of lead and was called *plumbago*. Native graphite is found in Ceylon, Siberia, Madagascar, Korea, Austria, Germany, Mexico, Canada, Italy, and the United States (New York).

7. Production

The Acheson process is used to make graphite on a large scale from coal. An electric furnace (Figure 185) is employed to heat a charge consisting of coarse grains of hard coal. A small central core of finely granulated carbon connects the electrodes and acts as a conductor of the current, since the coarse grains of coal conduct very poorly. The charge is covered with a layer

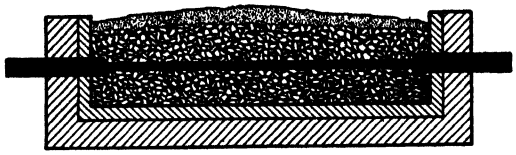


Figure 185. The Production of Graphite in the Electric Furnace

of sand and carbon to exclude the air. An alternating current passes through the charge and, because of the resistance, liberates enormous quantities of heat, which converts the carbon in the coal into graphite. Ferric oxide acts as a catalyst in the transformation. Coal usually contains a sufficient quantity of this substance to render the change sufficiently rapid. Powdered coal and pitch are sometimes mixed and made into electrodes and other objects of the desired form and size before graphitization. These objects are then heated in the electric furnace, and the carbon in them is converted into graphite.

8. Properties

The density of graphite is 2.25 g. per cc. It is grayish black in color and is so soft that it leaves marks when rubbed across a sheet of paper. The name graphite, from the Greek word which means "to write," was given to the substance because of this property. It is a better conductor of electricity than any other form of carbon. Like diamond it is chemically inactive and resists the attack of most reagents. It burns in oxygen at a temperature around 700°. The melting point of graphite is around 3500° and the boiling point slightly above 4800°.

9. Uses

Because of its chemical inactivity, graphite is used to make crucibles in which metals are melted in the manufacture of alloys and high-grade steel. A mixture of graphite and clay is used to make the crucible, the clay acting as a binding agent for the crystals of graphite and rendering them somewhat more resistant to oxidation at high temperatures. It is also widely used in the manufacture of electrodes, brushes, and other parts of electrical devices. Powdered graphite is used to coat wax forms which are later used as electrodes for the deposition of metals. This is the method of producing the plates used in the electrotyping process of printing. Graphite is an important lubricant because of the tendency of its small crystalline plates to slide over one another under pressure. It is used to lubricate wooden parts of machines and also metal bearings that are exposed to sand, and dust, or high temperature, which would render a lubricating oil valueless. Suspensions of graphite in water and in oil are also used as lubricants. Graphite is also used as a pigment in paints, and in stove polish, and as a lining for foundry furnaces. The "lead" of a pencil is composed of a mixture of graphite, clay, and wax. Sometimes, lampblack, silica, and other substances are added to produce pencils of special grades. The softer "leads" contain relatively more graphite.

10. Structures of Crystals of Graphite and Diamond

In the diamond lattice each carbon atom is surrounded by four other carbon atoms, which are joined by covalent bonds, and which form the four corners of a tetrahedron. The diamond crystal is a compact structure, in which the atoms of a single unit lie *in different planes*. The whole crystal is a "giant molecule." In graphite the atoms of the crystal unit are arranged in a hexagonal ring in a single plane (Figure 186). The bonds between the atoms in parallel planes are weak, and one plane, under pressure, can be made to slide over another, or it can be separated easily from the planes that lie above or below it. The use of graphite as a lubricant depends upon this feature of its crystalline structure.

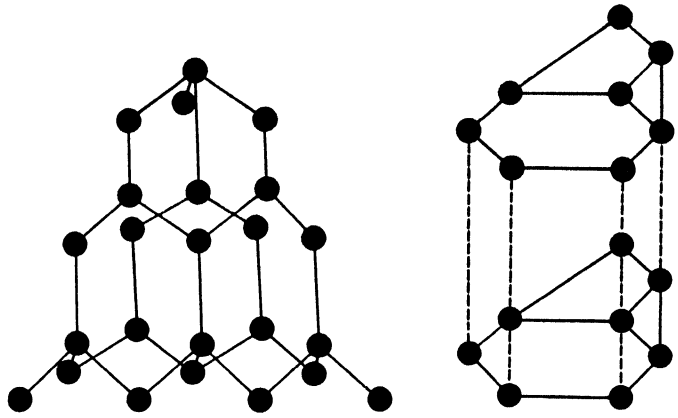


Figure 186. The Structures of Diamond Crystals (left) and Graphite Crystals (right)

11. Amorphous Carbon

Many forms of carbon are said to be amorphous, although X-ray analysis shows that they are composed of very small crystals which resemble those of graphite. These forms, such as charcoal, usually show more porous structures than graphite or form soft and very bulky powders. The most important forms of "amorphous" carbon are coke, charcoal, lampblack, gas carbon, and bone-black.

12. Coal

Because of coal's importance as a fuel, as a reducing agent in the production of metals and especially of iron from their ores, and as a source of many important compounds, the industrial prosperity of a country depends to no small extent upon that country's supply of this natural resource. From coal we obtain coke, coal gas, water gas, ammonia, and many substances such as benzene, toluene, naphthalene, anthracene, carbolic acid, and others that are widely used in the manufacture of dyes, drugs, explosives, and many other organic compounds. The world produces in normal times about one and one-half billion tons of coal each year. The United States produces about 650,000,000 tons annually from deposits in Pennsylvania, West Virginia, Indiana, Kentucky, Illinois, and Tennessee.

13. Coal's Origin

The origin of coal goes back to an early geological age, called the Carboniferous Period, when the earth was covered by very dense vegetation. This vegetable matter, as it died, collected in deep layers. Decay was prevented in some places by geological changes that submerged the deposits beneath the sea and covered them with layers of sediment, thus excluding the air. Chemical changes then slowly converted the deposited vegetable matter, first into what we call *peat*, then into *lignite* or brown coal, then into *bituminous* or soft coal, and, if the process continued long enough and under the proper conditions, finally into *anthracite* or hard coal. This process is called *carbonization*, because the slow changes by which coal was formed resulted in the partial liberation of the hydrogen, oxygen, and nitrogen originally present in the plants, and in an increase in the percentage of carbon. Table 13 shows the relative amounts of these elements, and also the percentages of uncombined water and ash, in wood and in different forms of coal. High pressures and temperatures have undoubtedly influenced the extent of carbonization in many cases.

14. Coke

When coal is heated in the absence of air,

TABLE 13. ANALYSES OF DIFFERENT KINDS OF COAL
(Percentages)

Sample	Water	Volatile matter	Fixed carbon	Ash	Dried Sample				Heating value (B.T.U. per lb.)
					Carbon	Hydrogen	Nitrogen	Oxygen	
Wood	7.4			0.4	50.0	6.0	0.1	43.0	4,500
Peat-air dried	10.0	50.0	25.0	10.0	59.0	5.0	2.9	32.0	4,300
Lignite	33.0	29.0	29.0	7.0	42.5	7.0	0.8	42.0	6,500
Bituminous coal	3.4	35.5	51.3	9.7	71.0	5.2	1.4	9.0	13,000
Anthracite coal	3.3	3.27	85.0	9.1	85.5	3.3	1.1	3.5	13,350

The analyses given in this table are representative values and are not to be considered as indicating the percentages of the various constituents to be found in every sample of fuel in a certain class. The percentages of water and ash are especially likely to vary over wide ranges.

the volatile constituents are driven off, leaving behind free carbon and mineral substances. This process is sometimes spoken of as the *destructive distillation* of coal. The residue is called *coke*. During the conversion of coal into coke, many of the complex compounds found in coal and containing carbon, oxygen, nitrogen, and hydrogen are broken down into simple and more readily volatile substances, which are distilled. The extensive amounts of coke used to produce water gas (page 70) and in the metallurgy of iron, where it is employed to reduce the oxides of iron to the free metal, make the coke industry one of great importance. Some coke is used as a household fuel, where its high heat value and its combustion, without the production of smoke, make it very desirable. Its use is restricted, however, because of its price. It is also difficult to ignite, because it contains none of the volatile substances, which have low kindling temperatures, and which are present in coal, especially in coal of the bituminous variety.

15. Production of Coke

Coke was formerly produced entirely in beehive ovens (Figure 187). The coal was loosely placed in the oven and heated in a limited supply of air. The combustion of a part of the coal converted the remainder into coke. The volatile substances were allowed to burn at the top of the oven. The beehive type of oven has now been largely replaced by ovens designed to provide for the recovery of the by-products distilled from the coal. These products include ammonia, coal gas (consisting principally of hydrocarbons), benzene, toluene, and coal tar. Many substances used in the manufacture of dyes, drugs, and other chemicals are obtained by further distillation of the tar.

Coke ovens that permit the recovery of the volatile parts of the coal are called *by-product* ovens. A diagram of such an oven is shown in Figure 188. The coal is heated by burning a part of the coal gas produced in the plant. Soft, or bituminous, coals

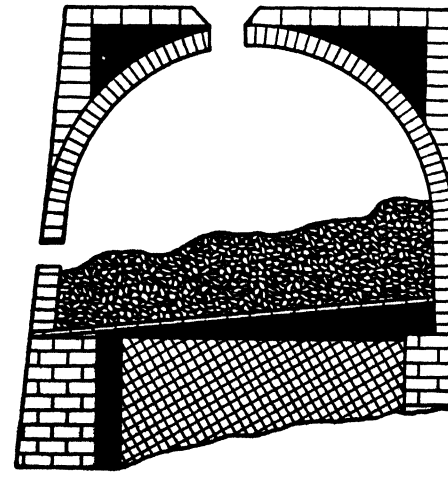


Figure 187. Beehive Coke Oven

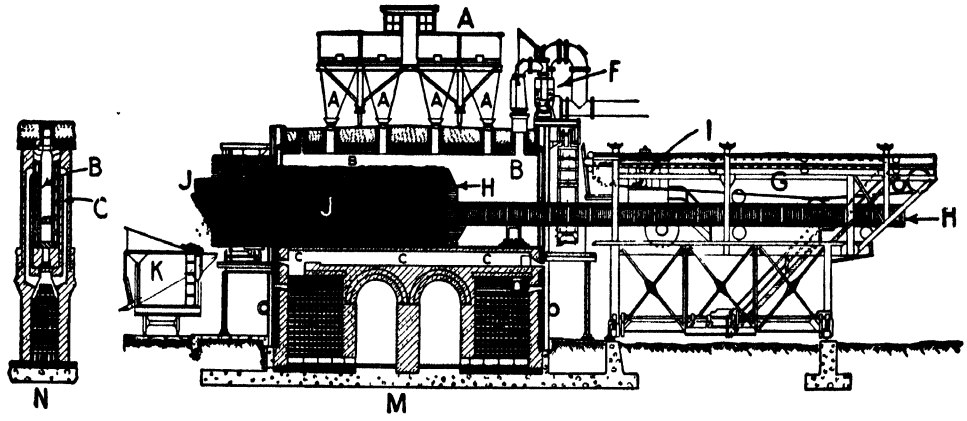


Figure 188. Cross-Section of a By-Product Coke Plant

N, section through retort (B) as seen from one end. M, a section taken lengthwise of the retorts. The coal is fed into the retorts through the carriers (A) and is heated by flames and hot gases, produced in C by the burning of coal gas in air that has been heated in E. The gases resulting from the combustion pass out through one compartment E, thereby heating it, while air is entering through the other. The coke (J) is pushed out of the retort by the pusher (H) into cars (K) where it is quenched. The coal gas passes out of the retort through F to the various units of the purifying plant.

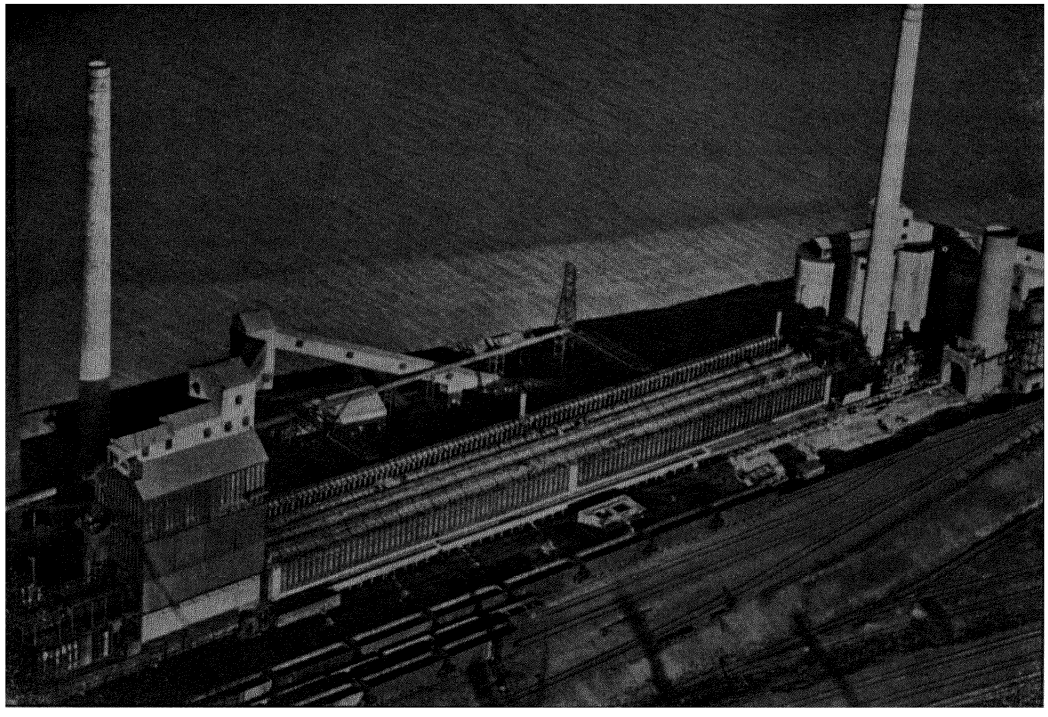


Figure 189. Battery of Coke Ovens

The battery consists of 106 ovens. At the left of the ovens is the coal storage bin, and at the right are the mixing bins, where different grades of coal are mixed to the proper blend for coking, and the quenching tower where the coke is cooled.

(Courtesy of Koppers Company)

give the largest yields of by-products, but anthracite or semi-anthracite give the best grades of coke. When used in metallurgical operations, coke must be fairly hard and strong to withstand the weight of the charges in the furnaces without crumbling. Coke from bituminous coal is usually too soft, although a good metallurgical grade can be produced, it is claimed, if the soft coal is preheated before it is placed in the coking ovens.

16. Charcoal

Wood is largely composed of cellulose $(C_6H_{10}O_5)_x$. Charcoal is made by heating wood in the absence of air, a process in which wood is *destructively distilled*. The hydrogen, oxygen, nitrogen, some of the carbon, and other elements are removed when the wood decomposes, upon heating, into volatile compounds of these elements. The charcoal that is left is a fairly pure form of carbon.

In the modern charcoal plant, iron cars are loaded with hard woods and pushed, on a track, into a large retort, which is heated by fires underneath. The volatile products escape through pipes in the top of the retort into condensers, where they are cooled and condensed to a liquid called *pyroligneous acid*. From it three very important products — acetic acid, acetone, and methyl (wood) alcohol — are produced.

Charcoal is used in limited quantities as a fuel. Its greatest use is as a clarifying and decolorizing agent for certain liquids, such as sugar solutions, syrups, acids, extracts, vegetable oils, and petroleum products. This use depends upon the ability of charcoal to *adsorb* certain substances that cause discoloration of the liquids.

Gas masks are used in war to protect troops or other persons who may be exposed to poisonous gases. The air to be breathed is passed through canisters filled with materials which remove the poisonous gases but allow the air to pass through. The efficiency of the mask depends, in part, upon the adsorption of poisonous gases by charcoal. The best charcoal for this purpose is a hard variety, prepared from cocoanut shells, peach pits, sugar, or from certain varieties of wood carbonized under pressure. Charcoal-filled gas masks are used in peace times to protect workers who may be exposed to poisonous gases. Activated charcoal is used, also, to adsorb the vapors of gasoline from natural gas. The gasoline is recovered by heating the charcoal. *Soft*, activated charcoal is most efficient in clarifying and decolorizing liquids. Charcoal is activated by heating it in steam to break down the larger granules, thus increasing the surface. The steam also removes gases already adsorbed.

17. Lampblack

This form of carbon is produced by burning natural gas, tar, or oils in a limited supply of air. The best grade is produced from natural gas and is called *carbon black*. If the oxygen supply is limited, burning produces a smoky flame because of the small particles of carbon that escape combustion. This flame plays upon one side of a revolving drum upon which the soot, or lampblack, is deposited. A knife on the other side scrapes off the deposit as the drum rotates. The product is a very finely divided black powder, composed of almost pure free carbon. Its principal use is in the compounding of the mixture used in manufacturing automobile tires. Carbon increases the resistance to wear, and makes a tougher, stronger, and more resilient material. It is also used in the manufacture of many other rubber articles. Large quantities of carbon black are used to make printer's ink, typewriter ribbons, India ink, and carbon paper. Carbon-inks are not bleached by chlorine and other reagents that destroy records made with other inks, and they do not run or smear when wet. Carbon black is also used as a paint and

enamel pigment, in phonograph records, and shoe, stove, and other polishes.

18. Bone-Black

Bone-black, or animal charcoal, is produced by the destructive distillation of bones and, sometimes, other organic materials from meat-packing plants. It contains about 10 per cent of charcoal and considerable mineral matter. Its chief use is in the sugar refinery. Crude sugar has a yellow or brown color. This color is removed by dissolving the sugar in water and filtering the colored solution through beds of bone-black, which adsorbs the discoloring materials. The dispersion of the finely divided carbon through the mass of mineral matter insures an enormous surface of the adsorbing material. The coloring matter of the sugar solution is thus removed, and a white crystalline product of a high degree of purity is then prepared by the evaporation of the filtrate.

19. Gas Carbon

Soft coal is distilled in coke ovens to produce illuminating gas and other by-products. The gas supply of many cities is produced in this manner. Some of the hydrocarbons in the gas are decomposed, or "cracked," by the high temperature of the retorts. As a result, some hydrogen escapes in the gas and carbon is deposited on the walls. This carbon is gray in color, and is harder and more crystalline than other forms. It conducts the current fairly well, and is used, therefore, to make the carbon rods or pencils used in arc lights, and the electrodes for electrolytic cells in which either the solutions or the substances liberated would attack electrodes made of metal or other materials.

PROPERTIES OF CARBON

20. Physical Properties of Carbon

In addition to the specific properties possessed by the different forms of carbon, certain other properties are common to all the forms. Carbon is odorless and tasteless. It is insoluble in water and in all ordinary solvents, such as alcohol, ether, benzene, and chloroform. It does dissolve slightly in some fused metals, in which it produces marked changes in properties. The solution of carbon in iron is important in the metallurgy of iron and steel. Carbon has extremely high boiling and melting points (page 292). When heated to a sufficiently high temperature, it becomes incandescent (emits light). The filaments used in the first electric lamps were made of carbon, but they are now made of tungsten, which has considerably less resistance than carbon and is more efficient in producing light.

21. Chemical Properties of Carbon

Carbon combines only very slowly, or not at all, with other elements at ordinary temperatures. At higher temperatures, it combines with many metals to form *carbides*, such as those of calcium, CaC_2, and iron, Fe_3C. It also combines with several non-metals. When carbon burns in an adequate supply of air or in pure oxygen, carbon dioxide, CO_2, is produced, but with a deficiency of air, carbon monoxide, CO, results. The use of carbonaceous materials as fuels depends largely upon the heat liberated by this reaction:

$$C + O_2 \longrightarrow CO_2 + 94{,}385 \text{ calories.}$$

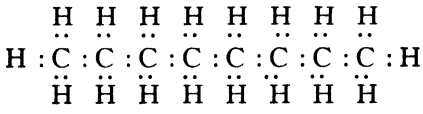
Carbon also reacts with sulfur at elevated temperatures to form carbon disulfide (CS_2) and with silicon to form the carbide (SiC). It also combines directly, but not very readily, with hydrogen to form hydrocarbons, such as CH_4. Hot carbon is an inexpensive and efficient reducing agent. Thus, it reduces hydrogen in the production of water gas from steam, forming carbon monoxide and setting hydrogen free. Its use in metallurgy also depends upon its

ability to reduce the metals from their oxides to the free state.

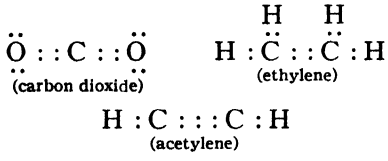
The carbon atom has four electrons in its outermost shell and, in keeping with this structure, carbon has a maximum valence of four. It sometimes has a valence of two, as in carbon monoxide. The element almost always forms covalent bonds with other elements. This behavior indicates that carbon has little tendency either to lose or to gain electrons.

22. Examples of Carbon Compounds

Two carbon atoms may share electrons with each other. This property gives rise to molecules of carbon compounds in which many carbon atoms may be bound together to form a long chain, as in *octane*,



One, two, or even three pairs of electrons may be shared by two carbon atoms or by a carbon atom and an atom of some other element:



The remarkable tendency of carbon to form covalent linkages — particularly linkages uniting carbon to carbon — is responsible, in part, for the extremely large number of compounds of this element. This number is further increased by the fact that some or all of the hydrogen atoms attached to atoms of carbon in compounds such as octane can be replaced by other elements, e.g., chlorine, or by radicals, e.g., NO_2 or OH.

REVIEW EXERCISES

1. How are the allotropic forms of carbon alike and how are they different?
2. How could you prove that a sample of graphite is pure carbon? How does a sample of graphite differ from a sample of anthracite coal?
3. How do the different kinds of coal differ? Which kind of coal is best for producing illuminating and fuel gas? Which has the highest and which the lowest heating value?
4. Name four kinds of amorphous carbon.
5. Describe "destructive distillation" as applied to coal and wood.
6. How is graphite prepared? What are four uses of graphite?
7. How is gas carbon made? Lampblack? What are their uses?
8. Why is coal or wood a better fuel than graphite?
9. Describe the action of charcoal in a gas mask.
10. What is a carbide? Give three examples.
11. How is coke produced from coal? Why is more and more coke being produced in "by-product" ovens rather than in "beehive" ovens, although the latter is the cheaper process?
12. What is the origin of coal? How do you think the natural forms of graphite have been produced?
13. How does coal differ in composition from wood?
14. What properties of carbon are predictable from its position in the periodic table? What other properties can you add to these?
15. How are artificial diamonds produced?
16. What was the approximate volume of the uncut Cullinan diamond?
17. What weight of graphite would occupy approximately the same volume as the Cullinan diamond?
18. What (standard) volume of carbon dioxide is produced when 1 g. of diamond burns? 1 g. of graphite?
19. Why does bituminous coal burn with the formation of so much more smoke than anthracite?

REFERENCES FOR FURTHER READING

Carbon Black and Lampblack: *Chem. and Met. Eng.*, **39**, 380, 449 (1932); *Ind. and Eng. Chem.*,

23, 612, 646 (1931); *J. Chem. Ed.*, **3,** 408 (1926); **13,** 45 (1936).

Charcoal: *Ind. and Eng. Chem.*, **23,** 631 (1931); **32,** 1166 (1940); *Chem. and Met. Eng.*, **32,** 13 (1925); **39,** 534, 604, 664 (1932).

Coal: *Chem. and Met. Eng.*, **34,** 668 (1927); *Fortune*, **3,** 2, 72 (1931); **8,** 4, 60 (1933); *Ind. and Eng. Chem.*, **26,** 164 (1934).

Diamonds: *Science*, **72,** 515 (1930); *Fortune*, **11,** 66, 96 (1935); *J. Chem. Ed.*, **26,** 509 (1949).

Gas Masks: *Chem. and Met. Eng.*, **46,** 136, 143 (1939); *Ind. and Eng. Chem.*, **11**, 93, 281, 402, 1105 (1919).

Graphite: *Chem. and Met. Eng.*, **38,** 282 (1931); *Ind. and Eng. Chem.*, **16,** 971 (1924); *J. Chem. Ed.*, **16,** 413 (1939).

24

THE OXIDES AND OTHER SIMPLE COMPOUNDS OF CARBON

1. Carbon Monoxide

Impure carbon monoxide is produced whenever carbon or carbonaceous materials are burned in a limited supply of air. Thus, every stove or furnace may act as the producer of a mixture of gases containing carbon monoxide, if combustion is not complete. The exhaust from automobile engines always contains this oxide in quantities ranging up to 10 or 12 per cent.

The production of carbon monoxide in an ordinary coal stove or furnace is shown in Figure 190. Air enters the stove at the bottom and, passing through the grate-bars, converts the carbon in the bottom layer (B) of coal into carbon dioxide. The oxygen of the air may be completely consumed by this reaction. In the middle and upper layers (C), where the temperature is higher, carbon dioxide reacts with hot carbon, forming carbon monoxide:

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

Above the coal, the carbon monoxide may burn to form the dioxide, provided an additional supply of air is admitted through the upper damper (D):

$$2\ CO + O_2 \longrightarrow 2\ CO_2.$$

Impure carbon monoxide is produced in the reactions involved in many industrial processes. In the reduction of iron, large quantities of carbon monoxide escape from the top of the furnaces along with carbon dioxide, nitrogen, a little hydrogen, and other gases. This mixture, called *blast-furnace gas*, is used as a cheap but very low-grade fuel. *Water gas* (page 70) contains carbon monoxide and hydrogen. This is an important source of carbon monoxide.

To produce a more nearly pure form of carbon monoxide a mixture of oxygen and pure carbon dioxide is passed over carbon. The carbon dioxide dilutes the oxygen, slows down the reaction,

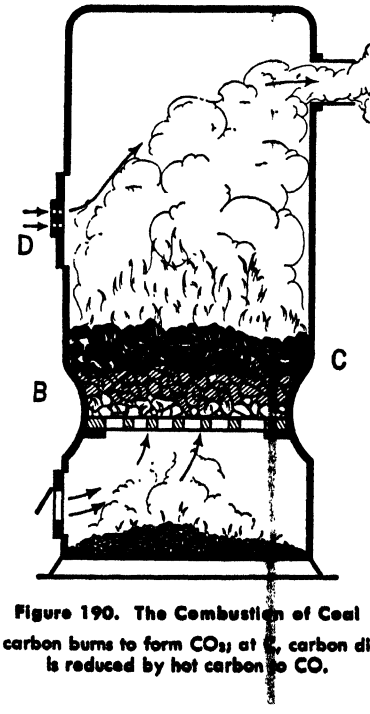


Figure 190. The Combustion of Coal
At B, carbon burns to form CO_2; at C, carbon dioxide is reduced by hot carbon to CO.

$$C + O_2 \longrightarrow CO_2 + 94{,}390 \text{ calories},$$

and consumes some of the energy that it releases, because the reduction of carbon dioxide by carbon is an endothermic reaction:

$$41{,}530 \text{ calories} + C + CO_2 \longrightarrow 2\ CO.$$

Pure carbon monoxide may be produced in the laboratory by heating formic or oxalic acid,

$$\underset{\text{(formic acid)}}{HCOOH} \longrightarrow H_2O + CO$$

$$\underset{\text{(oxalic acid)}}{(COOH)_2} \longrightarrow H_2O + CO_2 + CO,$$

or by treating these acids with concentrated sulfuric acid, which extracts water from them. If present, carbon dioxide can be removed by liquefying it and leaving carbon monoxide still in its gaseous state, or by passing the mixture of the oxides through a solution of sodium hydroxide:

$$2\ (Na^+ + OH^-) + CO_2 \longrightarrow (2\ Na^+ + CO_3^{=}) + H_2O.$$

Carbon monoxide does not react with sodium hydroxide.

2. The Molecular Structure of Carbon Monoxide

The electronic formula of carbon monoxide is usually written as :C:::O:, but there appears to be good evidence that the pairs of electrons may shift from one position to another in the molecule, thus making possible the following formulas:

$$:C \cdot \ddot{O}: \text{ and } :C::\ddot{O}$$

At a given instant, a molecule may have any one of these three arrangements of its electrons, and in a sample of carbon monoxide all three types of molecular structure are present at the same time. This and similar shifting structures are examples of the behavior known as *resonance.*

3. Properties and Uses

Carbon monoxide is a colorless, odorless, and tasteless gas. It dissolves very slightly in water, is slightly lighter than air (density 0.967 compared to the weight of an equal volume of air), and is liquefied with much greater difficulty than carbon dioxide. It condenses at − 190° under a pressure of one atmosphere.

The oxidation number of carbon in carbon monoxide is +2. Since the usual oxidation number of the element is four, carbon monoxide is a *reducing agent* and, at elevated temperatures, combines readily with oxygen. When heated in air, it burns with a characteristic blue flame. This flame is often observed above a red-hot bed of coals.

Formaldehyde and *methyl (wood) alcohol* can be produced from carbon monoxide and hydrogen with the aid of a catalyst and under the proper conditions of temperature and pressure. This oxide of carbon also combines with chlorine to form *phosgene*, $COCl_2$, which is used in the manufacture of dyes and drugs and is one of the poisonous gases that have been used in warfare. Carbon monoxide also unites with some of the metals, forming compounds called *carbonyls*: $Fe(CO)_5$, $Ni(CO)_4$, $Cr(CO)_6$, and $Co(CO)_4$. These compounds are sometimes formed in the purification of certain metals, e.g. nickel.

Carbon monoxide's most important use is as a fuel, usually in such mixtures as water gas, producer gas, and blast-furnace gas. It is an extremely important reducing agent in the metallurgical industries in which the reduction of the oxides of many of the metals, such as iron, copper, and zinc, depends upon its reaction with oxygen of the oxides, thus freeing the metals.

4. Poisoning by Carbon Monoxide

Carbon monoxide is the most common poisonous gas. Constant care must be exercised in many peacetime activities, against the dangers of this odorless and therefore treacherous poison. The ordinary automobile engine, while idling, or when being warmed-up, will produce a dangerous proportion of carbon monoxide in a small closed garage in three minutes. Explosions in coal mines and those resulting from the combustion of

finely divided carbonaceous materials, such as coal or flour, always result in the formation of some carbon monoxide. The Bureau of Mines has shown that not more than one part of carbon monoxide should be present in 2500 parts of air. A person exposed to air containing one part of the monoxide in 500–750 parts of air for a period of an hour is in grave danger, while greater concentrations are fatal in a few minutes.

The poisonous effect of carbon monoxide results from its combination with the hemoglobin, or red coloring matter, of the blood. The function of *hemoglobin* is the transportation of oxygen from the lungs to the various parts of the body, where it is used in oxidation. To perform this function, the hemoglobin forms a relatively unstable compound with oxygen. This compound, called oxyhemoglobin, is responsible for the red color of arterial blood. Carbon monoxide also combines with hemoglobin, and since it combines much more readily than oxygen, its presence in inhaled air causes a decrease in the amount of oxyhemoglobin that the blood can form. The compound of the monoxide is moderately stable, and the hemoglobin that combines with it is not released very readily. Death results when the blood loses its ability to absorb and transport an adequate supply of oxygen.

CARBON DIOXIDE

5. Laboratory Preparation

Small samples of carbon dioxide are usually prepared by the action of hydrochloric acid upon calcium carbonate, $CaCO_3$. Limestone or marble, which are natural forms of calcium carbonate, are used. The generator used for the preparation may be one of the Kipp variety (Figure 54) or one made from a bottle and a thistle tube (Figure 53). The dioxide is not very soluble in water and escapes through the delivery tube into the receiver, where it may be collected by the upward displacement of air. It may also be collected over water with some loss.

$$CaCO_3 + 2\,(H^+ + Cl^-) \longrightarrow (Ca^{++} + 2\,Cl^-) + H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2 \uparrow .$$

6. Commercial Production

In this country, some of the carbon dioxide that is used for commercial purposes is produced by the combustion of coke, coal or gaseous fuels. The gases that escape from a coal-burning furnace contain nitrogen, carbon monoxide, steam, and many other substances in addition to carbon dioxide. To remove the carbon dioxide the gases are passed, under increased pressure, through a tower filled with coke which is sprayed with a solution of potassium carbonate. The carbon dioxide dissolves in water, forming carbonic acid, which then reacts with the potassium carbonate to form potassium bicarbonate:

$$(2\,K^+ + CO_3^=) + H_2CO_3 \longrightarrow 2\,(K^+ + HCO_3^-).$$

The resulting solution is removed to another container, in which it is heated, usually, under reduced pressure. Here the reactions proceed in the opposite direction:

$$2\,(K^+ + HCO_3^-) \longrightarrow (2\,K^+ + CO_3^=) + H_2CO_3,$$
$$H_2CO_3 \longrightarrow H_2O + CO_2 \uparrow .$$

Potassium carbonate is formed and may be used over again. Fairly pure carbon dioxide is obtained and compressed in steel cylinders.

Carbon dioxide is produced as a by-product of several industries: (1) The production of lime from limestone:

$$CaCO_3 \longrightarrow CaO + CO_2.$$

(2) The alcohol industry in which glucose (a sugar) and other substances are converted by fermentation into ethyl alcohol:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2.$$

This industry is the source of a very pure supply of carbon dioxide.

(3) Metallurgical operations in which the reducing action of carbon upon the oxides of certain metals produces large amounts of carbon dioxide.

(4) The production of hydrogen from water gas (page 70) in which carbon monoxide is converted

into carbon dioxide, which is recovered by dissolving it in cold water under pressure.

7. Physical Properties

Carbon dioxide is a colorless, odorless gas. At 15° and under one atmosphere of pressure, one liter of water dissolves about one liter of the gas. The solubility is greater than might normally be expected because carbon dioxide reacts with water to form carbonic acid. *Soda water* is a solution under a pressure of 3 to 4 atmospheres. The gas is about 1.53 times as heavy as air, and at 0° and 760 mm. one liter weighs 1.977 g. The critical temperature is 31.4°, and, therefore, carbon dioxide can be liquefied at room temperature by increasing the pressure. At 20° it is liquefied by a pressure of about 56 atmospheres. The liquid solidifies to form a white solid at − 79°. The solid changes directly into the gaseous state at ordinary pressure. The carbon dioxide sold in steel cylinders is in the liquid state.

8. Its Solid State

Solid carbon dioxide — carbon dioxide snow — is now used as a refrigerant under the trade name of *Dry Ice*. Since it changes directly to a gas, Dry Ice has certain advantages as a refrigerant over ordinary ice, which melts to form water that must be disposed of. Small paper cartons may be used, therefore, instead of the heavy containers used for ice, and its use does not require salt and sawdust. Lower temperatures can also be attained by using smaller volumes and weights of this refrigerant

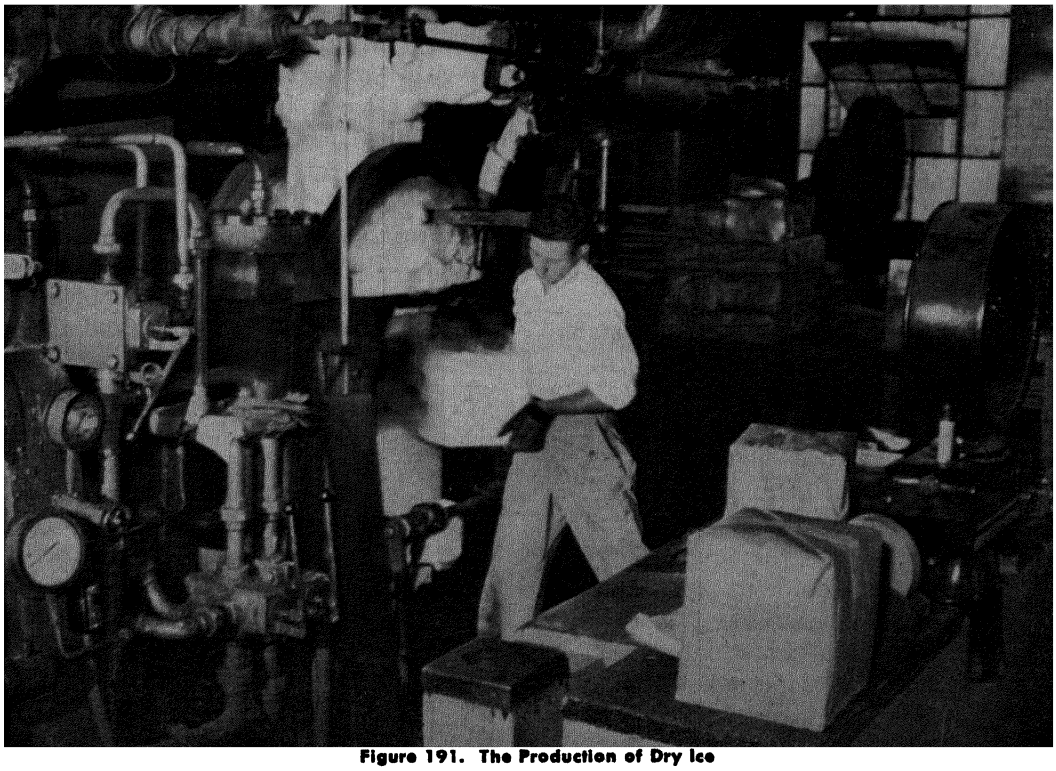


Figure 191. The Production of Dry Ice

In this plant Dry Ice is produced as a by-product of the manufacture of alcohol.
(Courtesy of Monsanto Chemical Co.)

than would be necessary if ice were used. The evaporation of carbon dioxide requires heat, and the removal of this heat from the surroundings is responsible for the refrigerating action. Dry Ice is extensively used for the refrigeration of fruit, meat, and fish, ice cream, and other foods.

9. Chemical Properties

Carbon dioxide is reduced at high temperatures by a few vigorous reducing agents such as sodium and magnesium. An ignited strip of magnesium ribbon will continue to burn in an atmosphere of carbon dioxide and will even reduce the solid:

$$2\ Mg + CO_2 \longrightarrow 2\ MgO + C.$$

The most familiar reducing agent for carbon dioxide is carbon:

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

This reduction occurs whenever carbon dioxide (in the absence of oxygen) passes over hot carbon (page 300) at about 1000°.

The aqueous solution of the dioxide contains carbonic acid, H_2CO_3, which is produced by the reaction:

$$H_2O + CO_2 \longrightarrow H_2CO_3.$$

10. Carbonic Acid and the Carbonates

Carbonic acid, H_2CO_3, is an unstable compound. The solution formed by bubbling carbon dioxide into cold water, at one atmosphere of pressure, contains a relatively small amount of the acid, but larger amounts are formed if the gas is dissolved in the liquid under high pressures. The aqueous solution has the properties of a *very weak acid* as shown by a comparison with hydrochloric, sulfuric, and even acetic, a relatively weak acid found in vinegar.

The reaction of carbonic acid with a base, such as sodium hydroxide, may produce sodium carbonate or sodium bicarbonate, depending upon the relative amounts of sodium hydroxide and acid available for the reaction. In the presence of a sufficient quantity of NaOH, sodium carbonate is produced:

$$2\ (Na^+ + OH^-) + H_2CO_3 \longrightarrow (2\ Na^+ + CO_3^{=}) + 2\ H_2O.$$

When an excess of carbon dioxide is passed into the solution, sodium bicarbonate is produced:

$$(2\ Na^+ + CO_3^{=}) + H_2CO_3 \longrightarrow 2\ (Na^+ + HCO_3^-).$$

Since the molecule of carbonic acid contains two replaceable atoms of hydrogen, or two atoms that it can release as protons, this substance is a *dibasic acid*, i.e., two gram-molecular (or formula) weights of sodium hydroxide are required to react with one gram-molecular weight of the acid. When carbon dioxide is bubbled into a solution of lime water ($Ca(OH)_2$), carbonic acid and calcium hydroxide react to form calcium carbonate, $CaCO_3$, which is only slightly soluble and precipitates. If carbon dioxide is added in excess, this precipitate dissolves, because calcium bicarbonate, $Ca(HCO_3)_2$, is formed. This compound is soluble.

$$CaCO_3 + H_2CO_3 \longrightarrow (Ca^{++} + 2\ HCO_3^-).$$

These reactions are used as a test for carbon dioxide. Barium hydroxide ($Ba(OH)_2$) is sometimes used in place of calcium hydroxide, because it is more soluble, and a more concentrated solution can be prepared.

Ground water contains small amounts of carbonic acid. When it comes into contact with limestone, $CaCO_3$, in the earth, calcium bicarbonate is produced and, since it is relatively soluble, is carried away in solution. This action is one of the ways in which caves are produced in limestone. It also explains the formation of hard water (page 186) which contains calcium bicarbonate in solution. When this water is boiled, the bicarbonate is converted into calcium carbonate and carbon dioxide is released:

$$(Ca^{++} + 2\ HCO_3^-) \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow.$$

Since the calcium ions are removed as the slightly soluble calcium carbonate, hard water of this kind can be softened by boiling.

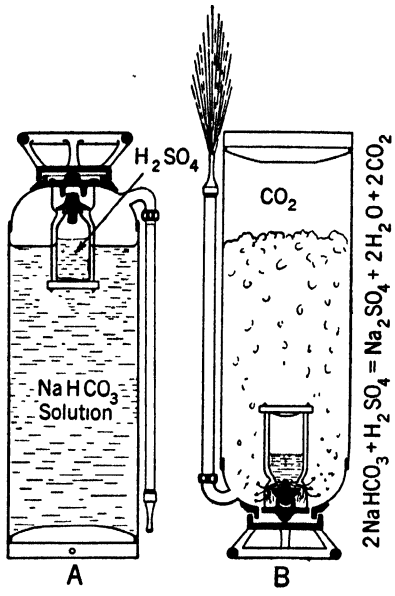


Figure 192. Fire Extinguisher

11. Uses of Carbon Dioxide

Many thousands of tons are used annually in this country in producing carbonated water and soft drinks, which are solutions of carbon dioxide or carbonic acid, various flavors, sugar, and sometimes other acids such as citric or phosphoric.

Carbon dioxide is also used to extinguish fires. One of the familiar types of fire extinguishers (Figure 192) contains a solution of sodium bicarbonate. A bottle containing sulfuric acid is held in place near the top. Until required for use the container is kept in an upright position. To use it the cylinder is inverted, and the stopper then drops out of the bottle containing the acid. The following reaction takes place:

$$2\,(Na^+ + HCO_3^-) + (2\,H^+ + SO_4^{=}) \longrightarrow (2\,Na^+ + SO_4^{=}) + 2\,H_2O + 2\,CO_2\uparrow .$$

Considerable pressure develops in the container, and the solution becomes saturated with the dioxide. The pressure forces the solution out through the nozzle. The carbon dioxide accompanying the stream of solution, and escaping from it as the pressure is reduced, helps to extinguish the fire, because it excludes the air and thus prevents the continuation of combustion.

Another type of extinguisher now widely used produces a stream of foam, called "Firefoam" or "Foamite." Carbon dixoide is the gas of which the foam is composed. An inner container of the extinguisher contains a solution of alum or aluminum sulfate, and an outer cylinder contains a solution of sodium bicarbonate and licorice. The aluminum sulfate reacts with water to form sulfuric acid and aluminum hydroxide:



A B

Figure 193. The Use of Firefoam

A. Burning oil. B. After the use of Firefoam.

$$(2\ Al^{+++} + 3\ SO_4^{=}) + 6\ HOH \longrightarrow 2\ Al(OH)_3\downarrow + 3(2\ H^+ + SO_4^{=}).$$

The aluminum hydroxide, or hydrous aluminum oxide, forms a gelatinous precipitate. When the cylinder is inverted, the solutions are mixed, and the acid reacts with sodium bicarbonate, liberating carbon dioxide. The carbon dioxide and the aluminum hydroxide produced by these reactions form a froth, or foam, which is stabilized — made to remain a foam longer — by *licorice*. The pressure produced by the carbon dioxide forces the mixture out of the container. This extinguisher is especially useful in fighting oil-fires. Such fires are not easily extinguished with water, because the fire is largely in the vapors above the surface of the oil. The water sinks, floating the oil on top of it. The foam, on the other hand, flows over the surface of the oil, effectively blanketing it. Because of the stable nature of the foam, the carbon dioxide is not carried away from the fire immediately by convection currents. Cylinders of liquid carbon dioxide are also used as fire extinguishers.

Carbon dioxide is used extensively in the manufacture of sodium bicarbonate (baking soda, $NaHCO_3$). It is also used in the manufacture of white lead, which is an important constituent of many paints.

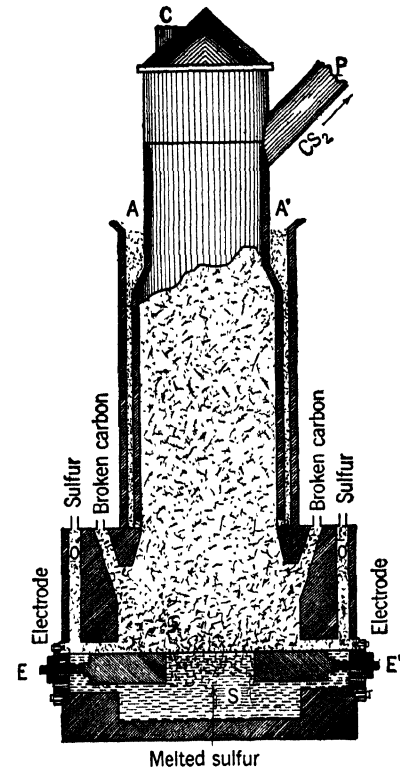


Figure 194. Production of Carbon Disulfide in the Electric Furnace

Charcoal is fed in at C and sulfur at A and O.

12. Carbon Disulfide

Carbon disulfide, CS_2, is produced in an electric furnace of the type shown in Figure 194. Sulfur and coke are fed into the furnace continuously. The sulfur is vaporized, and the carbon is heated to the required temperature by the heat liberated when the electric current flows between the two electrodes. The disulfide is volatile and distills as rapidly as it is formed. The vapor is passed from the top of the furnace into a condenser in which it is converted into the liquid state.

Carbon disulfide has a yellow color, that is usually caused by dissolved sulfur, and an unpleasant odor, which is not that of carbon disulfide but of traces of impurities. It is about one and one-fourth times as heavy as water. It does not mix with water, has a high index of refraction, and has a boiling point of 46° C. at 760 mm.

Carbon disulfide is used commercially as a solvent for rubber, phosphorus, sulfur, and fats. The sulfur solution finds some use as a medium for the vulcanization of rubber. Carbon disulfide is also used as a solvent for resins in the manufacture of varnishes and lacquers. It is one of the essential substances in the manufacture of cellophane and rayon. The heavy, poisonous vapor is used to kill weevil in grain and to kill moths, mice, rats, woodchucks, and other small animal pests. Since it is a solvent for fat and grease, it might be used as a dry-cleaning agent, if it were not poisonous and inflammable.

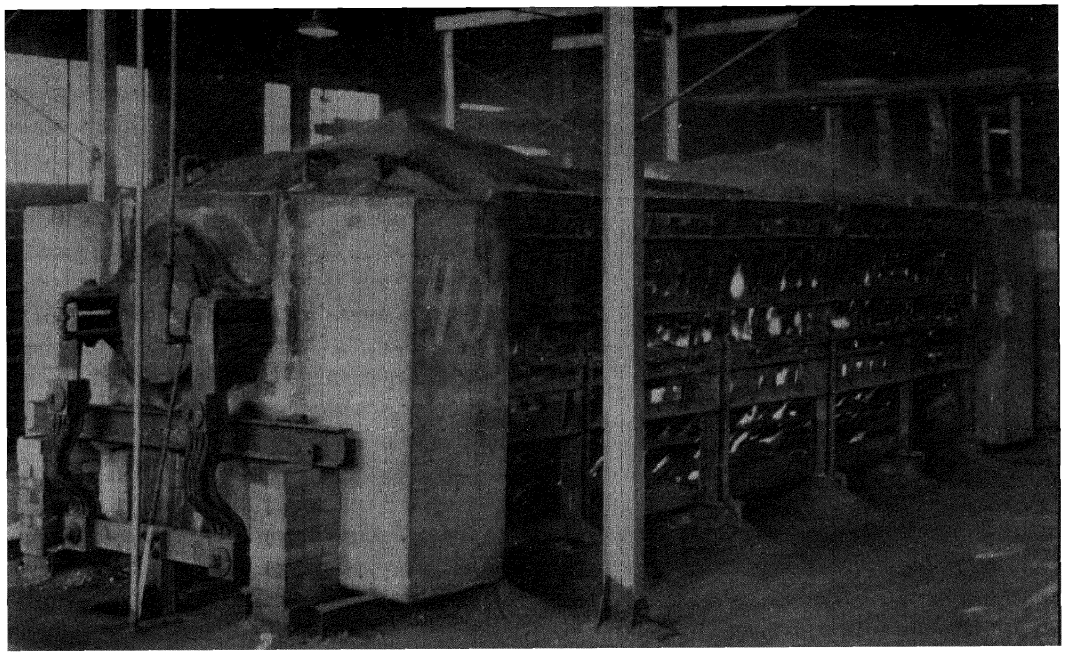


Figure 195. Resistance Type of Electric Furnace in Which Sand and Coke Are Converted Into Silicon Carbide

13. Carbon Tetrachloride

This substance is produced by treating carbon disulfide with dry chlorine:

$$CS_2 + 3\ Cl_2 \longrightarrow CCl_4 + S_2Cl_2.$$

Iodine is used as a catalyst of this reaction. The two products of the reaction can be separated by fractional distillation, since they boil at widely different temperatures.

The vapor of carbon tetrachloride is considerably heavier than air and is not combustible. For these reasons, and also because the liquid is readily volatile, carbon tetrachloride, usually mixed with other substances, is a very efficient fire extinguisher. A mixture of carbon tetrachloride and certain organic solvents is used for dry-cleaning, a use which depends upon carbon tetrachloride's properties as a solvent for grease and oils and upon the fact that it is safe, because it is not combustible.

Carbon tetrachloride is also used as a solvent for grease in cleaning wool, and as a solvent for vegetable oils in the extraction of oils from crushed seeds of various kinds. The tetrachloride is recovered by distillation, and the last traces of it are removed by blowing steam through the oil. Carbon tetrachloride has a limited use in medicine in the destruction of intestinal parasites, such as hookworm. It is also used as a fumigant to kill insects.

14. Silicon Carbide

When a mixture of sand (silica, SiO_2) and powdered coke is heated to a temperature of about 3000°, silicon carbide, SiC, is produced:

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

Silicon carbide is made in an electric furnace (Figure 195), which is built up of fire brick each time it is used. The charge consists of a mixture of powdered coke, sand, sawdust, and salt. The sawdust makes a more porous mass and aids in the escape of carbon monoxide. The salt aids in the removal of iron by forming the volatile chlo-

ride. A cross-section of the furnace and its charge is shown in Figure 196. A core of carbon (graphite) serves as a conductor. The resistance encountered by the current causes the liberation of heat and the central portion of the charge becomes white hot. The portion of the charge next to the core is converted into silicon carbide crystals.

Silicon carbide is used principally for grinding-stones, polishing powders, and other forms of abrasives. It will scratch glass and is almost as hard as diamond. Carborundum is one trade name for it.

15. Carbides of Metals

Several metals form binary compounds with carbon. One of the most important of these compounds is calcium carbide, CaC_2. It is produced by heating a mixture of lime and coke in an electric furnace:

$$CaO + 3\,C \longrightarrow CaC_2 + CO.$$

The carbide melts and flows out through an opening in the bottom of the furnace.

Calcium carbide reacts with water to form calcium hydroxide and the combustible gas, acetylene (C_2H_2), which is an important starting material in the synthesis of several organic compounds:

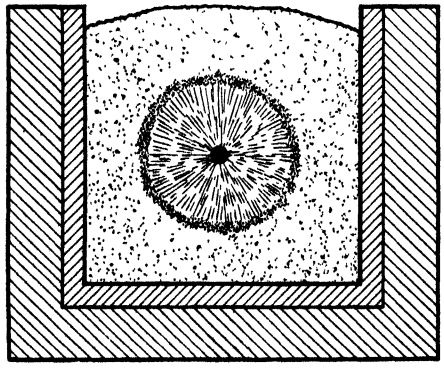


Figure 196. Cross Section of a Silicon Carbide Furnace

The carbon core is surrounded by crystals of silicon carbide.

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 \downarrow + C_2H_2 \uparrow.$$

Calcium carbide also reacts with nitrogen under certain conditions to form calcium cyanamide, $CaCN_2$. This substance is used in the manufacture of fertilizers. It may also be made to react with steam to form ammonia, and with sodium chloride or with sodium carbonate and carbon, to form sodium cyanide, NaCN.

Other metallic carbides include Al_4C_3, Fe_3C, W_2C, B_4C, TiC, and TaC. Some of the latter, notably W_2C, are very hard and are used as abrasives in cutting-tools.

REVIEW EXERCISES

1. How is carbon monoxide produced in a stove or furnace?
2. How would you determine whether a sample of gas is carbon monoxide or carbon dioxide?
3. Why is carbonic acid called a dibasic acid?
4. What volume of carbon dioxide, at 20° and 760 mm., can be produced (1) by heating 100 g. of $CaCO_3$, (2) by the fermentation of 100 g. of glucose, (3) by burning 100 g. of carbon, and (4) by heating 100 g. of sodium bicarbonate?
5. What are the names and some of the uses of each of the following carbon compounds: $NaHCO_3$, $CaCO_3$, $CaCN_2$, Na_2CO_3, C_2H_2, SiC, CCl_4, $COCl_2$, HCOOH, and CaC_2.
6. Suggest one reason why carbon forms more compounds than any other element.
7. What weight of calcium carbonate could be converted into calcium bicarbonate by 10 liters (standard conditions) of carbon dioxide, assuming that 10 per cent of the carbon dioxide is not used in the reaction?
8. What weight of calcium carbonate is precipitated (0.0013 g. dissolves in 100 cc. at 18°) when one liter of carbon dixoide (at 0° and 760 mm.) is completely absorbed in one liter of a solution containing an excess of calcium hydroxide?
9. What volume of carbon dioxide and water vapor at 100° and 760 mm. would be produced by the complete combustion of the acetylene which is made when 5 g. of calcium carbide reacts with an excess of water?

10. Why is carbon dioxide absorbed to a greater extent by a solution of sodium carbonate than by pure water?
11. Identify: Water gas, blast furnace gas, nickel carbonyl, phosgene, Dry Ice, soda water, dolomite, and Firefoam.
12. What are the sources or methods of producing (1) carbon monoxide and (2) carbon dioxide for commercial uses?
13. How can carbon dioxide be separated from carbon monoxide?
14. Account for the poisonous effect of carbon monoxide. Why should carbon dioxide not be expected to have the same effect?
15. How are the caves that are found in beds of limestone produced?
16. How can calcium bicarbonate be changed into calcium carbonate? What is one application of this reaction?
17. Account for the action of carbon dioxide in extinguishing fires, and as a leavening agent in baking.
18. How are the following compounds produced? CS_2, CaC_2, SiC, CCl_4.
19. A fire extinguisher contains 25 liters of a solution in which there is 10 g. of sodium bicarbonate per 100 ml. of solution. What (standard) volume of carbon dioxide can be produced from the contents of the extinguisher?
20. Carbon disulfide burns to form carbon dioxide and sulfur dioxide, SO_2. What (standard) volume of oxygen is required for the combustion of one gram-molecular weight of carbon disulfide?
21. Give what you think may be the electronic formulas for CS_2 and $COCl_2$.
22. Why does carbon dioxide escape from a bottle of soda water when the cap is removed?
23. How does carbon dioxide react with hot carbon, water, calcium hydroxide, burning magnesium, and sodium carbonate?
24. What is the difference in the nature of the reactions and of the bonds formed when CO is converted into $COCl_2$ and when CO_2 forms H_2CO_3?
25. Why should the formula of the chloride of sulfur mentioned on page 307 be written as S_2Cl_2 instead of SCl?

REFERENCES FOR FURTHER READING

Baking Powders: *J. Chem. Ed.*, **3,** 493 (1926); **9,** 1340 (1932).

Carbon Dioxide: *Ind. and Eng. Chem.*, **22,** 140, 437, 1086, 1186 (1930); **24,** 613 (1932); **27,** 1305, 1452 (1935); **29,** 632 (1937); *Chem. and Met. Eng.*, **28,** 5 (1923); **37,** 416 (1930); **38,** 136, 270 (1931); **39,** 433 (1932); **40,** 250 (1933); *J. Chem. Ed.*, **5,** 1321 (1928); **7,** 151, 403, 637 (1930); **9,** 1503, 1523 (1932).

Carbon Disulfide: *J. Chem. Ed.*, **8,** 867 (1931).

Carbon Monoxide: *Ind. and Eng. Chem.*, **20,** 564 (1928); **21,** 389 (1929); **22,** 1096 (1930); **29,** 495 (1937); *Chem. and Met. Eng.*, **30,** 824 (1924); **43,** 590 (1936).

Carbon Tetrachloride: *Chem. and Met. Eng.*, **43,** 313 (1936).

Dry Ice: *J. Chem. Ed.*, **22,** 1087 (1930); **24,** 615 (1932).

Fire Extinguishers: *J. Chem. Ed.*, **9,** 1503 (1932)

Silicon Carbide: *Chem. and Met. Eng.*, **31,** 501 (1924); *Ind. and Eng. Chem.*, **19,** 1127 (1927).

25

CHEMICAL EQUILIBRIUM

1. Introduction

We have frequently employed the general principle of equilibrium in describing the final condition that is reached when two changes operating in opposite directions occur simultaneously. Most of our examples of equilibrium, however, have dealt with physical rather than chemical changes. We have defined a saturated solution, for example, as one which is in equilibrium with the undissolved solute. Chemical equilibrium is like physical equilibrium in that the two changes must finally occur at the same speed. The principal difference is that in chemical equilibrium the changes produce different substances.

2. The Importance of Information Concerning Equilibrium Conditions

When we use a reaction, we usually desire to produce as much of the products from the starting materials as possible, and ideally the yield should be 100 per cent. It is evident, however, that the yield actually obtained is limited by the equilibrium conditions of the reaction. Thus, the reaction

$$\text{Heat} + 2\,H_2O \rightleftarrows 2\,H_2 + O_2,$$

is apparently complete toward the *left* at ordinary temperatures, although theoretically at least, it is reversible at all temperatures. At 2000° C., equilibrium is reached when about 2 per cent of the water has decomposed into hydrogen and oxygen. Knowing the equilibrium conditions of this reaction, we should not select this as a method of producing hydrogen and oxygen.

The equilibrium state of a given reaction is not the same under all conditions. The decomposition of water in a closed vessel reaches equilibrium at 2000° when about 2 per cent has decomposed, but at 1000° only about 0.01 per cent decomposes before the equilibrium is attained. A knowledge of the equilibrium states of a reaction under different conditions is, therefore, of great importance in many cases, because it is possible to produce larger quantities of the products of the reaction by proper selection of conditions.

The effect of a change in the conditions upon the equilibrium depends upon the manner in which the change affects the speeds of the two opposing reactions. It is to this subject, therefore, that we now give our attention.

CONDITIONS THAT AFFECT THE SPEED OF A REACTION

The speed of a reaction is measured by determining the quantities of the reacting materials that are changed into the products in a definite period of time, or by measuring the rate at which the products are formed. Usually, it is sufficient to determine the rate at which one substance —

either a reactant or a product — is consumed or produced. Thus, we might follow the speed of a reaction in which a sample of zinc reacts with hydrochloric acid in several ways: (1) By removing the zinc, drying it, and weighing it at definite intervals; (2) by measuring the volume of hydrogen evolved in different periods of time; or (3) by analyzing samples of the acid to determine the rate at which it is consumed. The speed of a reaction depends upon a number of factors which are discussed in the sections that follow

3. The Nature of the Reacting Substances

The chemical nature of the reacting substances has a great deal to do with the rate at which the reaction proceeds. We explain differences in the tendencies of various substances to react upon the basis of their atomic, ionic, or molecular structures and the changes in energy that accompany their reactions. Thus, sodium reacts more readily with chlorine than iron does, because the sodium atom gives up its valence electron to chlorine more readily. In general, reactions between ions are very rapid and their speeds can be measured only with difficulty, if they can be measured at all. Reactions between molecules in solution are often relatively slow.

4. Effect of Temperature

The effect of changes in temperature upon the speed of chemical reactions has been discussed in a previous chapter (page 63).

To some extent the increase in speed with increasing temperature can be explained by the greater number of collisions between molecules that results from the greater velocity of the molecules at the higher temperatures, but this effect cannot explain all the change in speed. An increase in temperature of 10° does not, by any means, double the number of collisions; and hence, if this were the only factor involved, it should not double the speed of the reaction. Molecules that react must meet — i.e., collide — but mere collision does not always result in a reaction. It is probable that, at a higher temperature, more of the molecules that collide will react, because more of them possess sufficient energy to break the bonds that hold their atoms or radicals together, thus making possible *other* combinations of these same particles. As the temperature rises, more molecules are *activated*, i.e., they possess the energy required to allow them to react when they collide with other molecules. For most reactions it appears, therefore, that a rise in temperature of 10° approximately doubles the speed, because this change in temperature doubles, approximately, the number of activated molecules.

5. The Effect of Catalysts

The speeds of many reactions are greatly influenced by certain substances called catalysts, which are not permanently affected during the chemical changes. A substance that accelerates a reaction is usually referred to as a catalyst, while one that retards a reaction is called a retarder, inhibitor, anti-oxidant, etc. Catalysts are often employed to modify the speed of a reaction instead of increasing the temperature. The latter may not only be more expensive than a catalyst, but it may be actually undesirable, because many reactions are less complete at high temperatures, and some substances that we may wish to make are decomposed at such temperatures.

A catalyst does not change the equilibrium conditions of a reaction, because it affects equally the speeds of the two opposing reactions. Hence, we cannot increase the quantity of the products that can be made from a definite quantity of the starting materials, but we can decrease the time required to produce this same quantity, at constant temperature, by the use of a suitable catalyst.

6. How Catalysts Affect the Velocities of Reactions

The actions of catalytic agents in some reactions have not yet been fully explained. In some cases, fairly satisfactory theories have been advanced.

(1) If the catalyst and the reactants are in the same physical state, the effect of the catalyst is called *homogeneous catalysis*. In most reactions of this kind the catalyst accelerates the reaction by forming an intermediate compound. If C is the catalyst and A and B are the reacting substances, the mechanism of the reaction may be explained by the following equations. The reactions are assumed to occur in the order indicated.

$$(1)\ A + C \longrightarrow AC.$$
$$(2)\ AC + B \longrightarrow AB + C.$$

The speed with which the product AB is formed will be increased if the speed of the two reactions is greater than the speed of the simple reaction:

$$A + B \longrightarrow AB.$$

The substance designated as C acts as a catalyst, therefore, by making possible certain intermediate reactions, which take place with a greater velocity, but which lead to the formation of the same product as the simple, uncatalyzed reaction. Although C takes part in the reaction, it is not converted ultimately into any new substance.

(2) The oxidation of alcohol may be catalyzed by the mere presence of a piece of platinum foil or wire. We assume that this reaction is catalyzed on the surface of the catalyst. Similar action is observed when a mixture of hydrogen and oxygen is exploded at ordinary temperature by finely divided platinum; and when ammonia is oxidized to nitric acid in the presence of a platinum foil or gauze. Substances that influence the speeds of reactions in this manner are said to act as *contact* catalysts, and, since catalyst and reactants are in different physical states, we may speak of the action as non-homogeneous or *heterogeneous* catalysis. In the action of these substances, it is probable that the catalytic effect is due to increases in the concentrations of the reacting substances. The concentrations are increased because the catalyst adsorbs the reacting substances upon its surface.

Adsorption by the catalyst may depend upon the irregular arrangement of atoms upon its surface; Figure 197 shows the condition of the surface of a crystal of nickel. If we could examine the surface of such a crystal, we would find, probably, that it is not smooth, but that it consists of numerous "hills" and "valleys" because of the irregular spacing of its surface atoms. This irregularity of surface would not be noticeable for a highly polished metal plate, but it would be pronounced for the finely divided, or grovular, state of the metal. The atoms in the body of the crystal are attracted equally in all directions, but the atoms on the surface, especially those in the "valleys" and along the sides of the "hills," exert attractions by means of which they may be able to hold the reacting particles — atoms, molecules, or ions — in much the same manner as they attract atoms of their own kind. In some instances, the attraction may be sufficiently great to split molecules, such as O_2 and H_2, allowing single atoms of the elements to be adsorbed. If this happens, the subsequent reaction that occurs between *atoms* of hydrogen and oxygen might be expected to occur more rapidly than the reaction between undissociated molecules of the two elements. Furthermore, the speed of the reaction should also be increased, because the adsorption of the two elements amounts

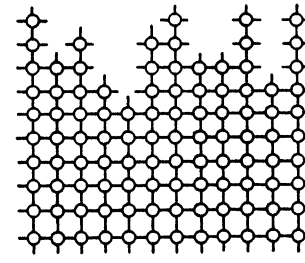


Figure 197. The Surface of a Crystal of Nickel

to an increase in their concentrations; more of the molecules — or atoms — are crowded into a small space on the surface of the crystal than are present in the same space when it is occupied by the two gases under normal conditions.

7. The Effect of Concentration

Reactions occur between particles — atoms, molecules, or ions — and the speed of a reaction depends to some extent upon the number of collisions occurring between particles of different kinds in a definite period of time. The number of collisions depends, in turn, upon the number of particles of each kind in a given volume and upon their velocities. The greater the number of ions or molecules within a given space, the greater will be the speed of the reaction, at constant temperature. For gases, the concentration increases with the partial pressures of the reactants; and hence, actions involving gases occur more rapidly under increased pressure. It is for this reason that pure oxygen reacts more vigorously than air under the same pressure; only about one fifth of the air consists of the active element, and its partial pressure is one fifth of the total pressure.

8. The Law of Mass Action

The effect of concentration upon the speed of a reaction was stated by Guldberg and Waage, in 1867, as a general principle now called the Law of Mass Action: *The speed of a reaction is proportional to the molecular concentration of each of the substances taking part in the reaction.* Concentration is usually expressed as the number of gram-molecular weights of each reacting substance per liter.

9. A Mathematical Statement of the Law of Mass Action

Let us consider the reaction of hydrogen and iodine vapor to form hydrogen iodide. At a sufficiently high temperature, all the substances involved can be studied in their gaseous states.

$$H_2 + I_2 \rightleftarrows 2\,HI.$$

Although the reaction is reversible, we shall speak, for the present only, of the forward reaction. The speed of the reaction at a constant temperature, is proportional to the number of hydrogen molecules in a definite volume, let us say in one liter; it is also proportional to the number of iodine molecules in the same volume. Now the number of molecules of each substance per liter is usually expressed in terms of the number of gram-molecular weights, or moles, of each substance per liter. This is the concentration of the substance. Let us represent the concentration of hydrogen as $[H_2]$ and that of iodine as $[I_2]$. Since the speed of the reaction is proportional to each of these quantities, it is also proportional to their product, $[H_2] \times [I_2]$, as long as conditions other than concentration are not changed.

Let us represent the speed of the reaction between hydrogen and iodine, when the concentration of each of the reactants is one gram-molecular weight, or one mole, per liter, by the symbol K, which is called the *velocity constant* of the reaction at the given temperature. If $[H_2]$ and $[I_2]$ are each equal to one gram-molecular weight per liter,

$$S = K \times 1 \times 1 = K.$$

For other concentrations of hydrogen and iodine, the speed of the reaction is given by the equation:

$$S = K \times [H_2] \times [I_2].$$

Thus, the speed when $[H_2] = 2$ and $[I_2] = 3$ g. mol. wts. per liter is

$$S = K \times 2 \times 3 = 6\,K,$$

or six times the speed in the first case (Figure 198).

The increase in speed with increase in concentration can be understood with the help of Figure 198, in which we represent concentration by the

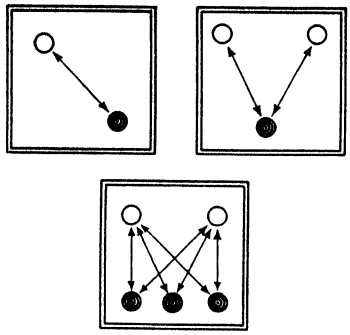


Figure 198. The Effects Produced Upon the Speed of a Reaction by Changes in Concentration

number of molecules in a definite volume; there are two molecules of hydrogen in the second reaction for each molecule in the first. If the number of molecules of iodine remains unchanged, the number of chances that a hydrogen molecule will meet an iodine molecule and that the reaction producing hydrogen iodide will occur is twice as great as the number of chances that these events will occur when the concentration of hydrogen is 1. If the number of molecules of iodine per unit of volume is trebled, when the number of hydrogen molecules is doubled, the number of chances that one molecule of hydrogen will meet and react with one molecule of iodine is six times as great as it is when $[H_2]$ and $[I_2]$ are each 1.

10. Reactions Involving More than One Molecule of a Reactant

If more than one molecule of a substance, as indicated by the equation, takes part in a reaction, *the concentration of that substance must be used as many times in the mass action equation as there are molecules of the substance in the balanced equation for the reaction.* Let us consider as an example the following reaction:

$$2\ NO + O_2 \rightleftarrows 2\ NO_2.$$

This reaction requires that two molecules of nitric oxide react with one of oxygen. Hence, the speed of the reaction is not proportional simply to the product $[NO] \times [O_2]$ but to the product, $[NO] \times [NO] \times [O_2]$, and the equation for the speed is

$$S = K \times [NO]^2 \times [O_2].$$

EQUILIBRIUM

11. Reversible Reactions

There are some reactions that appear to be *irreversible*, i.e., the products of the reaction cannot be made to form the original substances under any conditions now known. Thus, potassium chlorate, when heated sufficiently, decomposes to form potassium chloride and oxygen, but these two substances will not noticeably, under any known conditions, react to form potassium chlorate. This does not preclude the possibility, however, that such a reaction, under proper conditions, might occur. We are now concerned with reactions that are clearly *reversible* under conditions that can be provided. The products of these reactions do react to form the original substances. Unless disturbed by the removal of one or more of the substances involved, such reactions reach a state of equilibrium, at which time the two reactions, forward and reverse, occur at the same speed.

12. The Equilibrium Constant

Let us now consider a reaction in which molecules of substance A change into molecules of substance B. We shall think of the reaction as reversible, i.e., molecules of B also change into molecules of A.

$$A \rightleftarrows B.$$

We assume that one molecule of A produces one molecule of B. The speed (S_1) of the forward reaction, at equilibrium, is expressed as

$$S_1 = [A] \times K_1,$$

where $[A]$ is the molecular concentration of A, and K_1 is the velocity constant which expresses the rate at which A changes into B when $[A]$ is one mole per liter, and temperature is constant.

The speed (S_2) of the reverse reaction at equilibrium is expressed as

$$S_2 = [B] \times K_2,$$

where K_2 is the velocity constant of this reaction and is different, of course, from K_1. We understand that $[A]$ and $[B]$ represent the concentrations of A and B *at equilibrium*; $[A]$ does not represent the concentration of A at the beginning of the reaction.

At equilibrium,

$$S_1 = S_2.$$

Hence, it is also true that,

$$[A] \times K_1 = [B] \times K_2.$$

Dividing each side of this equation by $[A] \times K_2$, we obtain

$$\frac{K_1}{K_2} = \frac{[B].}{[A]}$$

Since K_1 and K_2 are constants, $\frac{K_1}{K_2}$ is also a constant. Hence, we may designate the quotient of one constant by the other as K_e, which we call the *equilibrium constant* of the reaction.

13. The Equilibrium Equation for the Reaction $A + B \rightleftarrows C + D$

Let us now consider the equation for the equilibrium constant of a reaction in which two substances, A and B, change into two other substances, C and D. If these symbols, which we have adopted for a perfectly general case, appear meaningless, the student may think of the reaction,

$$\begin{array}{ccccccc} \text{Ethyl Alcohol} & + & \text{Acetic acid} & \longrightarrow & \text{Water} & + & \text{Ethyl acetate} \\ C_2H_5OH & + & HC_2H_3O_2 & \longrightarrow & HOH & + & C_2H_5C_2H_3O_2. \\ A & + & B & \longrightarrow & C & + & D \end{array}$$

as a specific example. We may write the equations for the speeds S_1 of the forward reaction and S_2 of the reverse reaction, at equilibrium, as

$$S_1 = [A] \times [B] \times K_1.$$
$$S_2 = [C] \times [D] \times K_2.$$

At equilibrium, $S_1 = S_2$.
Hence,

$$[A] \times [B] \times K_1 = [C] \times [D] \times K_2.$$

Dividing each side of this equation by

$$[A] \times [B] \times K_2,$$

we obtain:

$$\frac{K_1}{K_2} = \frac{[C] \times [D]}{[A] \times [B]} = K_e.$$

14. An Example of the Equilibrium Constant of a Reaction

The equilibrium constant, K_e, as defined in the above equation is a number which states the value of a ratio. It may be found by analyzing the equilibrium mixture and determining from the results of the analysis the molecular concentrations of A, B, C, and D. Knowing the relative numbers of molecules (as shown by the equation) of the substances involved in the reaction, and knowing the concentrations of A and B in the beginning, it is sufficient to find by analysis the equilibrium concentration of a single substance in the reaction mixture. Thus, if we have three gram-molecular weights of A per liter and two of B in the beginning of the reaction, $A + B \rightleftarrows C + D$, and if we find, when the reaction has reached equilibrium that there has been formed one gram-molecular weight of C per liter, it is easy to see that the *equilibrium concentrations* of the four substances are

$[D]$, 1 gram-molecular weight per liter
$[C]$, 1 " " " " "
$[B]$, 1 " " " " "
$[A]$, 2 " " " " "

since one molecule each of A and B react to form one molecule each of C and D.

Under the conditions which result in this state of equilibrium, the value of K_e is

$$\frac{1 \times 1}{2 \times 1} = K_e = \frac{1}{2} \text{ or } 0.5.$$

15. Meaning of the Equilibrium Constant

Stated in words, the equilibrium equation has the following meaning: When a reversible reaction (of the type $A + B \rightleftarrows C + D$) has reached equilibrium, the ratio of the product of the concentrations of the substances formed to the product of the concentrations of the substances originally

present has a definite numerical value. The value of this ratio is quite independent of the original concentrations of the reacting substances. It is also independent of the effects of any catalysts, since such agents affect the speeds of the forward and the reverse reactions equally. It does vary, however, with the temperature.

The value of K_e for a given reaction is important, because it shows to what extent the reaction may be completed; a large value denotes a reaction that is more complete in the direction of the products, while a small value of K_e shows that the forward reaction occurs only slightly before equilibrium is reached. Information concerning the values of K_e for different temperatures is often of extreme importance. If these values are known, the conditions most favorable to the reaction in which we are interested can be selected.

16. The Equilibrium Equation for the Reaction $2A + B \rightleftarrows C + 3D$

For reactions in which two or more molecules of a given substance are involved, as indicated in the equation, the equilibrium equation takes a slightly different form. For the reaction $2A + B \longrightarrow$, we have shown (page 314) that the speed (S_1) is expressed by the equation:

$$S_1 = [A]^2 \times [B] \times K_1.$$

The speed (S_2) of the reverse reaction $C + 3D \longrightarrow$ is expressed by the equation

$$S_2 = [C] \times [D]^3 \times K_2.$$

Hence, the equilibrium constant for the reaction $A + B \rightleftarrows C + 3D$ is given by the equation:

$$K_e = \frac{[C] \times [D]^3}{[A]^2 \times [B]}.$$

FACTORS THAT DISTURB EQUILIBRIUM

17. The Effect of Changes in Concentration

What is the effect upon a reaction at equilibrium of adding or removing one of the substances that participates in the reaction either as a reactant or as a product? Let us consider that the reaction,

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic acid}}{HC_2H_3O_2} \rightleftarrows \underset{\text{water}}{HOH} + \underset{\text{ethyl acetate}}{C_2H_5C_2H_3O_2},$$

is at equilibrium. The concentrations of the four substances, therefore, are such that the equilibrium equation is satisfied:

$$\frac{[\text{Water}] \times [\text{Ethyl acetate}]}{[\text{Ethyl alcohol}] \times [\text{Acetic acid}]} = K_e.$$

This equilibrium is disturbed if some of the water, for example, is removed from the mixture by adding some substance that will react only with water to form, let us say, a hydrate. When this water is removed, then the ratio of the concentration products will be smaller, for the time at least, than the equilibrium constant (K_e) of this reaction. Hence, the reaction will readjust itself in such a manner that the value of K_e will be restored. To fulfill this requirement, the concentrations of alcohol and acetic acid must become smaller, and those of ethyl acetate and water must increase, until the ratio again has the constant value of K_e. This means, of course, that the *forward reaction* becomes more nearly completed as one of the *products* is removed.

As shown above, it is often possible to convert one substance more nearly completely into the products of a reaction by increasing the concentration of the substance that reacts with it but without increasing its own concentration. In the reaction that we have just considered, for example, more alcohol can be converted into ethyl acetate and water, if a large excess of acetic acid in proportion to the quantity of alcohol is used. This principle is often of great importance and value. Let us assume, for example, that A, in the reaction

$$A + B \rightleftarrows C + D$$

is a very expensive substance, which we must use to produce the two products C and D. Let us assume that B is relatively inexpensive. Without changing other conditions such as temperature, it is possible to convert A into the products more

nearly completely, if we use several times the theoretically required concentration of B, which is one molecule of B for each molecule of A.

18. Le Chatelier's Principle

This principle states that *a reaction, at equilibrium, will adjust itself in such a way as to counteract and relieve the effect of any change, or "stress" which disturbs the equilibrium state.* Thus, a change of concentration of H_2 in the reaction

$$3\ Fe + 4\ H_2O \rightleftarrows Fe_3O_4 + 4\ H_2$$

may be thought of as a 'stress." In overcoming, or counteracting, the effect of this stress the reaction toward the right becomes more nearly complete, if hydrogen is allowed to escape, and the reaction toward the left (the reverse reaction) becomes more nearly complete, if additional hydrogen is added in such a way that the quantity per liter (the concentration) is increased. Stresses are also produced by changes in temperature and, for reactions involving gases, by changes in pressure.

19. Effect of Changes in Pressure upon Equilibrium

In the reaction

$$CaCO_3 \rightleftarrows CaO + CO_2$$

the only gaseous substance participating is carbon dioxide. The concentration of a solid or a pure liquid is proportional to the density, which remains the same, of course, as long as there is any of the substance. Hence, the concentrations of both solids, CaO and $CaCO_3$, in the above reaction can be regarded as constant, and the equilibrium constant for this reaction may be written as

$$[CO_2] = K_c.$$

This equation signifies that the concentration of carbon dioxide in equilibrium with both the carbonate and the oxide, at a given temperature, is constant. But since the concentration of the carbon dioxide is proportional to its pressure, we must conclude that the pressure of carbon dioxide in equilibrium with the two solids is also constant for a definite temperature. If the pressure of the gas were made greater than its constant equilibrium pressure, the reaction would adjust itself to restore equilibrium. This means that the reaction would occur to the left more rapidly than to the right, until only sufficient carbon dioxide remained to establish the pressure and, therefore, the concentration required for equilibrium. This pressure is the same as it was before equilibrium was disturbed and is independent of the total weight of calcium carbonate or calcium oxide involved. Therefore, since $[CO_2] = K_c$, the value of the equilibrium constant is not affected by changes in pressure. It should be noted, however, if the reaction takes place in an open container, that carbon dioxide escapes, and its partial pressure cannot become equal to the equilibrium's dissociation pressure of calcium carbonate. Under such conditions, therefore, the carbonate may be converted completely into the oxide.

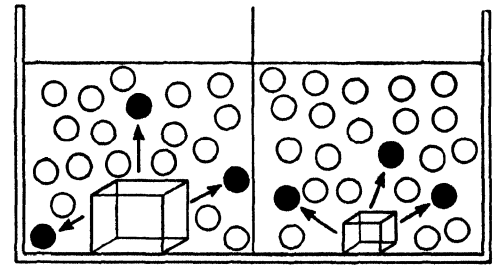


Figure 199

In a reaction involving solids with liquids or gases the concentration of the solid remains constant. As long as any solid exists, its density, or weight per unit of volume, remains constant.

As a general rule, we may say that, for reactions involving gases, an increase in pressure will favor the formation of those substances which are represented in the equation by the smaller total number of molecules of gases. In the decomposition

of calcium carbonate, for example, an increase in the pressure of carbon dioxide favors the formation of calcium carbonate, thus reducing the number of carbon dioxide molecules per unit of volume. The stress produced by the increased pressure is thus relieved in keeping with Le Chatelier's principle, because the increase in pressure is counteracted by a decrease in the number of molecules, a change that *lowers* the pressure.

20. Two Examples of the Effect of Pressure upon Reactions

Let us refer to the reaction by which ammonia is produced from nitrogen and hydrogen:

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

The equation shows that *two* molecules of ammonia are produced from one molecule of nitrogen and three of hydrogen, or from four molecules in all. If a mixture containing these three gases in equilibrium is subjected to an increase in pressure, the reaction toward the right is favored, and the yield of ammonia is increased. This effect is in keeping with Le Chatelier's principle because, if the volume and temperature are unchanged, two molecules of ammonia will exert less pressure than four molecules in all of hydrogen and nitrogen; the only way in which the increase in pressure can be counteracted at constant temperature and volume is by reducing the number of molecules that exert the pressure, and this is the result when nitrogen and hydrogen are converted into ammonia. To produce ammonia by this reaction a relatively high pressure, therefore, is desirable.

In the reaction of carbon monoxide with water vapor,

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

there is no change in the total number of molecules per unit of volume as the reaction occurs — two molecules are produced from two molecules. Hence, changes in pressure have no effect upon this reaction; the yield of hydrogen cannot be increased by either an increase or a decrease of pressure.

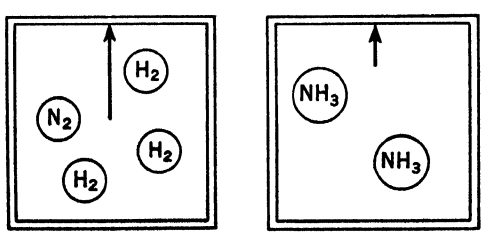


Figure 20. Reduction in Pressure at Constant Volume when Nitrogen and Hydrogen Form Ammonia

21. Effect of Changes in Temperature upon Equilibrium

Heat may be applied in a chemical reaction for two reasons: (1) To raise the temperature in order that the velocity of the reaction may be increased; and (2) to change the equilibrium so that the reaction is more complete in the direction of the substance that we desire to produce.

In considering the desirability of applying heat to raise the temperature, we must bear in mind the effect of the heat added upon the equilibrium conditions of the reaction. The addition of heat constitutes a "stress" in the sense in which that term is used in Le Chatelier's principle. When heat is applied, this means that the equilibrium will be shifted in the direction in which heat is absorbed.

Let us consider again the reaction,

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3 + 24{,}400 \text{ calories.}$$

When two gram-molecular weights of ammonia are produced from nitrogen and hydrogen, 24,400 calories of heat are liberated. A like quantity of heat is absorbed when the reverse reaction takes place. If heat is added from an outside source, the reaction that absorbs heat will be favored. If the reaction is carried out under conditions in which heat is removed, the temperature will be kept at a lower value, and the reaction that evolves heat will be favored. Since the addition or removal of heat results in a change in temperature, and since this change almost never is likely to cause the same change in the speeds of the forward and reverse reactions, the equilibrium constant has a different value for each temperature. To produce ammonia by

this reaction it is evident that a low temperature is desirable.

On the other hand, a high temperature is favorable to the conversion of steam and coke into carbon monoxide and hydrogen:

$$H_2O + C \rightleftarrows CO + H_2 - 28{,}500 \text{ calories.}$$

REVIEW EXERCISES

1. Why do some chemical changes appear to stop long before the quantities of substances added in the beginning are consumed?
2. What factors or conditions determine the equilibrium state of a reaction?
3. Would the search for a catalyst to accelerate the decomposition of water into hydrogen and oxygen at 20° be worth while? Explain.
4. Why does the reaction of hydrogen and oxygen at temperatures below 1000° appear to be irreversible? What evidence is there that this reaction is reversible?
5. The compound called zeolite, NaH_6AlSiO_7, is used to soften water. When hard water flows through a layer of this material, the sodium is replaced by calcium and $Ca(H_6AlSiO_7)_2$ is formed, the sodium ion remaining in solution. To restore the zeolite to its former condition, so that it may be used again, the calcium compound is treated with a concentrated solution of NaCl. Account for the action of NaCl.
6. Describe and account for the effect of (1) increased pressure, (2) decreased temperature, (3) increased concentration of chlorine, and (4) of decreased concentration of chlorine upon the following reversible reaction: $PCl_5 \rightleftarrows PCl_3 + Cl_2 - 39{,}500$ calories. (All the substances involved are gases.)
7. $A + B \rightleftarrows C + D$. Compare the speeds of the forward and reverse reactions (1) when A and B are first mixed, (2) at equilibrium, and (3) at time intervals between (1) and (2). How do the concentrations of A, B, C, and D change from the time the mixture of A and B is first made until equilibrium is reached?
8. What effect does an increase in pressure have upon each of the following reactions?

$$H_2S \rightleftarrows H_2 + S \text{ (solid)}$$
$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$$
$$2\,C \text{ (solid)} + O_2 \rightleftarrows 2\,CO$$

9. What is the distinction between the quantity of a substance and the concentration of the same substance? When should each of these terms be used?
10. State in words the meaning of the equilibrium constant of a reaction.
11. How is the speed of a reaction determined? Name the different factors which influence the speed of a reaction.
12. Correct the following statement: Equilibrium is the condition which is reached when a reversible reaction has proceeded as far as it can be made to go in one direction.
13. Correct the following statement: When a reaction has reached equilibrium no further reaction takes place.
14. The conversion of a mixture of nitrogen and hydrogen into ammonia (page 318) is very slow at 400°. Why is it not practical to carry out this reaction at 1000°, at which the speed of the reaction would be much faster?
15. What factors which influence the speed of a reaction may be changed without affecting the equilibrium constant of the reaction?
16. The equilibrium constant for the reaction, $N_2 + O_2 \rightleftarrows 2\,NO$, at a given temperature is 0.0035. Explain this statement. What use might be made of information of this kind?
17. State Le Chatelier's principle. Apply it to the effect of an increase in pressure upon a reversible reaction involving gases; to the effect of an increase in the concentration of one of the reacting substances; and to the effect of the addition of heat to a reaction in which heat is evolved by the forward reaction.
18. According to the general rule concerning the effect of temperature upon the speed of a reaction, how many grams of a substance can be produced per minute at 100° if 1 g. of the substance is produced in one minute at 0°? Assume concentrations and other conditions are the same for the two temperatures.
19. When the reaction, $A + B \rightleftarrows C$, has reached equilibrium, it is found that the concentrations of A, B, and C are, respectively, 2, 3, and 1 gram-molecular weights per liter. Calculate the equilibrium constant of the reaction.

20. What were the original concentrations of *A* and *B*, at constant volume, in the reaction of the preceding exercise if there was zero concentration of *C* at the beginning of the reaction?
21. Calculate the equilibrium constant for the reaction, $A + B \rightleftarrows 2\,C$, if the concentrations of *A*, *B*, and *C* at equilibrium are, respectively, 3, 3, and 2 gram-molecular weights per liter.
22. Why does an efflorescent hydrate in an open container decompose completely in a warm, dry atmosphere?
23. $2\,AB \longrightarrow A_2 + B_2$. One gram-molecular weight of the gaseous compound AB is placed in a closed container having a capacity of one liter and heated to 420° C. It is found that the concentration of each of the gaseous elements, A_2 and B_2, is 0.10 g. mol. wt. per liter at equilibrium. What is the equilibrium constant at this temperature?
24. Why does a catalyst have no effect upon the equilibrium constant of a reaction?
25. How would you expect the reaction by which ozone is produced from pure oxygen to be affected by (*a*) an increase in pressure and (*b*) by a decrease in temperature?
26. Why do changes in concentration and pressure (of gases) not affect the value of the equilibrium constant?

REFERENCES FOR FURTHER READING

Chapin and Steiner, *Second Year College Chemistry.*

Foster, W., *Romance of Chemistry.*

Hildebrand, J. H., *Principles of Chemistry.*

Hogness, T. R., and W. C. Johnson, *Qualitative Analysis and Chemical Equilibrium.* New York: Henry Holt and Company, 1937.

J. Am. Chem. Soc., **33,** 91 (1911).

J. Chem. Ed., **2,** 631 (1925); **7,** 2887 (1930); **9,** 261, 2026 (1932); **11,** 328, 617 (1934); **18,** 272 (1941); **22,** 387 (1945); **23,** 45 (1946).

Catalysis: *J. Chem. Ed.*, **23,** 579 (1946); **24,** 79 (1947).

26

EQUILIBRIA IN REACTIONS OF IONS

1. Introduction

In this chapter we shall be concerned with cases of equilibrium involving the ions and molecules of weak electrolytes, such as water and the weak acids. We shall find, in general, that the principles of equilibrium already discussed apply to the reactions of ions in solution, and that changes in the concentration of one ion may have profound effects upon the concentrations of certain other ions in the same solution.

ACIDS AND BASES

2. Modern Concept of Acids

The chemical nature of acids has already been discussed (page 121). As defined in an earlier chapter, an acid is a substance that gives up protons to another substance, and in keeping with this definition acids are sometimes called *proton donors*. Thus, the ammonium ion is formed in the solution of an acid (HA) in liquid ammonia, and the hydronium ion from the same acid in an aqueous solution:

$$NH_3 + HA \rightleftarrows NH_4^+ + A^-$$
$$H_2O + HA \rightleftarrows H_3O^+ + A^-.$$

Ordinarily the substances that we call acids and which we use as such in the laboratory are substances which in aqueous solution form hydrogen (actually hydronium) ions. For most purposes this definition of an acid is satisfactory, but we must remember that it holds true for aqueous solutions only. Our earlier definition (page 121) is more general, since it does not refer to any one solvent nor is it limited to the formation of hydronium ions. Thus, water itself can act as an acid with ammonia to form NH_4^+ and OH^- ions.

3. Bases and Their Reactions with Acids

Since we deal principally with aqueous solutions, it has been common practice to define a base as a substance which forms hydroxyl ions, OH^-, when dissolved in water. However, as for acids, this is a definition that fits a special situation. A more general definition of a base, and one that is in keeping with the general definition of an acid, may be stated as follows: *A base is a substance that accepts protons from an acid.* The following general equation serves to illustrate the rôles played by both bases and acids:

$$HA + B \rightleftarrows BH + A^-.$$

B is the base and *HA* is the acid. Both may be electrically charged, or they may be uncharged molecules. The hydrogen ion (H^+) probably never exists free; it either remains in the acid molecule *HA* or it combines, when A^- is formed, with another substance which acts as a base. The following equations illustrate reactions between

acids and bases. In (1), for example, *HA* is $HC_2H_3O_2$, and *B* is the water molecule. In the reverse reaction (H_3O^+) is the acid and the $C_2H_3O_2^-$ ion is the base. We see, here, illustrations of an electrically charged acid, H_3O^+, and a neutral acid, $HC_2H_3O_2$. Likewise the base $C_2H_3O_2^-$ is charged, while H_2O is neutral. The reactions of other acids and bases are shown by the other equations:

	Acid	*Base*	*Acid*	*Base*
(1)	$HC_2H_3O_2$ +	H_2O ⇌	H_3O^+ +	$C_2H_3O_2^-$.
(2)	H_2O +	NH_3 ⇌	NH_4^+ +	OH^-.
(3)	HCO_3^- +	OH^- ⇌	H_2O +	$CO_3^=$.
(4)	$HC_2H_3O_2$ +	NH_3 ⇌	NH_4^+ +	$C_2H_3O_2^-$.
(5)	$HC_2H_3O_2$ +	OH^- ⇌	H_2O +	$C_2H_3O_2^-$.

Ammonia, the hydroxyl ion, water, and the acetate ion are bases in these reactions. In the forward reaction of (2) the water molecule reacts, however, as an acid in yielding a proton to the molecule of ammonia.

4. Neutralization; Protolysis

The neutralization of HCl and NaOH is explained as follows:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$
$$NaOH \longrightarrow Na^+ + OH^-$$
$$H_3O^+ + OH^- \rightleftarrows 2\,H_2O.$$

The acetate ion may act as a base in the same manner as the hydroxyl ion:

$$(Na^+ + C_2H_3O_2^-) + (H^+ + Cl^-) \rightleftarrows HC_2H_3O_2 + (Na^+ + Cl^-).$$

In this and the preceding section we have discussed acids and bases in terms of what is usually called the Brönsted concept, or theory. By this same concept we would call the reaction between an acid, such as HCl, and a base, such as NaOH, and all other reactions in which protons are removed from one substance and added to another, ***protolytic*** reactions. Protolysis is, therefore, a more generally applicable term than neutralization; for example, we could scarcely say that water neutralizes ammonia when it reacts with it to form NH_4^+ and OH^- ions.

5. Strengths of Acids and Bases in Aqueous Solutions

Since the advent of Arrhenius's theory of ionization, the strengths of acids and bases have been compared by determining the concentrations of hydrogen and hydroxyl ions, respectively, in aqueous solutions of the same molecular concentrations. These determinations have been based, for the most part, upon the apparent degree of ionization of different acids and different bases (page 324) as measured by the conductivity method (page 218).

In terms of the Brönsted concept of acids mentioned above the strongest acids are those that most readily give up protons to bases. The strongest bases are those that have the strongest tendencies to combine with protons. Thus, hydrochloric acid must be a strong acid as compared to acetic, because in aqueous solutions of acetic acid very few molecules of the acid react with water to form hydronium and acetate ions, as shown by the slight conductance of the solution and the small degree of ionization of the acid. On the other hand, the conductance of an aqueous solution of hydrogen chloride is high, and the molecules of water evidently remove most of the protons from molecules of HCl.

The hydroxyl ion is a stronger base than the carbonate ion, because the OH^- ion removes the proton from the HCO_3^- ion to form water and $CO_3^=$ ion. Likewise, the chloride ion must be a very weak base, because many ions and other substances (OH^-, $CO_3^=$, $C_2H_3O_2^-$, HCO_3^-, NH_3, H_2O) will remove protons from HCl molecules, while Cl^- ion when placed in solutions containing such substances as H_2CO_3, H_2S, $HC_2H_3O_2$, NH_4OH, and H_2O shows little if any tendency to remove the protons from such substances to form HCl.

From what we have just said, we should

be able to compare the strengths of acids in aqueous solutions by measuring the degree of ionization of the different acids, because these results should provide information concerning the capacity of the same base, H_2O, to remove protons from different acids. (It will be remembered that ions are formed from acids in aqueous solutions in exactly the same manner for all acids; i.e., by reactions in which protons are removed from the acids by water.) Likewise, bases, such as ammonia, produce ions by reacting with water to form ions. The extent to which ammonia acts in this way can be measured roughly by determining the degree of ionization of the ammonium hydroxide. The fact that the results show the degree of ionization to be small indicates that OH^- is a stronger base than NH_3, because most of the protons remain in water molecules and, relatively, only a few are removed by NH_3 to form NH_4^+.

The soluble hydroxides of the metals — e.g., NaOH — are completely ionized; hence, the real base in their solutions (page 123) is the OH^- ion. The degree of ionization as measured by the conductance of a 0.01N solution of NaOH is about 94 per cent and about 91 per cent for a 0.1N solution. These data, however, only indicate the extent to which the ions in the solution are hindered in their movement by interionic attraction (page 219).

6. The Ionization of Salts

If the interionic attraction theory is valid, we should expect that salts containing divalent or trivalent ions should exhibit smaller apparent degrees of ionization than salts containing two univalent ions. An ion which carries two units of positive charge should attract chloride ions, for example, more strongly and should produce a greater resistance to the movement of that ion through the solution than a positive ion possessing only one unit of positive charge. How well the facts support this proposition may be observed by an inspection of the degrees of ionization of different salts (Table 14). Salts consisting of univalent ions, such as NaCl, $NaNO_3$, and KCl, in 0.1N solutions are ionized to an extent of 80 to 90 per cent. Salts containing one divalent and one univalent ion are ionized to an extent which is about 10 per cent less, on the whole, than the first group. Salts containing two divalent ions show an apparent degree of ionization of approximately 40 per cent.

7. The Ionization of Dibasic and Tribasic Acids

Since a molecule of a dibasic acid contains two hydrogen atoms which may form hydrogen ions, the molecule ionizes in two steps. The steps are shown in the following equations, in which the part played by water in producing hydronium ions has been omitted.

$$(1)\ H_2SO_4 \rightleftarrows H^+ + HSO_4^-$$
$$(2)\ HSO_4^- \rightleftarrows H^+ + SO_4^{=}.$$

$$(1)\ H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$
$$(2)\ HCO_3^- \rightleftarrows H^+ + CO_3^{=}.$$

A tribasic acid ionizes in three stages. A moderately concentrated solution of phosphoric acid (H_3PO_4), for example, contains chiefly hydrogen ions and *dihydrogen phosphate* ions:

$$(1)\ H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-.$$

In more dilute solutions, the following reaction occurs, forming the *monohydrogen phosphate* ion:

$$(2)\ H_2PO_4^- \rightleftarrows H^+ + HPO_4^{=}.$$

In very dilute solutions appreciable concentrations of the simple phosphate ion may be formed:

$$(3)\ HPO_4^{=} \rightleftarrows H^+ + PO_4^{\equiv}.$$

Acids which yield more than one proton per molecule in reacting with a base are called *polyprotic* acids (or *polybasic* acids).

TABLE 14. THE STRENGTHS OF COMMON ELECTROLYTES * AS MEASURED BY THEIR DEGREES OF IONIZATION

			Percentage ionized
Acids			
Hydrochloric,	HCl	$\frac{N}{10}$	92
Nitric,	HNO_3	$\frac{N}{10}$	92
Sulfuric,	H_2SO_4	$\frac{N}{10}$ (H^+, HSO_4^-)	90
	H_2SO_4	$\frac{N}{10}$ $(HSO_4^- \longrightarrow H^+ + SO_4^{=})$	60
Oxalic,	$H_2C_2O_4$	$\frac{N}{10}$ $(H^+, HC_2O_4^-)$	40
	$H_2C_2O_4$	$\frac{N}{10}$ $(HC_2O_4^- \longrightarrow H^+ + C_2O_4^{=})$	1
Carbonic,	H_2CO_3	$\frac{M}{10}$ (H^+, HCO_3^-)	0.17
Hydrosulfuric,	H_2S	$\frac{M}{10}$ (H^+, HS^-)	0.07
	H_2S	$\frac{M}{10}$ $(HS^- \longrightarrow H^+ + S^{=})$	0.0001
Phosphoric,	H_3PO_4	$\frac{M}{10}$ $(H^+, H_2PO_4^-)$	27
	H_3PO_4	$\frac{M}{10}$ $(H_2PO_4^- \longrightarrow H^+ + HPO_4^{=})$	0.1
	H_3PO_4	$\frac{M}{10}$ $(HPO_4^{=} \longrightarrow H^+ + PO_4^{\equiv})$	0.0001
Acetic,	$HC_2H_3O_2$	$\frac{N}{10}$	1.34
Hydrocyanic,	HCN	$\frac{N}{10}$	0.01
Bases			
Potassium hydroxide,	KOH	$\frac{N}{10}$	91
Sodium hydroxide,	$NaOH$	$\frac{N}{10}$	91
Barium hydroxide,	$Ba(OH)_2$	$\frac{N}{10}$	77
Ammonium hydroxide,		$\frac{N}{10}$ $(NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-)$	1.3
Salts			
Potassium chloride,	KCl	$\frac{N}{10}$ (all salts of the type M^+X^-)	86
Calcium chloride,	$CaCl_2$	$\frac{N}{10}$ (salts of the type $M^{++}2X^-$)	75
Cupric sulfate,	$CuSO_4$	$\frac{N}{10}$ (salts of the type $M^{++}X^{=}$)	39
Mercuric chloride,	$HgCl_2$	$\frac{N}{10}$ (one of the few exceptions)	1

* The symbol H^+, used in the expressions for the ionization of acids, represents the ion responsible for acidity and is probably H_3O^+. The degree of ionization of a given substance varies with the temperature. Most of the values in this table were determined at 18° C. In the portion of the table dealing with salts M represents a metal and X a nonmetal or a negative radical; the valences are indicated by the + or − signs.

Thus, sulfuric acid is a *diprotic* and phosphoric acid is a *triprotic* acid.

The degrees of ionization of each of the three stages of ionization of phosphoric acid (Table 14) indicate that the strengths of H_3PO_4, $H_2PO_4^-$, and $HPO_4^{=}$ decrease in that order; i.e., H_3PO_4 most readily and $HPO_4^{=}$ least readily give up protons to a common base such as water.

EQUILIBRIA INVOLVING IONS AND MOLECULES OF WEAK ACIDS

8. Ionization Constants of Acids

A solution of a weak electrolyte, such as acetic acid, $HC_2H_3O_2$, contains ions and molecules in equilibrium with each other. For reactions of this kind the equilibrium constants are called ionization constants.

For the ionization of acetic acid the equation is

$$(1) \qquad HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-,$$

and the equation for the ionization constant of this reaction is

$$(2) \qquad \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_1.$$

If we take into account the reaction of acetic acid with the solvent (water), the equation for the ionization of the acid is

$$(3) \quad HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-,$$

and the ionization constant is defined as

$$(4) \qquad \frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2] \times [H_2O]} = K_2.$$

Of the four concentrations represented in this equation, the concentration of water, $[H_2O]$, is constant or may be so regarded for all practical purposes. The concentration of water is 1000 g. ÷ 18 g. = 55.5 moles per liter. This concentration is so many times greater than the concentration of any other substance in the solution that it would not be changed appreciably even if all of the H_3O^+ and $C_2H_3O_2^-$ ions were changed into molecules of acetic acid and water. Hence, considering $[H_2O]$ as constant and multiplying each side of equation (4) by it, we may write

$$\frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_2 \times [H_2O] = K_3$$

as the equation for the ionization constant. If, now, we replace $[H_3O^+]$ by $[H^+]$ since they are numerically equal (either represents the concentration of the positive ion in the solution), we have a mathematical expression for the ionization constant of acetic acid that is identical with equation (2).

9. Calculation of the Ionization Constant of Acetic Acid

To determine the numerical value of the ionization constant of acetic acid we must know the concentration at equilibrium of hydrogen ions, acetate ions, and acetic acid molecules. A 0.1N solution of acetic acid contains 0.1 of a gram-molecular weight of acid per liter, and of this quantity, 1.34 per cent, or $0.1 \times 0.0134 = 0.00134$ gram-molecule, produces ions. Since each molecule in ionizing produces one hydrogen and one acetate ion, the concentration of each ion in this solution is 0.00134 gram-ion per liter. The concentration of the acetic acid that is not ionized is the quantity added (per liter) minus the quantity that ionizes, or $0.1 - 0.00134 = 0.09866$ gram-molecular weight, per liter. These values can now be substituted in the equilibrium equation, thus permitting us to calculate K_1:

$$\frac{0.00134 \times 0.00134}{0.09866} = K_1 = \frac{0.00000179}{0.0987} = 0.000018.$$

The value 0.000018 may also be written as 1.8×10^{-5}. This same value for the ionization constant, K_1, is found for other concentrations of the acid, provided the solutions are dilute or only moderately concentrated.

10. Activity and Activity Coefficients

Because of interionic attraction, the attraction of particles of solute and solvent for each other, and other forces of a similar nature, we cannot expect the speed of a reaction to be directly proportional to the molecular concentration of the reacting particles, especially if the concentra-

tions are high. The deviations in reactions involving ions are usually much greater than those between molecules, because of the attraction between ions resulting from their electrical charges. In any reaction, however, the *effective* concentration of any particle (ion or molecule), as determined by the observed speed of the reaction in which that particle participates, is less than the *actual* concentration. The effective concentration is usually termed the *activity* (a) of the given ion or molecule. The ratio of the activity to the actual concentration (c) is called the activity *coefficient* (f):

$$a = fc.$$

The activity coefficient is not a constant. It varies with the concentration, and in infinitely dilute solutions, f is unity:

$$a = c.$$

If activities instead of concentrations are used in determining the speeds of a reaction, the law of molecular concentration and the equilibrium equation may be applied more accurately to the reacting system. Thus, for acetic acid the equation becomes:

$$\frac{a_{H^+} \times aC_2H_3O_2^-}{aHC_2H_3O_2} = K_a.$$

For dilute solutions of weak electrolytes, such as acetic acid, K_a and K_I, differ but little, since in the solutions of these substances the activities of the ions are almost the same as the actual concentrations. Since we shall be dealing usually with at least fairly dilute solutions, we shall use concentrations rather than activities in the discussions that follow.

IONS OF WATER

11. The Ionization of Water

The ionization of water results in the formation of hydronium and hydroxyl ions:

$$HOH + HOH \rightleftarrows H_3O^+ + OH^-.$$

Water is an extremely poor conductor of the electrical current, and the extent of its ionization, therefore, is very small. The conductance of pure water, at ordinary temperatures, indicates that it contains one gram-ion each of hydronium and hydroxyl ions in 10,000,000 liters, or a concentration in one liter of 0.0000001 gram-ion. This means that one molecule in 555,000,000 ionizes at ordinary temperatures.

12. The Ionization Constant of Water

Representing the positive ion as H^+ instead of H_3O^+, we may state the equation for the ionization constant of water as

$$\frac{[H^+] \times [OH^-]}{[HOH]} = K_{Iw}.$$

The numerical value of the constant may be calculated by substituting the values for the ionic concentrations and the concentration of the non-ionized water (as given above) in this equation. The portion of the water which does not ionize is almost equal to the total quantity and may be considered as constant and equal to 55.5 gram-molecules per liter; the concentration of each ion (at ordinary temperatures) is 0.0000001 gram-ion per liter. The dissociation constant, therefore, is

$$\frac{0.0000001 \times 0.0000001}{55.5 - 0.0000001} = \frac{1 \times 10^{-14}}{55.5} = 1.9 \times 10^{-16}.$$

Since the concentration of non-ionized water is practically constant, it is more convenient to write the equation as follows:

$$[H^+] \times [OH^+] = K_I \times [HOH] = K_{Iw}.$$

The constant, K_{Iw}, is equal, therefore, to the product of the gram-ion concentrations of the ions of water (H^+ and OH^-) and is called the *ion product* of water. At 25° K_{Iw} has the value 1.2×10^{-14}, which might also be written as $0.0_{13}12$. At higher temperatures, K_{Iw} has somewhat greater values.

13. Hydrogen and Hydroxyl Ion Concentrations of Solutions

If the product of their concentrations in pure water is 1×10^{-14}, the concentrations of hydrogen and hydroxyl ion are 1×10^{-7} gram-ion of *each* per liter. This statement does not mean that *any solution must con-*

tain the same concentration of each ion. If an acid is added to water, the concentration of the hydrogen ion is increased; if an hydroxide base is added the concentration of the hydroxyl ion is increased. As the concentration of one ion increases, the concentration of the other must decrease, and the product of the two concentrations (temperature remaining constant) must always be the same as it is in pure water, 1×10^{-14}.

Let us consider the ionic concentrations in a 0.1 N solution of hydrochloric acid. If we assume that the acid is completely ionized, the concentration of the hydrogen ion in this solution is 0.1 gram-ion per liter. The concentration of the hydroxyl ion expressed as gram-ion per liter is found by solving for $[OH^-]$ in the equation:

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$
$$0.1 \times [OH^-] = 1 \times 10^{-14}$$
$$[OH^-] = \frac{1 \times 10^{-14}}{0.1} = 1 \times 10^{-13}.$$

14. The Hydrogen Electrode; Comparisons of Hydrogen Ion Concentrations

A direct method of determining the hydrogen ion concentration depends upon the determination of the electromotive force, or potential, between hydrogen ions in a solution and free hydrogen. An electrode consisting of a gold or platinum wire or foil and covered with finely divided platinum, is placed in the solution and pure hydrogen under 1 atm. of pressure is passed over it. The hydrogen is absorbed by the platinum, and then establishes equilibrium with the hydrogen ions of the solution. The reaction may be represented by the following equation:

$$H_2 \rightleftarrows 2\,H^+ + 2\,e,$$

where e represents an electron. When the concentration of the hydrogen ion is decreased, the equilibrium is disturbed and the reaction proceeds towards the right. As hydrogen atoms change into ions, electrons are left on the electrode and increase its negative charge. On the other hand, an increase in the concentration of the ions causes the reaction to go to the left, and ions are converted into neutral atoms and molecules. This change removes electrons from the electrode and decreases its negative charge. If the hydrogen electrode is placed in a circuit with another electrode whose charge remains constant, changes in the electromotive force between the two electrodes may be regarded as changes in the electrical charge of the hydrogen electrode resulting from changes in hydrogen ion concentration.

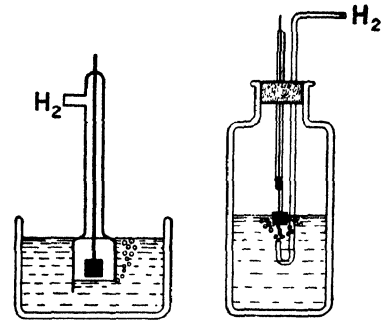


Figure 201. Hydrogen Electrodes

15. pH or Hydrogen Ion Index

Instead of expressing the concentration of hydrogen ion as gram-ions per liter, the concentration is often expressed in terms of *p*H, or the hydrogen ion index. The term *p*H is an abbreviation of the expression "potential of hydrogen."

Numerically, the *p*H of a solution is the *logarithm of the number of liters of the solution that contains one gram-atomic weight (1.008 g.) of hydrogen as H^+ ion.* The same statement may be expressed in the form of an equation:

$$p\text{H} = \log \frac{1}{[H^+]},$$

in which $\frac{1}{[H^+]}$ is the reciprocal of the

concentration of H^+ per liter, and is equal to the number of liters containing one gram-ion weight of hydrogen ion (1.008 g.).

16. The pH of Water and of Solutions

Pure water contains 0.0000001 gram-ion of H^+ per liter. Hence, the *p*H of water is

$$p\text{H} = \log \frac{1}{0.0000001} = \log 10{,}000{,}000.$$

Now the logarithm of a number is the exponent of 10 which shows the power to which 10 must be raised to give the number. The logarithm of 10 is 1; of 100, 2; of 1000, 3; and 10,000,000, 7. The *p*H of pure water therefore is 7.

In a solution containing an acid the concentration of H^+ is greater than it is in water. This means that the number of liters in which 1 gram-ion of H^+ is contained is smaller for the solution of the acid than for water; consequently, *the pH is smaller the greater the concentration of* H^+. In an alkaline solution, the *p*H is greater than 7.

If we may assume that a 0.001 N solution of HCl is completely ionized, the concentration of the hydrogen ion is 0.001 N, and one gram-ion weight is contained in 1000 liters. The logarithm of 1000 is 3 ($1000 = 1 \times 10^3$) and 3, therefore, is the *p*H of this solution.

A slightly different explanation of the *p*H index may be helpful to the student. We can define *p*H as the exponent of the H^+ concentration written as a power of 10 with the sign reversed. Thus, if the hydrogen ion concentration of a solution is 1×10^{-6}, the exponent of 10 that must be used to express the concentration is -6, and the *p*H is 6. If the concentration is, let us say, 4×10^{-6}, we can refer to a table of logarithms to find the logarithm of 4, which is 0.6, and the logarithm of 10^{-6}, which is -6.0. The logarithm of the product of the two numbers is the sum of the logarithms of the two numbers; and hence, the logarithm of 4×10^{-6} is $-6.0 + 0.6 = -5.4$. If the sign of this number is reversed, we have the *p*H of the solution, 5.4.

17. Use of Indicators in Measuring pH

The concentration of hydrogen ion, or the *p*H, of a solution can be measured approximately by noting the colors obtained when different indicators are added to the solution. The colors depend upon the hydrogen ion concentration of the solution.

Let us consider an indicator that is a weak acid, HX, in which X represents a complex group of atoms that compose the negative ion of the indicator. An indicator that has two colors under different conditions has two different structural arrangements of its atoms. One of these may be regarded as a non-electrolyte and the other as a weak acid or a weak base, usually the former. Let us indicate the non-ionizing form of the indicator as (HX) and the ionizing form as HX. In an aqueous solution the following equilibrium is established:

$$(\text{HX}) \rightleftarrows \text{HX} \rightleftarrows \text{H}^+ + \text{X}^-.$$

Let us say that the (HX) form is blue and that the ion X^- is red. When an acid is added to this solution, the concentration of H^+ is increased, thus increasing the speed of the reaction to the left and increasing the concentration of the (HX) molecules and decreasing the concentration of the X^- ions. An acid, therefore, tends to change the color from red to blue. A base like sodium hydroxide reduces the concentration of the H^+ ion and shifts the equilibrium toward the right with an increase in the concentration of X^- at the expense of (HX). The color is changed, therefore, by a base from blue to red.

The colors of solutions of some of the common indicators corresponding to different *p*H values are shown in Table 15. It should be understood that the change from one color to another usually does not occur at a definite *p*H but occurs, sometimes, through a considerable range.

The use of indicators in determining the *p*H of a solution is illustrated by the following examples. If a solution gives a yellow color when methyl red is added, we know that the *p*H of this solution is above 5 (Table 15). If the same solution gives a yellow color with rosolic acid, we know that

TABLE 15. INDICATOR COLORS IN SOLUTIONS OF DIFFERENT PH

R, red; B, blue; Y, yellow; V, violet; P, purple; O, orange; C, colorless; G, green; Ch., changing.

Methyl violet	Methyl yellow	Methyl orange	Brom phenol blue	Congo red	Sodium alizarin sulfonate	Methyl red	Brom cresol purple	Brom thymol blue	Litmus	Neutral red	Rosolic acid	Thymol blue	Phenolphthalein	Trinitrobenzene	Indigo carmine	pH
Y	R	R	Y	B	Y	R	Y	Y	R	R	Y	R	C	C	B	0
G	R	R	Y	B	Y	R	Y	Y	R	R	Y	R	C	C	B	1
B	R	R	Y	B	Y	R	Y	Y	R	R	Y	O	C	C	B	2
V	Ch	R	Y	V	Y	R	Y	Y	R	R	Y	Y	C	C	B	3
V	Y	O	G	V	Y	R	Y	Y	R	R	Y	Y	C	C	B	4
V	Y	Y	B	R	Y	Ch	Y	Y	Ch	R	Y	Y	C	C	B	5
V	Y	Y	B	R	Ch	Y	Ch	Y	Ch	R	Y	Y	C	C	B	6
V	Y	Y	B	R	V	Y	P	G	Ch	Ch	Ch	Y	C	C	B	7
V	Y	Y	B	R	V	Y	P	B	Ch	Y	R	Y	C	C	B	8
V	Y	Y	B	R	V	Y	P	B	Ch	Y	R	G	Ch	C	B	9
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	C	B	10
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	C	B	11
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	C	B	12
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	O	G	13
V	Y	Y	B	R	V	Y	P	B	B	Y	R	B	R	O	Y	14

the *p*H is less than 7. We may conclude, therefore, that the *p*H of this solution is approximately 6. If another solution gives a yellow color with methyl orange, and yellow with brom thymol blue, its *p*H must be 5 to 6. If the same solution gives a definite yellow color with brom cresol purple, its *p*H must be nearer 5 than 6. If standard solutions are prepared having known *p*H values increasing by tenths from, let us say, 4.5 to 6.5, and if the same number of drops of the solution of the indicator (brom cresol purple) is added to each, we can obtain a set of solutions varying in color throughout the *p*H range that we wish to study in this particular case. From these we can select the solution that most nearly matches in color the solution under study. We must use the same volume of this solution, of course, and add the same quantity of the indicator as is used in preparing the standards.

18. The Importance of Hydrogen Ion Measurements and Control

The proper hydrogen ion concentration must be maintained to secure the results desired from many kinds of chemical change in nature, in industry, and in scientific investigations. The *p*H of the blood of man must be maintained at the average value of 7.35 and must not vary far in either direction from this mean. This *p*H indicates

that the blood is slightly alkaline. The *p*H usually increases a little after eating, because the stomach draws upon the hydrogen ions of the blood to produce the hydrochloric acid needed for digestion. Measurements and control of hydrogen ion concentration are of importance in the following: Bleaching, dyeing, purification of water (*p*H affects the rate of filtration), corrosion of metals, manufacture of dyes and drugs, acidity of soils, sizing of paper, fermentations of sugar and starches, baking, and candy making. In analytical chemistry the separation and detection of several of the metallic ions depend upon the *p*H of the solutions containing the ions.

REACTIONS BETWEEN IONS

19. Will Ions A^+ and B^- Combine?

Many compounds are formed by reactions between ions in solutions. In all solutions containing two electrolytes, combinations of two pairs of ions are possible and may, or may not, occur. Let us consider two electrolytes, A^+B^- and C^+D^-. Ions A^+ and D^- may combine to form AD, and ions C^+ and B^- may form CB. The extent to which they combine depends upon (1) the solubility of the compound that they form, and (2) upon its degree of ionization, if it is soluble. Let us consider three specific examples.

20. Reactions That Form a Slightly Soluble Gas

A solution of sodium carbonate and hydrochloric acid contains hydrogen, chloride, sodium, and carbonate ions. Hydrogen ion will combine with carbonate ion to form, first, bicarbonate, HCO_3^-, ion and carbonic acid, H_2CO_3. This acid is unstable and decomposes into water and carbon dioxide, which is only slightly soluble and, consequently, escapes:

$$H^+ + CO_3^= \rightleftarrows HCO_3^- + H^+ \rightleftarrows H_2CO_3.$$

The escape of carbon dioxide from the solution disturbs this equilibrium and results, eventually, in almost complete removal of the carbonate ion, provided that a sufficient quantity of hydrochloric acid is added to convert all of the carbonate ion into carbonic acid.

21. The Formation of a Slightly Soluble Solid

A solution of barium chloride contains barium and chloride ions. A solution of sodium sulfate contains sodium and sulfate ions. When these two solutions are mixed, a white solid, which can be identified as barium sulfate, is precipitated. Barium sulfate is only slightly soluble in water; about 0.00001 gram-molecular weight dissolves in one liter at 20° C. It is possible, therefore, for a solution to contain only small concentrations of barium and sulfate

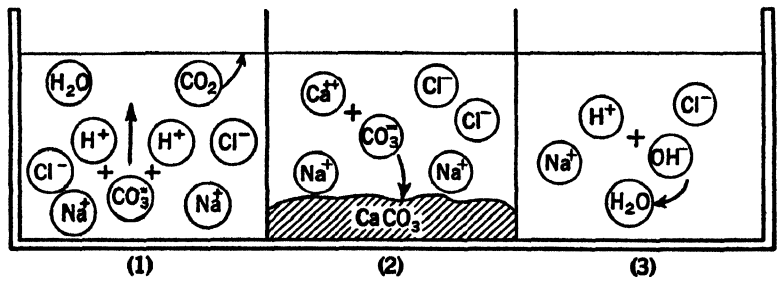


Figure 202

Reactions between ions. In (1) a slightly soluble gas is produced; in (2) a slightly soluble solid; and in (3) a slightly ionized compound. These three reactions are typical of the three kinds of reactions between ions (oxidation and reduction excluded) that are likely to occur.

ions. When they are mixed, these ions form crystals of barium sulfate, leaving only as many ions in the solution as are required to produce saturation. The removal of these ions from the solution, therefore, is almost complete.

$$(Ba^{++} + 2\ Cl^-) + (2\ Na^+ + SO_4^=) \longrightarrow BaSO_4 \downarrow + 2\ (Na^+ + Cl^-).$$

22. The Formation of Slightly Ionized Substances

When HCl and NaOH are placed in the same solution, the solution contains, at first, four ions — H^+, Cl^-, Na^+, and OH^-.

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-) + H_2O.$$

The sodium and chloride ions do not combine, of course, since sodium chloride is soluble and completely ionized, but the situation for hydrogen and hydroxyl ions is very different. Water is only slightly ionized; to have a solution containing, simultaneously, large numbers of these ions is to have, obviously, an impossible condition — an abundant supply of the ions of a substance that can produce very few ions. The ions must combine to form molecules of water until the ionic concentrations remaining are just sufficient to give, when multiplied together, 1×10^{-14}. Since this is a very small number, the reaction between these two ions must be almost complete.

Whenever the ions of any weak electrolyte are brought together in solution, they react to form molecules of the electrolyte until equilibrium between ions and molecules is established. Thus, when hydrogen ions and acetate ions are brought together, they combine to form molecules of acetic acid until, at equilibrium, the ratio of the product of the ionic concentrations to the concentration of acetic acid molecules is 0.000018 (page 325). The reaction of these ions is an example of protolysis (page 322).

23. The Hydrolysis of Salts

We might expect the solution of a salt, which is made by neutralizing an acid and a base, to be neutral. We must consider, however, the possible reactions that may occur between the ions of the salt and the ions of water.

Let us consider the hydrolysis of salts and the condition (acidic, alkaline, or neutral) of their solutions in terms of the Brönsted concept. Sodium acetate forms an alkaline solution because the acetate ion, being a strong base, reacts with molecules of water to form acetic acid molecules and hydroxyl ions. The latter are responsible for the alkaline properties of the solution. Ammonium acetate hydrolyzes considerably, but its solution is neutral:

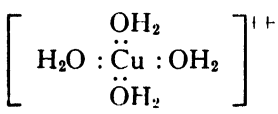
$$NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$$
$$C_2H_3O_2^- + H_2O \longrightarrow HC_2H_3O_2 + OH^-.$$

Both the ammonium and the acetate ions react with water, the former as an acid and the latter as a base. Since both H_3O^+ and OH^- ions are formed, the concentration of neither can increase very much because of the extremely slight degree of ionization of water which they form by reacting with each other. Ammonium chloride gives an acidic reaction in solution because NH_4 ions react with water to form NH_3 and H_3O^+ ions, while Cl^- ions do not act as a base. Hence, the formation of H_3O^+ ions produces an acidic solution.

24. The Hydrolysis of Hydrates of Salts

In the hydrates of salts (page 189) molecules of water are combined with metallic ions, which share pairs of electrons with the oxygen atoms of the water molecules. Such ions may be hydrolyzed by reacting with water to produce hydrogen, or hydronium, ions, thus causing the solution to have a decided acidic reaction. For example, the cupric ion, Cu^{++}, may combine in aqueous

solution with molecules of water to form the hydrated cupric ion:



Now this ion may react with water:

$$Cu(H_2O)_4^{++} + H_2O \rightleftarrows H_3O^+ + Cu(OH)(H_2O)_3^+.$$

According to this reaction a hydrated metallic ion acts as an acid, or proton donor.

25. The Common Ion Effect

This effect is observed when one of the ions of a weak electrolyte is added in excess to a solution of the electrolyte. The general effect, is to render the electrolyte less ionized.

Let us illustrate by referring once again to a solution of acetic acid. The common ion effect will be observed if crystals of sodium acetate are added to the solution; the acetate ion is the common ion. We shall assume that equilibrium had been established before the sodium acetate was added.

$$HC_2H_3O_2 \underset{(2)}{\overset{(1)}{\rightleftarrows}} H^+ + C_2H_3O_2^-.$$

The salt is ionized completely, and its addition, therefore, increases the concentration of the acetate ion considerably. Since the speed of reaction (2) is increased by this change of concentration, while that of reaction (1) is not, molecules of acetic acid will be produced, temporarily, in greater numbers than they ionize. But as the ions are consumed, and the number of non-ionized molecules increases, the two speeds will become equal again, and equilibrium will be established once more. For the new equilibrium, the concentration of hydrogen ion will be less than for the first, and the concentrations of acetate ions and acetic acid molecules will be greater. This amounts to a decrease in the ionization of the acid.

26. The Effect of Different Ions upon the Acidity of Solutions

The *p*H of the solution of any weak acid is always increased by the addition of a salt of the acid, as, for example, by the addition of sodium acetate to a solution of acetic acid. This effect means that the percentage of the acid that is ionized and, consequently, the H^+ ion concentration is decreased by the addition of the salt.

Solutions of strong acids, such as HCl, are not appreciably affected by the addition of their salts. The concentration of hydrogen ion in a solution of HCl is reduced, however, by the addition of an acetate, or the salt of any weak acid because the negative ion of such an acid acts as a base:

$$H^+ + C_2H_3O_2^- \rightleftarrows HC_2H_3O_2.$$

The addition of ammonium chloride likewise reduces the concentration of hydroxyl ion in the solution of a strong (hydroxide) base because the ammonium ion acts as an acid with the hydroxyl ion:

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O.$$

EQUILIBRIA IN SATURATED SOLUTIONS

27. The Solubility Product

Let us consider a saturated solution of silver chloride, AgCl. Since the ions and solid silver chloride are in equilibrium, the equilibrium equation for this system is

$$\frac{[Ag^+] \times [Cl^-]}{[AgCl(s)]} = K_c.$$

The concentration of solid AgCl is constant, and, therefore,

$$[Ag^+] \times [Cl^-] = \text{constant}.$$

This constant is called the *solubility product* of silver chloride.

If we add sodium chloride to a saturated solution of silver chloride, we are placing in the solution more Cl^- ions than can be in equilibrium with Ag^+ ions and undissolved

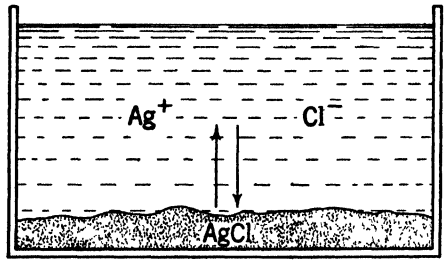


Figure 203

The solubility product of silver chloride (at a given temperature) is the product of the concentrations of the silver and the chloride ions in a saturated solution.

silver chloride. Therefore, some of the Cl^- and Ag^+ ions in the solution must be precipitated as AgCl in order that the concentrations of the two ions remaining in the solution will be just sufficient to make the solution saturated. The product of the ionic concentrations $[Ag^+] \times [Cl^-]$ remains unchanged.

In silver sulfate, Ag_2SO_4, there are two silver ions for each sulfate ion, and the equilibrium equation is

$$\frac{[Ag^+]^2 \times [SO_4^=]}{[Ag_2SO_4(S)]} = \text{Ke.}$$

Since the concentration of solid silver sulfate is constant, the numerator is also constant, and so we may write

$$[Ag^+]^2 \times [SO_4^=] = \text{Solubility Product.}$$

The solubility product may be defined for a definite temperature as *the product of the ionic concentrations in a saturated solution and is obtained by taking as a factor the concentration of each ion as many times as that ion appears in the formula of the substance.* This principle holds true only for slightly soluble ionic compounds, because in any but very dilute solutions interionic and other effects cause the activities of the ions to differ considerably from the actual concentrations.

28. Calculations of Solubility Product

Let us calculate the solubility product of silver chloride. The solubility of silver chloride is 0.00001 mole per liter at 18°. Since the two ions are produced in equal numbers, the saturated solution contains 0.00001 gram-ion each of Ag^+ and Cl^- per liter. The solubility product, therefore, is

$$0.00001 \times 0.00001 = 0.0000000001, \text{ or } 1 \times 10^{-10}.$$

The solubility of magnesium hydroxide, $Mg(OH)_2$, is 0.0002 gram-molecular weight per liter. Assuming that this substance is completely ionized, the concentration of the magnesium ion (Mg^{++}) is 0.0002 gram-ion per liter. But the ion-concentration of the hydroxyl ion is twice this amount (0.0004 gram-ion per liter), since two hydroxyl ions are formed for each magnesium ion. The solubility product, therefore, is equal to:

$$0.0002 \times (0.0004)^2 = 0.000000000032, \text{ or } 3.2 \times 10^{-10}.$$

The solubility products of other substances are given in Table 2, Appendix.

29. Conditions that Determine the Completeness of Precipitation

When the ions of a slightly soluble compound are mixed in a solution, *the extent to which the precipitate is formed depends upon the extent to which the product of the ionic concentrations as added exceeds the solubility product.* Consider, for example, the precipitation of silver chloride, when 1 gram-ion each of silver and chloride ions are brought together in one liter of an aqueous solution. The ions must precipitate until the product of their concentrations equals 1×10^{-10}, or each concentration is reduced to 0.00001 gram-ion per liter. This means that $1 - 0.00001$ or 0.99999 gram-molecular weight of silver chloride will precipitate. This quantity varies slightly, of course, with the temperature. Unless the product of the concentrations of the ions as added exceeds 1×10^{-10}, no precipitate will form. For example, no precipitate forms when 0.1 gram-ion of silver is placed in a solution containing 1×10^{-11} gram-ion of chloride per liter, because $0.1 \times (1 \times 10^{-11}) = 1 \times 10^{-12}$, and this product is smaller than 1×10^{-10}. This solution of silver chloride is not saturated.

30. How Can an Ion be More Completely Precipitated?

Let us say that we wish to remove silver ion as completely as possible from a solution by precipitating it as silver chloride. Since $[Ag^+] \times [Cl^-]$ must always equal 1×10^{-10}, it is obvious that the concentration of the silver ion at 18° must be reduced as the concentration of the chloride is increased. If we wish to leave as little silver ion as possible in the solution, we must add a large excess of the chloride ion. A solution which contains 1 gram-ion per liter of Cl^- can contain only 1×10^{-10} gram-ion of Ag^+.

$$[Ag^+] \times 1 = 1 \times 10^{-10}$$

$$[Ag^+] = \frac{1 \times 10^{-10}}{1} = 1 \times 10^{-10}.$$

If the concentration of the chloride ion is 0.001 gram-ion per liter, then the concentration of the silver ion must be 1×10^{-7} for a saturated solution, and so on.

THE INFLUENCE OF DIFFERENT IONS UPON THE PRECIPITATION OF SLIGHTLY SOLUBLE COMPOUNDS

31. The Precipitation of Calcium Carbonate

A solution containing sodium carbonate and calcium chloride will, ordinarily, yield a precipitate of calcium carbonate, since the solubility product of this substance is small (1×10^{-8}). In the presence of an acid, however, the following reactions reduce the concentration of the carbonate ion.

(1) $H^+ + CO_3^= \rightleftarrows HCO_3^-$
(2) $H^+ + HCO_3^- \rightleftarrows H_2CO_3$
(3) $H_2CO_3 \rightleftarrows H_2O + CO_2 \uparrow$.

Even if the reaction proceeds no further than to form bicarbonate ion, the concentration of carbonate ion is considerably reduced because in reaction (1) the bicarbonate ion, HCO_3^-, is only slightly ionized, or, to put the matter in another way, the $CO_3^=$ ion is a fairly strong base and therefore has a strong tendency to combine with protons. If sufficient acid is added, the concentration of the carbonate ion will be reduced to such a low value that the solubility product of calcium carbonate cannot be exceeded, and no precipitate can form.

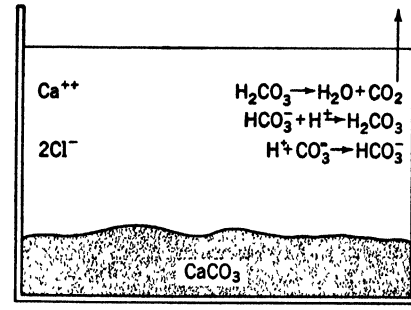


Figure 204. The Solubility of Calcium Carbonate in a Solution Containing Hydrochloric Acid

32. The Precipitation of Metallic Sulfides

In qualitative analysis, some of the cations (metals) are separated from others by the precipitation of their sulfides. A solution containing the metallic ions is treated with hydrogen sulfide. Although this acid is very slightly ionized, its saturated solution contains a sufficient concentration of sulfide ions to allow the solubility products of the sulfides of many of the metals to be exceeded (Table 2, Appendix). If an acid, such as HCl, is added the concentration of the sulfide ion is reduced because the following reactions occur:

$$H^+ + S^= \rightleftarrows HS^-.$$
$$HS^- + H^+ \rightleftarrows H_2S.$$

Both HS^- and H_2S are only very slightly ionized. If the concentration of the sulfide ion is reduced to just the right amount, it will be possible to exceed the smaller solubility products of the least soluble sulfides (HgS, CuS, As_2S_3, PbS, etc.) without exceeding the larger solubility products of the more soluble sulfides (FeS, ZnS, MnS, etc.). In this manner, it is possible to precipitate mercuric and cupric sulfides, for example, without precipitating zinc and manganese

sulfides at the same time. After the removal of the less soluble sulfides by filtration, the others may be precipitated from the filtrate by making this solution alkaline and again treating with hydrogen sulfide. The addition of the base reduces the concentration of the hydrogen ion and increases the concentration of the sulfide ion. It becomes possible, therefore, to exceed the larger solubility products of the more soluble sulfides, which will then precipitate.

REVIEW EXERCISES

1. From the data concerning the percentages of ionization of different acids (page 324) calculate the concentration of H^+ in 0.1 M solutions of HCl, $HC_2H_3O_2$, and HCN. Assuming that only the first stage of ionization occurs, make a similar calculation for H_2S, H_2CO_3, and H_3PO_4, if the concentrations are 0.1 M.
2. From the data obtained in (1) and from page 324, calculate the ionization constants for the reactions:

$$HCN \rightleftarrows H^+ + CN^-$$
$$H_2S \rightleftarrows H^+ + HS^-$$
$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-.$$

   Assume 0.1 M solutions in each case.
3. Assuming that a solution of acetic acid contains molecules of the acid in equilibrium with the ions, H^+ and $C_2H_3O_2^-$, tell what will happen if you add (1) NaOH (solid); (2) $NaC_2H_3O_2$ (solid); (3) water; (4) HCl; (5) NaCl (solid).
4. If you have a solution of ammonium hydroxide in which the molecules of ammonia and water are in equilibrium with the ions, what would happen if you added (1) HCl; (2) NH_4Cl (solid); (3) NaOH (solid); (4) water; (5) $NaC_2H_3O_2$ (solid); (6) NaCl (solid)?
5. What is the concentration of OH^- ion in a 0.1 N solution of ammonium hydroxide? What is the concentration of H^+ ion in the same solution? What is the *p*H of the same solution?
6. Which of the following substances will give an acid reaction, and which will give an alkaline reaction when dissolved in water? Na_2S; $KC_2H_3O_2$; $FeCl_3$; $(NH_4)_2SO_4$; K_2CO_3.
7. In view of the fact that oxalic acid ($H_2C_2O_4$) is a relatively weaker acid than HCl, why does calcium oxalate dissolve in a solution to which HCl is added?
8. Suggest one reason why barium sulfate ($BaSO_4$) does not dissolve in a solution to which HCl has been added, while barium carbonate ($BaCO_3$) does.
9. Why is magnesium hydroxide not precipitated as completely in the presence of NH_4Cl as in its absence?
10. What is incorrect in the following statement? Phosphoric acid is a stronger acid than sulfuric, because it contains three replaceable atoms of hydrogen per molecule while sulfuric has but two.
11. Silver nitrate was added in excess to 100 ml. of a solution of HCl. The precipitated AgCl was filtered, dried, and weighed. The precipitate weighed 2.6 g. How much HCl was present in one liter of the original solution? What was the normality of the solution?
12. What is the approximate *p*H of a solution that gives a blue color with brom-phenol blue, violet with sodium alizarin sulfonate, blue with brom-thymol blue, and yellow with thymol blue?
13. Define solubility product. What factors determine the size of the solubility product of a substance?
14. What factor or condition determines the quantity of a substance which will precipitate from a solution in which the ions of the substance are brought together?
15. Calculate the solubility products of $BaCrO_4$ and $Pb(OH)_2$ if their solubilities (at 18°) are 0.000015 and 0.0004 gram-molecular weight per liter, respectively. Assume that the solutes are completely ionized.
16. Would a precipitate of $PbCl_2$ form in a solution containing 0.0001 g. ion of Pb^{++} per liter if 0.01 gram-molecular weight of solid sodium chloride were added? Why?
17. How does the concentration of the sodium chloride solution which is added to a solution of silver nitrate in precipitating AgCl affect the quantity of precipitate? Explain in terms of the solubility product principle.

18. What indicator could be used to distinguish between 0.1 N NaOH and 0.00001 N HCl; Pure water and 0.001 N NH_4OH; and 0.00001 N NaOH and 0.001 N NaOH?
19. Why is a solution of NaCl practically neutral while a solution of NH_4Cl is acid?
20. Give in detail the method which you would use to determine the approximate *p*H of a solution of NH_4Cl.
21. The *p*H of a solution of an acid is 5. What is the concentration of H^+ in this solution?
22. What is the concentration of Ag^+ ion in a saturated solution of silver chloride, at 18°, if the concentration of chloride ion is 0.01 gram-ion per liter? How could such a solution be prepared?
23. Why does cupric sulfide, CuS, precipitate from a solution containing Zn^{++}, Cu^{++}, $S^=$, and H^+ ions, while zinc sulfide, ZnS, does not, although the concentrations of Zn^{++} and Cu^{++} are the same?
24. A colorless solution of acetic acid containing phenolphthalein turns pink as sodium carbonate is added. What does the change in color indicate? How was the condition causing this change produced?
25. Are the following statements true or false?
    (*a*) The *p*H of a colorless solution containing phenolphthalein is greater than 7.
    (*b*) The *p*H of a 0.1 N HCl solution is approximately 1.
    (*c*) The *p*H of any solution containing an acid is greater than 7.
    (*d*) The *p*H of a solution of sodium acetate is greater than 7.
    (*e*) The *p*H of a solution of ammonium chloride is less than 7.
    (*f*) As an acid is added to a solution of sodium hydroxide, the color of any indicator in the solution changes when equivalent quantities of acid and base have been mixed.
26. $(Na^+ + OH^-) + (NH_4^+ + Cl^-) \longrightarrow (Na^+ + Cl^-) + NH_3 + H_2O$.
    Show that this equation represents a reaction between an acid and a base.
27. Give examples of reactions in which the following substances act as acids: HOH, NH_4^+, $HC_2H_3O_2$, HCO_3^-, H_3O^+. Give examples of reactions in which the following act as bases: HOH, OH^-, NH_3, $C_2H_3O_2^-$, $S^=$, $CO_3^=$, and HCO_3^-.
28. What is meant by the term *activity* of an ion? Under what conditions is the activity equal to the actual concentration?

REFERENCES FOR FURTHER READING

Hammett, L. P., *Solutions of Electrolytes.*

Hogness, T. R., and W. C. Johnson, *Qualitative Chemical Analysis and Chemical Equilibrium.*

Acids and Bases: *J. Chem. Ed.*, **7,** 782 (1930); **12,** 109 (1935); **18,** 206 (1941); **20,** 219, 250, 344 (1943).

Dissociation of Electrolytes: *J. Chem. Ed.*, **9,** 841, 1010, 1227 (1932).

Modern Theories of Solutions: *J. Chem. Ed.*, **10,** 677 (1933); **17,** 124, 128, 131, 132 (1940); **18,** 206 (1941).

*p*H and H^+ Ion Concentration: *J. Chem. Ed.*, **5,** 1647 (1928); **6,** 36, 1659 (1929); **9,** 1010 (1932).

27

NITROGEN AND AMMONIA

NITROGEN

1. Introduction

In 1772, Rutherford burned different substances, such as phosphorus and carbon, in air and noted that there was always left a residue of the air that would not support the combustion of any substance. For this reason, Rutherford regarded the residue as air saturated with phlogiston. Scheele later showed that the inactive gas prepared by Rutherford is always present in the air, but Lavoisier was the first to recognize the substance as an element. He named it *azote*, a name that refers to the failure of the substance to support life. Later, Chaptal suggested the name *nitrogen*, because the element is found in "niter," a substance we now call potassium nitrate.

2. Sources of the World's Nitrogen Supply

At the present time a large part of the world's nitrogen needs is obtained directly from the vast supply of *nitrogen in the air*. This nitrogen is converted on a commercial scale into ammonia from which other nitrogen compounds are made. One of the most important of these is nitric acid, which in turn is used to manufacture many materials of importance. The conversion of nitrogen in the atmosphere into useful compounds is sometimes referred to as the *fixation of nitrogen*.

There are other important sources of nitrogen compounds. When coal is distilled in the production of coal gas and coke, a portion of the nitrogen contained in the coal escapes in the gas as ammonia. This has, for a long time, been an important source of ammonia. Until fairly recent times, most of the nitric acid made in this country and elsewhere was prepared from sodium nitrate and sulfuric acid. An extensive deposit of sodium nitrate occurs in a desert region in the mountains along the Pacific coast of South America. Most of the deposit is in Chile. The material taken from the deposit is called *caliche*. This is leached with water, and a product that is richer in sodium nitrate than the crude material is obtained. This is called *Chile saltpeter*.

3. Production of Free Nitrogen

Nitrogen for commercial use is obtained from the air. The air is liquefied, and the liquid is fractionally distilled (page 49). The nitrogen obtained from liquid air contains about one per cent of other substances. The principal impurity is argon, which is inert and, therefore, does not interfere seriously in the use of nitrogen.

Laboratory samples of nitrogen can be produced by causing the oxygen of the air to combine with phosphorus, copper, hydrogen, carbon, or some other combustible

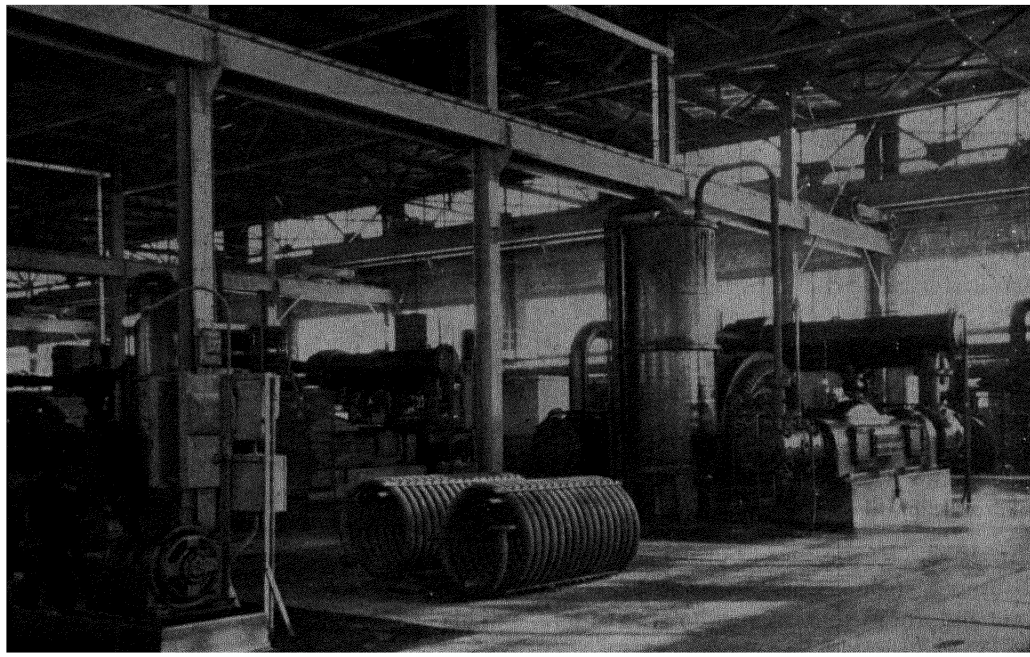


Figure 205. Plant in Which Nitrogen Gas is Distilled from Liquid Air
(Courtesy of American Cyanamid Company)

or easily oxidized substance. To obtain a fairly pure sample of nitrogen, the products formed by the combustion must be either non-volatile, or if they are gases, they should dissolve readily in water. The method shown in Figure 206 may be used when phosphorus is employed to remove the oxygen. The nitrogen is collected over water. Since only oxygen is removed, samples of nitrogen prepared in this manner are never pure.

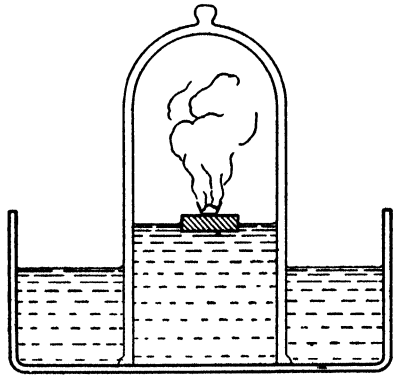


Figure 206. The Removal of Oxygen from a Sample of Air by the Combustion of Phosphorus

Small samples of *pure* nitrogen are prepared by heating ammonium nitrite:

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

Since ammonium nitrite is very unstable, some danger is involved in heating the pure, dry substance. In order to avoid this danger, the substance is usually prepared from a mixture containing sodium nitrite ($NaNO_2$) and ammonium chloride (NH_4Cl) in solution:

$$(Na^+ + NO_2^-) + (NH_4^+ + Cl^-) \longrightarrow N_2 + 2\ H_2O + (Na^+ + Cl^-).$$

4. Physical Properties

Nitrogen is colorless, odorless, and tasteless. At atmospheric pressure its boiling point is $-195.8°$, and its freezing point is $-209.8°$. Its critical temperature is $-147°$. The density of the gas under standard con-

ditions is 1.2506 grams per liter. Under standard conditions, 100 ml. of water dissolve about 2.3 ml. of nitrogen.

5. Chemical Properties

The nitrogen atom contains five valence electrons located in the second shell. The molecule consists of two atoms united by one or more pairs of shared electrons. The following structures seem the most probable:

$$:N:::N: \quad \text{or} \quad \dddot{N}:\dddot{N}$$

The molecule is very stable; 170,000 calories of heat are required to decompose a gram-molecular weight. This large quantity of energy accounts for the inactivity of the element, which shows very little tendency to form compounds with any other element under ordinary conditions. It combines with several metals at elevated temperatures. When magnesium is burned in air, the *nitride*, Mg_3N_2, as well as the oxide, is produced. Other nitrides of metals are Ca_3N_2, K_3N, and AlN. The nitride of hydrogen is called ammonia and has the formula, NH_3. At high temperatures, nitrogen combines with oxygen to form nitric oxide (NO).

6. Oxidation Numbers

Nitrogen has an oxidation number of -3 in ammonia and in the nitrides of the metals. In a few compounds, the element has oxidation numbers of -1 and -2. The positive oxidation numbers of the element are one, two, three, four, and five as indicated by the five oxides: N_2O; NO; N_2O_3; NO_2; and N_2O_5. Nitrogen trioxide and pentoxide are, respectively, the anhydrides of *nitrous* ($N_2O_3 + H_2O \longrightarrow 2\,HNO_2$) and *nitric* ($N_2O_5 + H_2O \longrightarrow 2\,HNO_3$) acids. These acids and their salts, the *nitrites* and the *nitrates*, are, along with ammonia, the most important inorganic compounds of the element.

7. Uses

The most important uses of nitrogen are those that involve its conversion into nitrogen compounds. The compound usually made directly from nitrogen is ammonia, but a large part of the production of that substance is, in turn converted into nitric acid, which is necessary for the manufacture of almost all explosives, many fertilizers, drugs, dyes, and other chemicals or materials of commerce.

Free nitrogen is often used to replace air when an inert, non-oxidizing and non-reducing atmosphere is desirable. Electric lamps are generally filled with nitrogen or with a mixture of nitrogen and argon. Mercury thermometers (especially those which are prepared for use at high temperatures) may contain nitrogen in the capillary space above the mercury.

8. Nitrogen in the Soil

The rocks and soils of the earth's surface contain naturally very little combined nitrogen. Compounds of this element are, however, essential substances among the nutritive materials that plants must acquire from the soil. The mixtures sold and used as fertilizers contain compounds of one or more of the three elements nitrogen, potassium, and phosphorus and, sometimes, smaller amounts of compounds of other elements as well. The nitrogen in these mixtures, usually, is in the form of nitrates or ammonium salts: KNO_3, $NaNO_3$, $Ca(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$, and $(NH_4)_3PO_4$. The manufacture of these compounds requires, in normal times, a large percentage of the world's production of ammonia and nitric acid.

In addition to the use of "chemical" fertilizers, there are various other agencies that contribute to the soil's supply of nitrogen, and there are other means by which the farmer can restore the nitrogen that is withdrawn by the removal of crops, such as corn and wheat. Some nitrogen and

oxygen combine in the atmosphere during electrical storms. The compounds produced in this manner dissolve in the rain and eventually find their way into the soil, where they add at least something to the fertility over a long period of time. Certain plants, called the *legumes*, have on their roots nodules, in which nitrifying bacteria live. With the aid of these bacteria, the legumes are able to feed upon the nitrogen from the air. In addition to supplying their own needs, they "fix" more nitrogen, which remains in the soil to serve as food for other plants. The leguminous plants include alfalfa, clover, beans, and peas. The wise farmer practices a system of crop rotation, in which each part of his cultivated land is planted in some leguminous crop at least once in four years. If the legume is "turned under," the soil is greatly enriched by the addition of all the nitrogen which the plants (and their coexisting bacteria) have been able to assimilate from the air. Crops turned beneath the soil in this manner are called "green" manures.

9. The Natural Nitrogen Cycle

Nitrogen appears to belong naturally only in the atmosphere of the earth. A small amount of it is always found, however, as nitrogen compounds on the earth's surface and in the soil. The changes that these nitrogen compounds undergo are a part of a natural cycle. Some nitrogen from the air is converted into compounds either by electrical discharges or by the action of the nitrifying bacteria that live upon the roots of leguminous plants. This nitrogen is then used by plants in synthesizing complex nitrogenous compounds called *proteins*, which compose plant structures, or which are stored away in seeds, fruits, roots, blades, branches, or leaves. These proteins serve, in part, as foods for animals, which convert them into other proteins, often of a more complex structure.

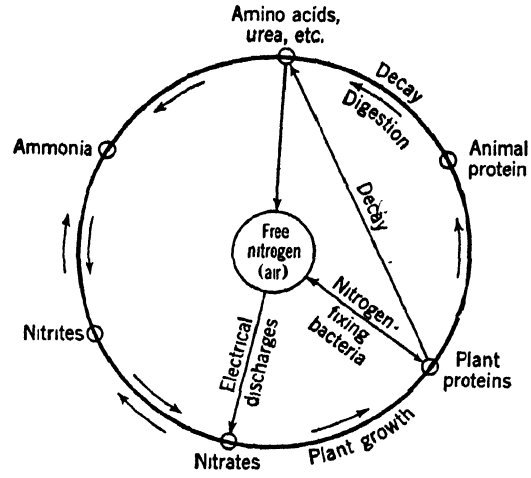


Figure 207. The Nitrogen Cycle

Eventually, many of them are eliminated as waste nitrogenous products of the animal body. Plant and animal proteins finally undergo decomposition and decay. Some may be destroyed by combustion. In these changes, some of the nitrogen may escape into the free state, while the remainder is converted into ammonia, nitrites, and nitrates and may again be used by plants.

AMMONIA

At one time ammonia was prepared by heating the horns and hoofs of animals in the absence of air. The gas produced during the decomposition of these materials, which contain nitrogenous (protein) organic compounds, was dissolved in water to form a solution called *spirits of hartshorn*. Pure ammonia was probably prepared for the first time by Priestley, about 1774, by heating *sal ammoniac* with slaked lime. The name *ammonia* was given to the gas by Bergman (1782), and Berthollet (1785) determined the composition of the compound.

10. Laboratory Methods of Preparation

When a solution of ammonium hydroxide is warmed, ammonia escapes and, being

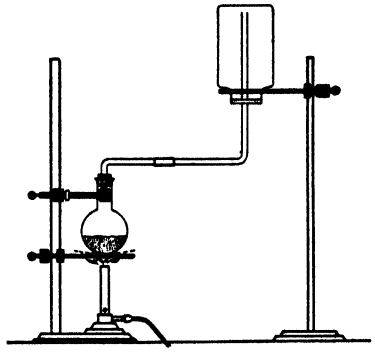


Figure 208. The Preparation of Ammonia and Its Collection by the Downward Displacement of Air

lighter than air, can be collected by the downward displacement of air (Figure 208).

Instead of using pure ammonium hydroxide solution, an ammonium salt may be treated with sodium hydroxide or calcium hydroxide. This brings together NH_4^+ and OH^- ions, which react to form ammonia and water. If the mixture is heated, ammonia is liberated and can be collected in the same manner as described above.

Ammonia may be produced by the hydrolysis of magnesium nitride:

$$Mg_3N_2 + 6\,HOH \longrightarrow 3\,Mg(OH)_2 + 2\,NH_3.$$

The magnesium nitride is prepared by passing nitrogen over heated magnesium.

11. The Production of Ammonia from Coal

Coal contains an average nitrogen content of about one per cent. When coal is destructively distilled, in the manufacture of coke, a portion of this nitrogen (about one fifth) is converted into ammonia. In the by-product coking process (page 294), the gases, including ammonia, produced by the distillation of coal are first passed through an extractor to remove the tar and are then washed by passing them through scrubbers containing water. The ammonia dissolves, forming a solution of ammonium hydroxide and ammonium salts. This solution is called *ammoniacal liquor*. It is treated with slaked lime to convert the ammonium salts into ammonium hydroxide, and the mixture is then treated with steam to drive off the ammonia. This purified ammonia is dissolved in water or in a solution of sulfuric acid with which it forms ammonium sulfate, which is used chiefly as a fertilizer. About 20 pounds of ammonium sulfate are produced from each ton of coal.

12. The Haber Synthetic Ammonia Process

Of the many proposed methods of converting the nitrogen in the atmosphere into useful compounds, the method called the *synthetic ammonia* or *Haber process* has proved most successful. This process involves the direct synthesis of ammonia from nitrogen and hydrogen. It was used on a large scale for the first time during the first World War to supplement the production of ammonia from coal and other sources. From this ammonia nitric acid, which was needed for the production

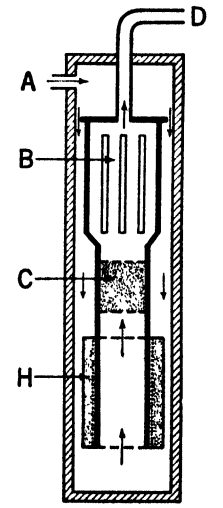


Figure 209. The Reaction Chamber of the Haber Synthetic Ammonia Process

The mixture of nitrogen and hydrogen enters at A, passes down around the catalytic chamber and finally over the catalyst at C. The gaseous mixture is heated, before passing over the catalyst, in H, where heat is supplied by the flow of an electric current through resistance wire. After the reaction in C, the gases flow out through the cooling chamber B and into absorbing towers through D.

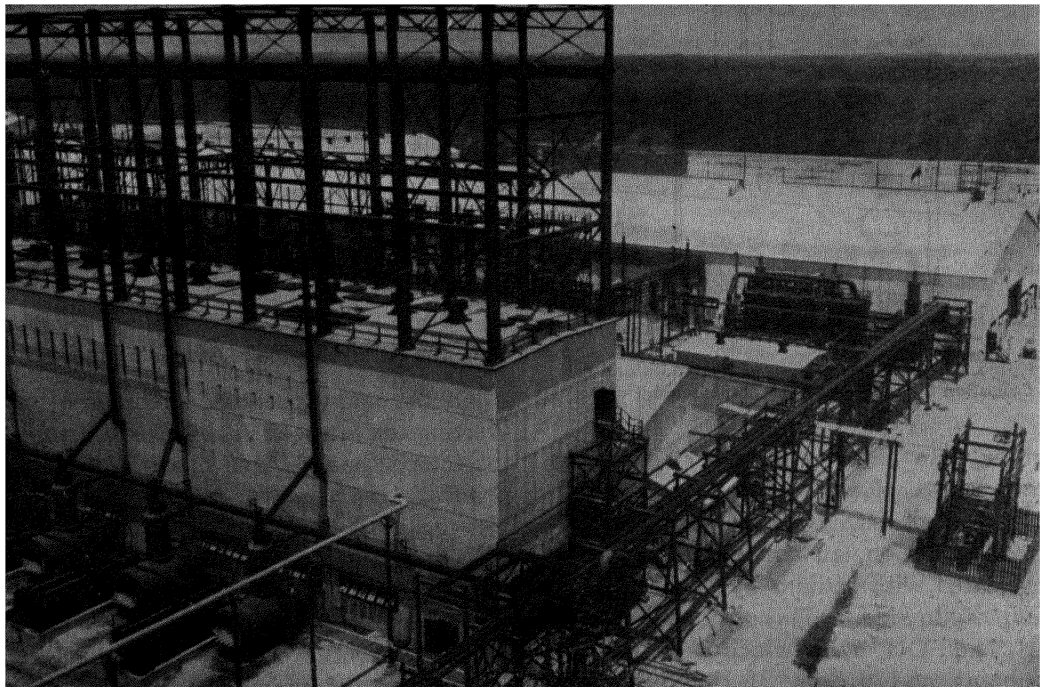


Figure 210. Synthetic Ammonia Plant
(Courtesy of Chemical Construction Co.)

of explosives, was produced. Between World Wars I and II, this method of producing ammonia and nitric acid became the chief source of these substances.

The reaction of nitrogen and hydrogen to produce ammonia is exothermic:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 24{,}400 \text{ calories.}$$

It is also reversible. According to Le Chatelier's principle (page 317), an increase in the temperature should reduce the percentage of nitrogen which is converted into ammonia. The actual effect of an increase in temperature is shown in Table 16, columns (1) and (2), in which the advantage of low temperature is clearly indicated. At low temperatures, however, the speed of the reaction is so slow that the rate at which ammonia is produced is not practical.

The only practical solution to a problem of this kind is the use of a catalyst that will accelerate the speed of the reaction at a low temperature. Among the catalytic substances which have been used are osmium, uranium, a mixture of iron and molybdenum, and a mixture of iron and potassium aluminate (potassium and aluminum oxides). One other factor may also be controlled in such a way that the percentage of ammonia is increased for a given temperature. From the equation for the reaction, it is evident that one volume of nitrogen reacts with three volumes of hydrogen to form two volumes of ammonia. The reaction is favored, therefore, by high pressure. This effect is shown by the data in Table 16, columns (2)–(5). The pressure employed in practice ranges from 200 to 1000 atmospheres and the temperature from 400° to 600°. The present producing capacity for synthetic ammonia in the United States is 1,200,000 short tons per year.

TABLE 16. EFFECT OF TEMPERATURE AND PRESSURE UPON THE PRODUCTION OF SYNTHETIC AMMONIA

Temperature Degrees C.	Percentage of Ammonia in the Equilibrium Mixture			
	1 atmosphere	100 atmospheres	200 atmospheres	250 atmospheres
200°	15.3	....	86.0	....
300°	2.2	....	...	....
500°	0.13	10.2	17.6	20.0
600°	0.05	4.5	8.2	9.5
700°	0.02	2.0	4.0	5.0
800°	0.01	1.1	2.2	2.8
900°	....	0.8	1.2	1.8
1000°	0.004	0.4	0.9	1.2

13. Calcium Cyanamide

Ammonia can be produced, also, from calcium cyanamide, $CaCN_2$, which is manufactured from coke, limestone, and free nitrogen. Although not nearly so widely used as a method of producing ammonia as the Haber process, it is an important nitrogen fixation method.

The steps involved in the production of calcium cyanamide employ inexpensive raw materials but require large amounts of energy.

(1) Limestone is heated with coke in an electric furnace. The coke reduces the limestone and forms calcium carbide.

$$CaCO_3 + 4\,C \longrightarrow CaC_2 + 3\,CO.$$

(2) Calcium carbide is heated to a temperature of about 1000° and nitrogen (obtained from liquid air) is passed over it. The reaction produces calcium cyanamide:

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C.$$

Calcium cyanamide is then treated in autoclaves with steam under pressure:

$$CaCN_2 + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3.$$

The cyanamide, itself, may be used as a fertilizer. As such it is sometimes called *lime nitrogen*. It is also converted into certain nitrogen compounds.

14. Physical Properties of Ammonia

Ammonia is a colorless gas. It is readily detected by its sharp, irritating, and suffocating odor. If pure ammonia is breathed, it is very poisonous in its effects and may cause death in a few minutes, but when greatly diluted with air, it appears to have no serious effects. Its density is a little more than half that of air; under standard conditions, one liter weighs 0.771 g. It can be collected, therefore, by the downward displacement of air. It cannot be collected over water because it is very soluble; one volume of water at 20° dissolves about 700 volumes of ammonia under one atmosphere of pressure. Its critical temperature is 132.9°, and its critical pressure is 112 atmospheres; therefore, it is easily liquefied. The liquid boils at − 33.4° and freezes at − 77.7°. Its heat of vaporization — 317 calories per gram — is relatively great as compared with that of most other liquids. This fact, together with the ease with which it can be liquefied, makes ammonia a suitable substance to use in refrigerators and in the manufacture of ice. The concentrated aqueous solution (aqua ammonia) contains about 28 per cent of ammonia at ordinary temperatures and weighs about 0.9 g. per ml. Liquid ammonia resembles water to some extent in its action as a solvent; it has a high dielectric constant and serves, therefore, as a good ionizing medium for electrolytes.

15. The Chemical Properties of Ammonia

The chemical behavior of ammonia is best described by the following specific reactions:

(1) Ammonia reacts with the water in which it dissolves to form small concentrations of ammonium and hydroxyl ions. The solution is referred to, usually, as a solution of the weak base, ammonium hydroxide (page 323).

It is possible that a solution of ammonia in water contains some molecules of NH_4OH, and if so it may be assumed that these molecules are in equilibrium with NH_4^+ and OH^- ions. Whether or not this is true can scarcely be tested experimentally, but, at least, it appears reasonable to believe that the high solubility of ammonia in water must be accounted for by the rather extensive hydration of ammonia to form not only the monohydrate, NH_4OH, but perhaps other hydrates as well. For our purposes, however, it is sufficient to think of the solution as containing only NH_4^+, NH_3 and OH^-.

If an acid is added to the solution, an ammonium salt of the acid is produced. When ammonia and hydrogen chloride are mixed as gases, ammonium chloride is produced in the form of a white cloud, which can serve as an effective smoke screen.

(2) Ammonia burns readily in pure oxygen to form water and nitrogen. Mixed with about ten times its volume of air and passed over a platinum gauze heated to 600°, ammonia is oxidized to form nitric oxide and water:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O.$$

This reaction is the basis of the Ostwald process of converting ammonia into nitric acid (page 352).

(3) Ammonia acts as a reducing agent. It reacts, for example, with hot cupric oxide to form free copper, water, and nitrogen:

$$3\ CuO + 2\ NH_3 \longrightarrow 3\ Cu + N_2 + 3\ H_2O.$$

(4) In some of its reactions ammonia acts as HNH_2. Thus, sodium reacts when heated with ammonia to replace hydrogen and to form *sodamide*, ($NaNH_2$), just as it reacts with water to form NaOH and hydrogen:

$$2\ Na + 2\ HNH_2 \longrightarrow 2\ NaNH_2 + H_2.$$

(5) Ammonia also reacts with some compounds in the same manner that water does when these compounds hydrolyze:

$$HgCl_2 + HNH_2 \longrightarrow HgNH_2Cl\downarrow + HCl.$$

Using water instead of ammonia, this reaction would be:

$$HgCl_2 + HOH \longrightarrow HgOHCl + HCl.$$

(6) It also reacts with some salts to form compounds corresponding to hydrates. With calcium chloride, ammonia forms the compound $CaCl_2.8\ NH_3$.

16. Complex Ions Containing Ammonia

Many metallic ions combine with ammonia to form *complex ions*. These are thought to be produced when the nitrogen atom of the ammonia molecule shares its unused pair of electrons with the metallic ion.

$$Cu^{++} + 4\ NH_3 \rightleftharpoons \left[\begin{array}{c} NH_3 \\ \vdots \\ H_3N : Cu : NH_3 \\ \vdots \\ NH_3 \end{array}\right]^{++}$$

$$Ag^+ + 2\ NH_3 \rightleftharpoons [H_3N : Ag : NH_3]^+.$$

These complex ions are only slightly dissociated,

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\ NH_3,$$

in solution. Hence, the concentration of the silver ion is easily reduced to a very small value by adding ammonia to a suspension of silver chloride in water. It becomes so small that the solubility product of silver chloride is not exceeded, and this substance then dissolves completely if enough ammonia is added.

17. Coordination Numbers

The complex ion of copper and ammonia

described above and many other similar structures result from the sharing of pairs of electrons belonging originally to one molecule or ion with a simple ion, such as Cu^{++}, that can accept such electrons. A bond of this kind is covalent in nature, but it is evidently somewhat different from the usual bond of this kind in which each of the atoms provide one electron of the pair that they share. It is called a *coordinate covalent*, or simply a coordination, bond. The numbers of such bonds that a central atom, as the copper atom in $Cu(NH_3)_4^{++}$, forms is called the *coordination number* of the central atom. Thus, in the examples cited above copper's coordination number is 4, and silver's is 2.

18. Liquid Ammonia as a Solvent

The behavior of liquid ammonia as a solvent is very much like that of water. There is, however, a great deal of difference in the solubility of certain substances in the two solvents. Ammonia, for example, dissolves silver chloride and other salts that are not soluble in water; on the other hand, some salts, like barium chloride, which are readily soluble in water, are very slightly soluble in ammonia. The alkali and alkaline earth metals (the calcium family of group two) dissolve in liquid ammonia to form blue solutions.

Liquid ammonia is a very feeble conductor of the electric current, but it does contain small concentrations of ions. These ions are formed, as in the case of water (page 326), by the interaction of two molecules of the liquid:

$$NH_3 + NH_3 \rightleftarrows NH_4^+ + NH_2^-.$$

Amide is the name of the NH_2^- ion, which corresponds to the hydroxyl ion of water, while the ammonium ion corresponds to the hydronium ion, H_3O^+ Salts that dissolve in liquid ammonia are highly ionized and can be electrolyzed.

Corresponding to the hydroxides of the active metals, e.g., KOH, are the amides, e.g., *potassium amide*, KNH_2. This substance dissolves in ammonia, and the solution affects indicators in the same manner as a solution of potassium hydroxide in water. The solution of an acid in liquid ammonia contains an ammonium salt of the acid that corresponds to the hydronium compound that the acid forms in water. For example in water hydrochloric acid forms $(H_3O^+ + Cl^-)$; in ammonia the corresponding compound is $(NH_4^+ + Cl^-)$. The similarity of the two ionic combinations is clearly indicated by their reactions with an active metal such as sodium:

$$2\,Na + 2\,(H_3O^+ + Cl^-) \longrightarrow 2\,(Na^+ + Cl^-) + H_2 + 2\,H_2O$$

$$2\,Na + 2\,(NH_4^+ + Cl^-) \longrightarrow 2\,(Na^+ + Cl^-) + H_2 + 2\,NH_3.$$

Furthermore, we can consider NH_4Cl as an acid that will neutralize amide-bases, just as a solution of HCl in water $(H_3O^+Cl^-)$ neutralizes hydroxide-bases:

$$(H_3O^+ + Cl^-) + (K^+ + OH^-) \longrightarrow (K^+ + Cl^-) + 2\,H_2O.$$

$$(NH_4^+ + Cl^-) + (K^+ + NH_2^-) \longrightarrow (K^+ + Cl^-) + 2\,NH_3.$$

19. Uses of Ammonia

Ammonia is used to form other compounds of nitrogen. Of these, nitric acid is most important, but large quantities are also converted into ammonium sulfate, ammonium carbonate, ammonium chloride, and other ammonium salts. It is also used in refrigeration and in the manufacture of ice (Figure 211). As *aqua ammonia*, it is used as a cleansing agent and water softener. The use of ammonia in the Solvay process for producing soda has already been discussed (page 244). It has some use in medicine, in manufacturing certain dyes, drugs, plastics and other organic compounds, and in bleaching and printing some kinds of cloth. Liquid ammonia, if allowed to boil rapidly under reduced pressure, can be used to produce temperatures as low as $-50°$. It is used in this way in one method of producing quickly frozen foods.

20. Ammonium Compounds

When an ammonium salt is treated with a base, such as Na^+OH^-, the ammonium and hydroxide ion react to form ammonia and water. The ammonia that escapes

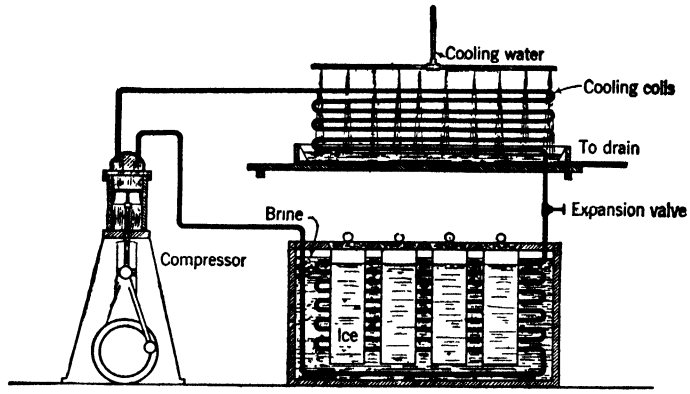


Figure 211. The Production of Ice by Means of Ammonia

The cooling that results in the formation of ice is brought about by allowing the compressed, liquefied ammonia to change into the gaseous state in the coils that surround the tanks in which the ice is formed.

from this solution can be detected by its odor or by its reaction with hydrogen chloride to form a white cloud of ammonium chloride. This procedure is used as a test for ammonium compounds.

Ammonium salts differ from the corresponding compounds of sodium and potassium in two respects: (1) They are hydrolyzed to a greater extent, because the ammonium ion reacts as an acid with water to form H_3O^+ ion, while Na^+ and K^+ ions do not react with water; and (2) ammonium salts are decomposed easily by heat.

$$NH_4Cl \rightleftarrows NH_3 + HCl$$
$$NH_4NO_3 \longrightarrow 2\ H_2O + N_2O$$
$$(NH_4)_2SO_4 \rightleftarrows 2\ NH_3 + H_2O + SO_3.$$

Ammonium chloride is used as a flux in soldering and in manufacturing dry cells. Ammonium sulfate is an important fertilizer (page 341). Ammonium nitrate is used as an ingredient in certain explosives. Ammonium carbonate, $(NH_4)_2CO_3$, mixed with alcohol and aromatic oils, is used as "smelling salts."

REVIEW EXERCISES

1. How does nitrogen that is prepared from air differ from nitrogen prepared from NH_4NO_2?
2. What are the three principal sources of compounds of nitrogen?
3. Why do molecules of nitrogen display little chemical activity?
4. What are some of the important types of the compounds of nitrogen?
5. In what natural ways is the soil enriched in nitrogen?
6. Describe the cycle of nitrogen and its compounds in nature.
7. Summarize the three principal methods of producing ammonia on an industrial scale. Compare these processes, showing what advantages, if any, each has over the other two.
8. State the conditions which favor the reactions of the Haber process and explain how each condition affects the reaction.
9. Illustrate each of the important chemical properties of ammonia by an equation. How is ammonia similar to water?
10. Why do the hydroxides of some metals dissolve in a solution of ammonia?
11. Describe the reactions employed in the cyanamide process. Why is this process not used as extensively as the Haber process?
12. How is the NH_4^+ ion prepared from NH_3?
13. What kinds of particles are contained in an aqueous solution of ammonia?
14. What is the maximum weight of nitrogen that can be obtained by passing 24 (standard) liters of ammonia over cupric oxide?
15. What volume (standard) of ammonia could be produced from 100 g. of calcium cyanamide?

16. If the ammonia is completely oxidized, in the presence of platinum, to form nitric oxide, NO, what volume of the latter, under standard conditions, can be produced from one liter of liquid ammonia, which has a density 0.62 g. per milliliter?
17. What (standard) volume of air must be used to produce the liquid ammonia required to fill a cylinder holding 100 liters? Assume that all the nitrogen of the air is converted into ammonia by the Haber process.
18. What (standard) volume of ammonia can be produced from 10 g. of ammonium chloride?
19. Write equations for reactions that occur when.
    (*a*) Ammonia is converted into nitric oxide.
    (*b*) Ammonium nitrite is heated.
    (*c*) Calcium cyanamide reacts with steam.
    (*d*) Magnesium nitride hydrolyzes.
    (*e*) Calcium hydroxide reacts with ammonium sulfate.
    (*f*) Silver chloride dissolves in a solution of ammonium hydroxide.
    (*g*) Calcium carbide reacts with nitrogen.
    (*h*) Sodium reacts with ammonia.
    (*i*) Mercuric chloride reacts with ammonia.
20. Explain the use of ammonia in a refrigerating unit.
21. What are the different oxidation states of nitrogen? Which are most important?
22. What changes in the oxidation numbers of nitrogen occur in the reaction of ammonium nitrite and ammonium chloride to form free nitrogen?
23. Of what importance to man is the fact that nitrogen and oxygen do not react readily?
24. In what ways is sodamide similar in properties to sodium hydroxide?
25. Compare ($H_3O^+Cl^-$) and ($NH_4^+Cl^-$) as to method of formation and chemical properties.
26. How is the NH_4^+ ion like the ions of the alkali metals and how is it different?

REFERENCES FOR FURTHER READING

U.S. Bureau of Mines, *Nitrogen and Its Compounds*, Information Circular 6385, Washington, D.C.

Ammonia: *J. Chem. Ed.*, **8,** 55 (1931); *Chem. and Met. Eng.*, **45,** 682 (1938); **48,** 117 (1941).

Liquid Ammonia: *J. Chem. Ed.*, **5,** 828 (1928); **6,** 441 (1929).

Nitrogen Fixation: *Chem. and Met. Eng.*, **19,** 574 (1918); **26,** 58 (1922); **28,** 498 (1923); **29,** 105 (1924); **32,** 321 (1925); **33,** 165 (1926); **38,** 82 (1931); **43,** 282 (1936); **47,** 253 (1940); *Ind. and Eng. Chem.*, **10,** 270 (1918); **11,** 541 (1919); **17,** 775, 862, 1000 (1925); **19,** 789, 1153, 1250 (1927); **20,** 1128 (1928); **22,** 433, 795, 1099 (1930); *J. Chem. Ed.*, **3,** 50, 170 (1926); **4,** 845 (1927); **6,** 894, 2097 (1929); **7,** 2571 (1930); **9,** 1113, 1829, 1847 (1932); **11,** 101, 457 (1934).

Nitrogen Industry: *Chem. and Met. Eng.*, **43,** 282 (1936); *Ind. and Eng. Chem., News Edition*, **17,** 86 (1939); **18,** 759 (1940).

28

OTHER COMPOUNDS OF NITROGEN: OXIDES, OXYGEN ACIDS, CYANIDES

OXIDES

Name	Formula	Physical Properties
Nitrous oxide	N_2O	Colorless gas; boiling point $-90°$
Nitric oxide	NO	Colorless gas; boiling point $-151°$
Nitrogen trioxide	N_2O_3	Blue liquid; boiling point 3.5°
Nitrogen dioxide	NO_2, N_2O_4	Red-brown gas; at low temperatures, a colorless gas, N_2O_4, or a light yellow liquid, boiling point 21.3°
Nitrogen pentoxide	N_2O_5	White solid

1. Nitrous Oxide

This oxide of nitrogen is a colorless gas at ordinary temperatures. It can be prepared by carefully heating ammonium nitrate:

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

If the heating is very vigorous, ammonium nitrate may decompose explosively. The gas is usually collected over warm water.

Nitrous oxide is an endothermic compound:

$$2\ N_2O\ (g) \longrightarrow 2\ N_2 + O_2 + 34{,}000 \text{ calories.}$$

It is, consequently, unstable and acts as a vigorous oxidizing agent. A glowing splint will burst into flame in an atmosphere of this gas almost as readily as in pure oxygen.

Sir Humphry Davy discovered that nitrous oxide when breathed produces peculiar exhilarating and intoxicating effects. It is called *laughing gas* because of the hysterical laughter or weeping which it produces. It is used as an anesthetic by dentists and for minor surgical cases. As such it is pleasant, quick in its action, and without harmful after-effects. When it is administered as an anesthetic, it must be mixed with oxygen. Oxygen does not oxidize nitrous oxide, under ordinary conditions, to any of the higher oxides.

2. Nitric Oxide

Small amounts of this oxide are produced from the oxygen and nitrogen in the air during thunder storms. Cavendish first prepared the compound by subjecting a mixture of the two elements to an electrical discharge. It has been made on an industrial scale by passing a mixture of oxygen and nitrogen through an electric arc. It is also produced by the oxidation of ammonia:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O.$$

In the laboratory, it is usually prepared by

the action of *dilute* (about 6 N) nitric acid upon copper:

$$3\ Cu + 8\ (H^+ + NO_3^-) \longrightarrow 3\ (Cu^{++} + 2\ NO_3^-) + 2\ NO\uparrow + 4\ H_2O.$$

Nitric oxide is a colorless gas and is only slightly soluble in water. Its most important chemical property is its reaction with oxygen to form nitrogen dioxide, a reaction involved in the production of nitric acid (page 352):

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

It acts, therefore, as a reducing agent. It may also act as an oxidizing agent, but only with the most active reducing agents. With some ions of metals it forms complex ions, as $Fe(NO)^{++}$.

3. Nitrogen Trioxide

This oxide is the anhydride of nitrous acid (HNO_2), which is formed, at least temporarily, when a nitrite is treated with sulfuric acid. Nitrous acid decomposes, under ordinary conditions, into water and a mixture of two gases, NO_2 and NO. When a mixture of the two oxides is cooled to 3.5°, there is produced a blue liquid, which is probably N_2O_3. At higher temperatures, there is probably an equilibrium between N_2O_3 and its decomposition products:

$$N_2O_3 \rightleftarrows NO_2 + NO.$$

4. Nitrogen Dioxide

This oxide can be prepared by allowing *concentrated* nitric acid to act upon copper:

$$Cu + 4\ (H^+ + NO_3^-) \longrightarrow (Cu^{++} + 2\ NO_3^-) + 2\ NO_2\uparrow + 2\ H_2O.$$

It is also prepared by heating the nitrate of a heavy metal:

$$2\ Cu(NO_3)_2 \longrightarrow 2\ CuO + 4\ NO_2 + O_2.$$

Nitrogen dioxide is produced on an industrial scale by allowing nitric oxide to react with the oxygen of the air.

This oxide exists in two forms: a red-brown gas, NO_2, at moderately high temperatures, and a colorless gas, or slightly yellow liquid, N_2O_4, at low temperatures. At ordinary temperature, both forms exist as a mixture. The oxide N_2O_4 is a *polymer* of NO_2. *Polymerization* refers to the process in which two or more molecules of the same kind combine with one another. In this case two molecules of the dioxide combine to form one of the tetroxide. The NO_2 molecule contains an odd number of valence electrons — twelve for the two atoms of oxygen and five for nitrogen; and hence there must be one electron in the molecule that is not paired. The combining of two molecules of NO_2 to form one of N_2O_4 is, no doubt, the result of the tendency of the odd electrons of the two molecules of NO_2 to form a pair.

Nitrogen dioxide is very poisonous. It acts as an oxidizing agent but supports combustion only at fairly high temperatures. It is also a reducing agent, since it can be converted into nitric acid and the nitrates. The most important property of NO_2 is its reaction with water:

$$2\ NO_2 + H_2O(cold) \longrightarrow HNO_2 + HNO_3$$
$$3\ NO_2 + H_2O(hot) \longrightarrow 2\ HNO_3 + NO.$$

5. Nitrogen Pentoxide

This oxide is the anhydride of nitric acid. It is a white crystalline solid. It may be produced by dehydrating nitric acid with phosphorus pentoxide:

$$4\ HNO_3 + P_4O_{10} \longrightarrow 2\ N_2O_5 + 4\ HPO_3.$$

6. Nitrous Acid and the Nitrites

Nitrous acid has never been prepared in the pure state. We assume, however, that it is formed whenever a mixture of NO and NO_2 is passed into cold water, because when this solution is neutralized with NaOH and evaporated, crystals of sodium nitrite ($NaNO_2$) are obtained.

Sodium and potassium nitrites are the

most important of the salts of this acid. They are used as laboratory reagents and in the manufacture of certain organic chemicals and dyestuffs.

Sodium nitrite is prepared by passing a mixture of NO and NO_2 into a solution of NaOH; by heating sodium nitrate at a temperature above its melting point; and by heating sodium nitrate with metallic lead:

$$NO + NO_2 + 2\,(Na^+ + OH^-) \longrightarrow 2\,(Na^+ + NO_2^-) + H_2O.$$

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

$$NaNO_3 + Pb \longrightarrow PbO + NaNO_2.$$

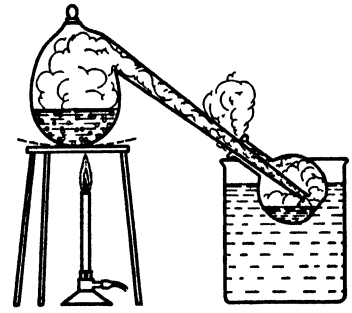


Figure 212. The Preparation of Nitric Acid in the Laboratory

Sodium nitrate and sulfuric acid are heated in the retort. Pure nitric acid is condensed in the neck of the retort.

7. The Production of Nitric Acid from Sodium Nitrate

The most convenient method of producing nitric acid in the laboratory involves the distillation of a mixture of sodium nitrate (solid) and concentrated sulfuric acid:

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

This reaction is similar to the one which is used to prepare HCl from NaCl. In producing nitric acid, however, the second step in which $NaHSO_4$ reacts with additional $NaNO_3$ is not carried out, since it requires a fairly high temperature, at which nitric acid is decomposed. This reaction has been used very extensively until recent years to produce HNO_3 on a commercial scale. The essentials of a nitric acid plant are shown in Figure 213. The nitric acid is distilled from an iron retort under reduced pressure in order to avoid decomposition. The acid is condensed in tubes made of some acid resisting material, such as glass, quartz, or duriron. Now, however, nitric acid is produced, for the most part, from ammonia. In fact, at the outbreak of World War II, sodium nitrate supplied only about 8 per cent of the world's

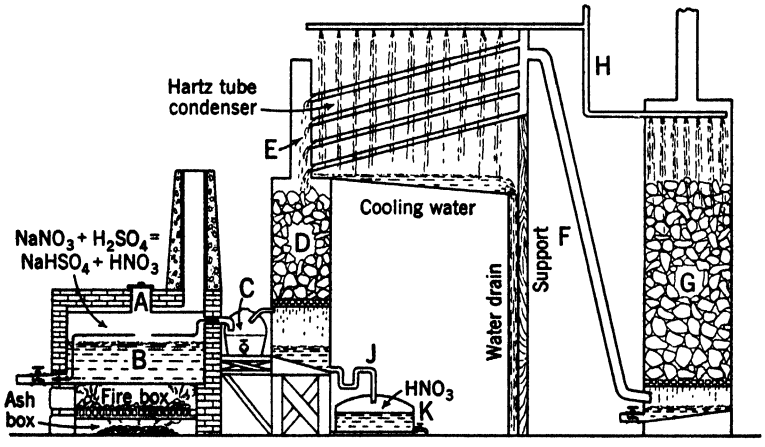


Figure 213. Nitric Acid Plant

The charge of sodium nitrate and sulfuric acid is added through A. B is the retort, C is a trap to catch the overflow from the retort, D is a tower containing quartz chips over which the nitric acid that is condensed in the tube condensers flows; in D the rising fumes of hot nitric acid remove the oxides of nitrogen that are present in the condensed acid. The last traces of HNO_3 are absorbed in the tower G by water which flows over the quartz chips with which the tower is filled.

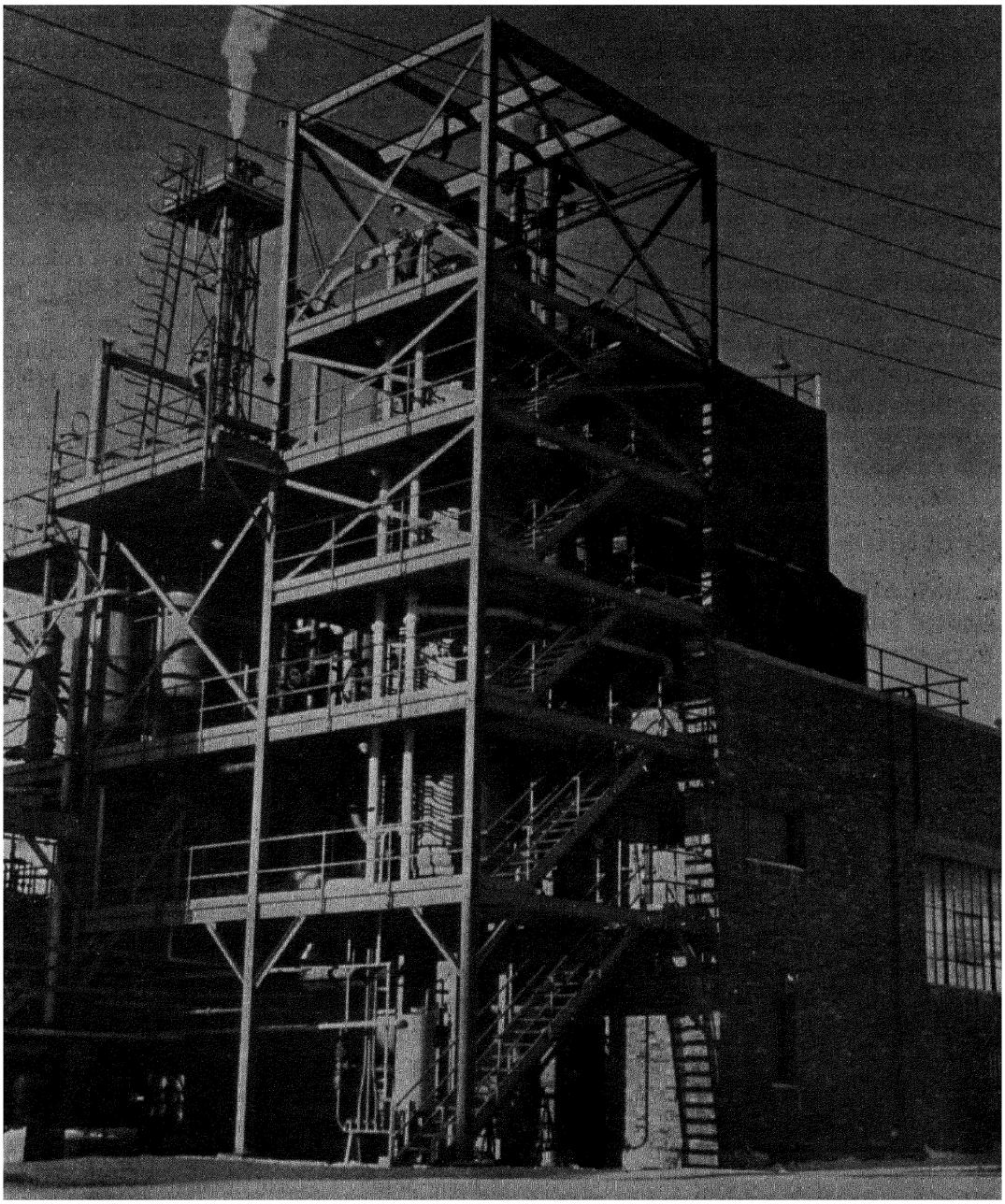


Figure 214. Synthetic Nitric Acid Plant
(Courtesy of Monsanto Chemical Company)

production of about 3,000,000 tons of combined nitrogen in all forms.

8. Production of Nitric Acid from Ammonia

This process, sometimes called the *Ostwald process*, depends upon the oxidation of ammonia by air in the presence of platinum as a catalyst. Ammonia is mixed with air and passed through a platinum gauze or screen, which is heated to about 700°, in the beginning, by means of an electric current, but when the reaction has started, it liberates sufficient heat to maintain this temperature without any outside help. Since the reaction is exothermic, high temperatures are unfavorable. The following reactions occur in the chamber containing the catalyst:

$$(1)\quad 4\,NH_3 + 5\,O_2 \longrightarrow 6\,H_2O + 4\,NO.$$

The nitric oxide is cooled and immediately converted into nitrogen dioxide by allowing it to react with oxygen in the air:

$$(2)\quad 2\,NO + O_2 \longrightarrow 2\,NO_2.$$

The nitrogen dioxide is then passed into an absorption tower, where it is allowed to react with warm water:

$$(3)\quad 3\,NO_2 + H_2O \longrightarrow 2\,(H^+ + NO_3^-) + NO.$$

The nitric oxide resulting from this reaction is returned to the process (2) and again converted into NO_2. Sometimes, this nitric oxide is mixed with air and converted directly into nitrates by passing it into a solution of a base, such as NaOH or $Ca(OH)_2$ (in suspension), or by allowing it to react upon a mixture of limestone and water:

$$2(Ca^{++} + 2\,OH^-) + 4\,NO + 3\,O_2 \longrightarrow 2\,H_2O + 2\,(Ca^{++} + 2\,NO_3^-)$$

$$2\,CaCO_3 + 3\,O_2 + 4\,NO \longrightarrow 2\,(Ca^{++} + 2\,NO_3^-) + 2\,CO_2.$$

The solution of nitric acid produced in this process contains about 60 per cent of HNO_3. It is further concentrated by distilling it from a mixture with sulfuric acid.

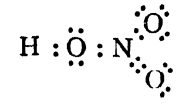
Coupled with the Haber process for producing ammonia, the Ostwald process has solved the problem of the production of nitric acid from the nitrogen in the air. Almost all the nitric acid manufactured in the United States is made in this way.

9. The Physical Properties of Nitric Acid

When nitric acid is pure, it is a colorless liquid, which has a density of 1.502 g. per cc. at 25°, boils at 86° and freezes at − 42°. The constant boiling aqueous solution (b.p. 120.5°) contains 68 per cent of HNO_3 and has a density of 1.4 g. per cc. at 25°. This is the ordinary concentrated nitric acid used in the laboratory and in the industries. This solution dissolves the oxides of nitrogen, especially NO_2, and forms a brown solution that is called *fuming nitric acid.* This contains about 96 per cent of HNO_3.

10. The Chemical Properties of Nitric Acid

The electronic formula of nitric acid appears to be



although other resonant electronic arrangements for the molecule and for the NO_3^- ion are possible.

Chemically, nitric acid acts (1) as a strong acid and (2) as a vigorous oxidizing agent. As an oxidizing agent, it reacts with many different kinds of substances. Sulfur is oxidized to sulfur dioxide or sulfuric acid. Carbon forms carbon dioxide. Charcoal which has been ignited will continue to burn when immersed in concentrated HNO_3. Phosphorus is converted into phosphoric acid (H_3PO_4 or HPO_3), and iodine into iodic acid (page 287). Some of the more important reactions of HNO_3 are discussed below.

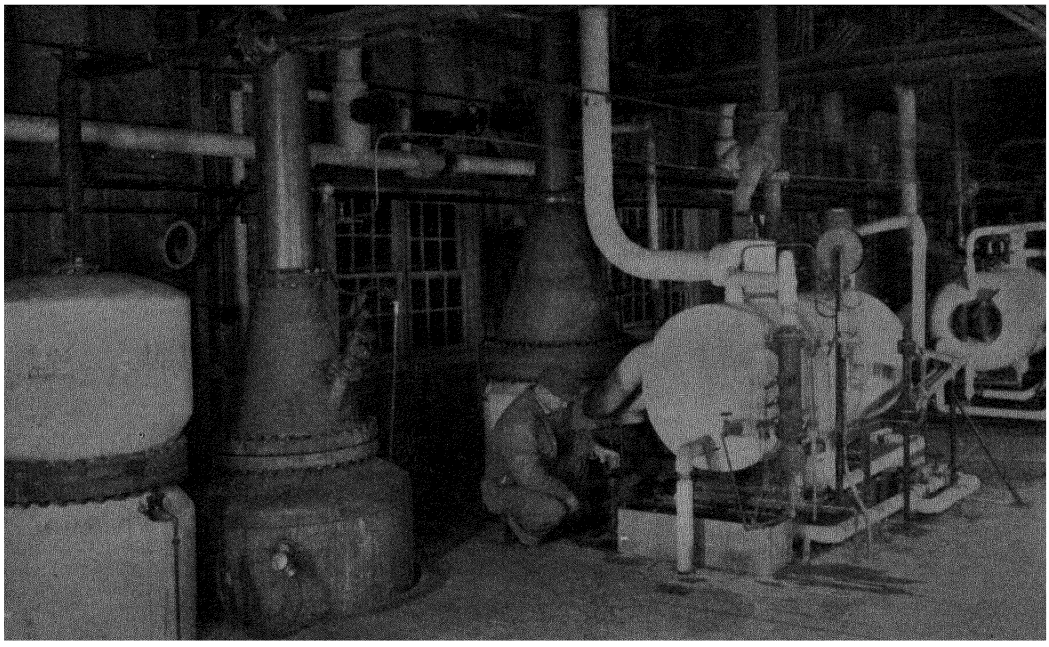


Figure 215. Ammonia Burners and Waste Heat Boilers in Plant Producing Nitric Acid from Ammonia
(Courtesy of Chemical Construction Company)

11. Action upon Metals

Nitric acid attacks all metals except platinum, gold, and some of the rarer ones. When moderately dilute (about 6 N), nitric acid acts upon copper or other metals well toward the bottom of the electrochemical series, nitric oxide is formed:

$$3\,Cu + 8\,(H^+ + NO_3^-) \longrightarrow 3\,(Cu^{++} + 2\,NO_3^-) + 2\,NO + 4\,H_2O.$$

If concentrated nitric acid is used, nitrogen dioxide, instead of nitric oxide, is formed:

$$Cu + 4\,(H^+ + NO_3^-) \longrightarrow (Cu^{++} + 2\,NO_3^-) + 2\,NO_2 + 2\,H_2O.$$

It is often impossible to predict the final state of the nitrogen when the acid acts upon the more active metals, such as zinc or aluminum. The nitrogen may appear among the products of the reaction as NO_2, NO, N_2O, N_2, NH_3, or NH_4NO_3. In general, the greater changes in the oxidation numbers of nitrogen occur when dilute nitric acid and an active reducing agent react. With more concentrated acid and a less vigorous reducing agent, the product is more likely to be NO or even NO_2. With zinc, for example, the usual reaction is:

$$3\,Zn + 8\,(H^+ + NO_3^-) \longrightarrow 3\,(Zn^{++} + 2\,NO_3^-) + 2\,NO + 4\,H_2O.$$

But if the acid is dilute any or all of the following reactions may occur:

(1) $$4\,Zn + 9\,(H^+ + NO_3^-) \longrightarrow NH_3 + 4\,(Zn^{++} + 2\,NO_3^-) + 3\,H_2O$$
$$NH_3 + (H^+ + NO_3^-) \longrightarrow NH_4^+ + NO_3^-$$

(2) $$4\,Zn + 10\,(H^+ + NO_3^-) \longrightarrow 4\,(Zn^{++} + 2\,NO_3^-) + 5\,H_2O + N_2O$$

(3) $$5\,Zn + 12\,(H^+ + NO_3^-) \longrightarrow 5\,(Zn^{++} + 2\,NO_3^-) + 6\,H_2O + N_2.$$

12. Action upon Hydrochloric Acid

Nitric acid oxidizes hydrochloric acid to form free chlorine and water:

$$2\,(H^+ + NO_3^-) + 6\,(H^+ + Cl^-) \longrightarrow 4\,H_2O + 2\,NO + 3\,Cl_2.$$

Some of the chlorine reacts with nitric oxide to form *nitrosyl chloride* (NOCl). A mixture of one part of nitric acid and three parts of hydrochloric is often called *aqua regia*. This name was first used by the alchemists because the mixture of acids dissolves gold, platinum, and other "noble" metals, which are not affected by either acid alone. Chlorine converts the metals into chlorides, $AuCl_3$ and $PtCl_4$, which may combine with chloride ions to form the complex ions, $AuCl_4^-$ and $PtCl_6^=$.

13. Action upon Glycerine

Nitric acid reacts with certain organic compounds that contain the hydroxyl (OH) radical to form nitrates. The reaction is illustrated by the formation of "nitroglycerine" from concentrated nitric acid and glycerine:

$$\underset{\text{(Glycerine)}}{C_3H_5(OH)_3} + 3\,(H^+ + NO_3^-) \longrightarrow 3\,H_2O + \underset{\text{(Nitroglycerine)}}{C_3H_5(NO_3)_3}.$$

The product is called "nitroglycerine" erroneously since it is really a nitrate — *glyceryl nitrate*. It is a powerful explosive.

14. Action upon Cellulose and Starch

Nitric acid acts in a similar manner upon cellulose and starch to form nitrates of these substances. The reactions are similar to that used in making glyceryl nitrate, since starch and cellulose, both of which are represented by the empirical formula $(C_6H_{10}O_5)_x$, [1] contain OH radicals in their molecules. With cellulose (of cotton or wood) the reaction is as follows:

$$[C_6H_7O_2(OH)_3]_x + 3\,x(H^+ + NO_3^-) \longrightarrow 3xH_2O + \underset{\text{(Cellulose nitrate)}}{[C_6H_7O_2(NO_3)_3]_x}$$

This nitrate of cellulose is called *gun cotton*. "Smokeless powder" is made from it. If the action of the nitric acid is allowed to proceed until the cellulose is only partially nitrated, a non-explosive compound called *pyroxylin*, which contains about 11 per cent of nitrogen, is formed. This substance is the basis of the production of lacquers ("Duco"), artificial leather, pyralin, photographic film, artificial silk, and other substances. Gelatin dynamite contains nitrated cellulose and nitroglycerine.

[1] The simplest formula for cellulose is $C_6H_{10}O_5$, but the actual molecules are made up of many of these simple units tied together in the form of long chains.

15. Action upon Benzene and Its Derivatives

Nitric acid reacts with certain compounds of carbon and hydrogen, and with certain derivatives of such compounds, to produce substances containing the *nitro*, $-NO_2$, group. With *benzene*, nitric acid reacts as follows:

$$\underset{\text{(Benzene)}}{C_6H_6} + (H^+ + NO_3^-) \longrightarrow HOH + \underset{\text{(Nitrobenzene)}}{C_6H_5NO_2}.$$

The product, called *nitrobenzene*, is not a nitrate, since it does not contain the nitrate (NO_3) radical. It is used to produce many organic compounds.

Toluene ($C_6H_5CH_3$) reacts with nitric acid to form the explosive, *trinitrotoluene* (T.N.T.):

$$C_6H_5CH_3 + 3\,(H^+ + NO_3^-) \longrightarrow C_6H_2(NO_2)_3CH_3 + 3\,H_2O.$$

With *phenol* (C_6H_5OH), also called *carbolic acid*, *trinitrophenol* or *picric acid* is produced:

$$C_6H_5OH + 3\,(H^+ + NO_3^-) \longrightarrow C_6H_2(NO_2)_3OH + 3\,H_2O.$$

Picric acid, a yellow solid, is used as an explosive, as a yellow dye, and in the treatment of burns.

16. Uses of Nitric Acid

Nitric acid is used both as a strong acid and as an oxidizing agent. Its use in the manufacture of explosives and various cellulose nitrate products has been mentioned

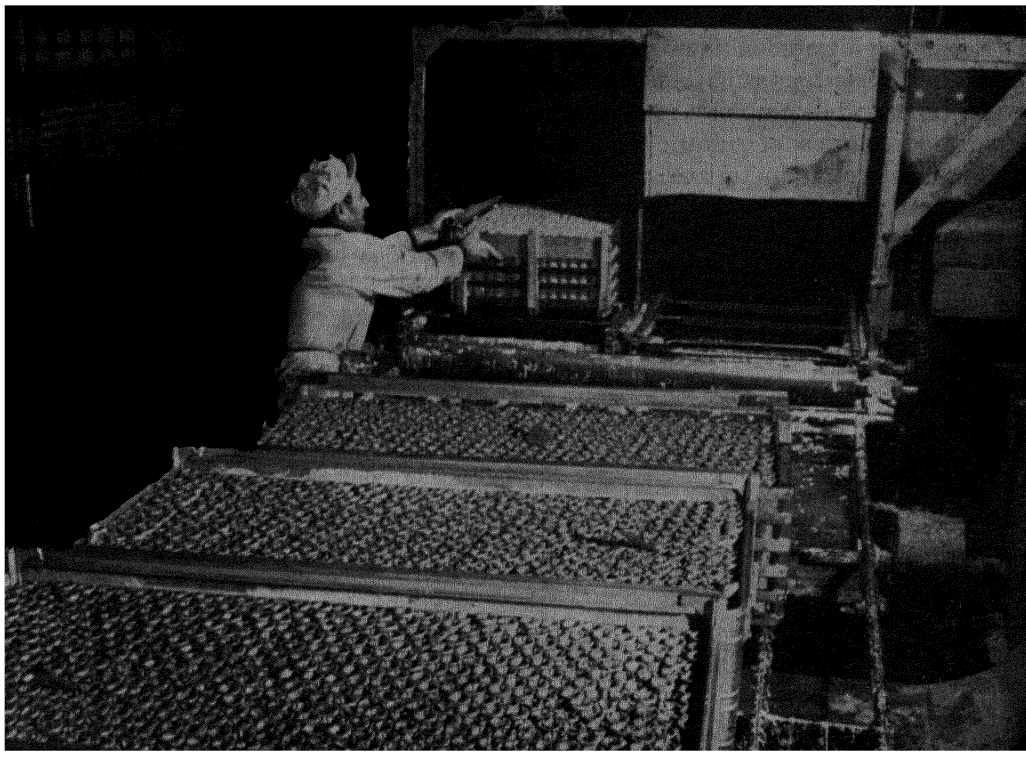


Figure 216. Production of Containers to be Filled with Dynamite
Dynamite is an explosive containing nitroglycerine.
(Courtesy of Du Pont Company)

in the preceding section. It is also used in the manufacture of many dyes and drugs. The nitrates, many of which are produced directly from nitric acid, also have many uses.

17. The Nitrates

The nitrates are produced by the action of nitric acid upon the metals or upon metallic oxides and hydroxides. All the nitrates of the metals are soluble in water, although some of them may hydrolyze to form slightly soluble basic salts:

$$(Bi^{+++} + 3\ NO_3^-) + H_2O \longrightarrow BiONO_3 \downarrow + 2\ (H^+ + NO_3^-).$$

When the nitrates of metals are heated, they are decomposed. Upon the basis of the products which they form when heated, the nitrates may be divided into the following classes:

(1) Those which decompose to give the oxide of the metal. This list includes the nitrates of the heavy metals.

$$2\ Cu(NO_3)_2 \longrightarrow 2\ CuO + 4\ NO_2 + O_2.$$

(2) Those which decompose to give oxygen but no oxide of nitrogen. These nitrates form nitrites of the metal.

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

Ammonium nitrate decomposes to give nitrous oxide and water vapor.

Nitrates are valuable fertilizers. The most important of those used for this purpose are calcium, sodium, and potassium nitrates. Ammonium nitrate mixed with powdered aluminum forms the explosive *ammonal*. With trinitrotoluene, it forms the explosive *amitol*.

18. Test for Nitrate Ion

To detect the nitrate ion a few milliliters of a solution of ferrous sulfate are placed in a test tube, and 2–3 ml. of a moderately concentrated solution of sulfuric acid are added by means of a pipette at the bottom of the tube so that the ferrous sulfate solution floats on the acid. A few drops of the solution to be tested are added. If a nitrate is present a brown compound, $Fe(NO)SO_4$, forms as a ring at the junction of the two solutions.

CYANOGEN AND THE CYANIDES

19. Cyanogen $(CN)_2$

The compound called *cyanogen* is somewhat like chlorine in a chemical sense. It reacts, for example, with potassium and sodium to form potassium or sodium cyanide, just as chlorine in similar reactions forms the chlorides:

$$2\ Na + (CN)_2 \longrightarrow 2\ NaCN$$

It is produced by heating mercuric cyanide:

$$Hg(CN)_2 \longrightarrow Hg + (CN)_2.$$

It can also be produced by an electrical discharge between carbon electrodes in an atmosphere of nitrogen. Cyanogen is a colorless, deadly poisonous gas. It burns to produce free nitrogen and carbon dioxide.

20. Hydrocyanic Acid (HCN) and Its Salts

This substance, which is commonly called *prussic acid*, is made by treating cyanides of the metals with sulfuric acid:

$$2\ (Na^+ + CN^-) + (2\ H^+ + SO_4^{=}) \longrightarrow (2\ Na^+ + SO_4^{=}) + 2\ HCN\uparrow .$$

Hydrogen cyanide is a colorless liquid below 26°. It dissolves readily in water, and its solution possesses the properties of a weak acid. The salts of the acid (NaCN, $Ca(CN)_2$, etc.) are called *cyanides*. These substances hydrolyze readily to liberate HCN. Both the acid and its salts are extremely poisonous, and when taken in even small amounts cause instant death.

The acid is used as a fumigant and insecticide. Pulverized calcium cyanide and sodium cyanide are used as insecticides and to destroy rats, mice, prairie dogs, and other small animal pests.

Solutions of sodium and potassium cyanides dissolve gold and silver, with which they form salts in which gold and silver are combined with cyanide ion in the form of complex ions: $(Na^+ + Au(CN)_2^-)$ and $(Na^+ + Ag(CN)_2^-)$. For this reason, sodium and potassium cyanides are used in extracting gold and silver from ores in which the metals occur in the free state. The same reaction is often used in cleaning gold and silver articles.

Sodium cyanide is produced directly from the nitrogen of the air by the following reaction:

$$Na_2CO_3 + 4\ C + N_2 \longrightarrow 2\ NaCN + 3\ CO.$$

It is also produced by heating calcium cyanamide with carbon and sodium carbonate:

$$CaCN_2 + C + Na_2CO_3 \longrightarrow 2\ NaCN + CaCO_3.$$

21. Other Cyanogen Compounds

Several other compounds containing the cyanide radical are used in the chemical laboratory. Some of these are: *potassium cyanate*, KOCN; *potassium sulfocyanate*, KSCN; *potassium ferrocyanide*, $K_4Fe(CN)_6$; and *potassium ferricyanide*, $K_3Fe(CN)_6$.

The ferrocyanides of sodium and potassium are usually produced from by-products obtained in the destructive distillation of coal. In the gas that escapes during the distillation, a portion of the nitrogen of the coal is present as hydrogen cyanide. If the gas is passed over iron oxide, the hydrogen cyanide is converted into the cyanide of iron from which, first, calcium ferrocyanide and, eventually, sodium or

potassium ferrocyanide are produced. The ferrocyanide ion $(Fe(CN)_6)^{-4}$ is used as a test for ferric ion, with which it forms dark blue ferric ferrocyanide, $Fe_4(Fe(CN)_6)_3$, *Prussian blue.* The ferricyanide ion, $(Fe(CN)_6)^{-3}$ contains trivalent iron. This ion is used to detect the presence of ferrous ion, with which it forms a dark blue precipitate of *Turnbull's blue.*

REVIEW EXERCISES

1. What are two methods of producing nitric acid? Compare the extents to which they are used.
2. Write equations to show how:
   Ammonia is converted into nitric oxide.
   Nitric acid is converted into ammonia.
   Nitric oxide is converted into nitric acid.
   Sodium nitrate is converted into sodium nitrite.
3. Write equations to show what happens when:
   Ammonium nitrate is heated.
   Cupric nitrate is heated.
   Nitric acid acts upon H_2S.
   Nitric acid oxidizes ferrous sulfate to ferric sulfate in the presence of H_2SO_4.
4. Illustrate by appropriate equations the chemical properties of nitric acid.
5. What volume of commercial (concentrated) nitric acid can be prepared from 50 kilograms of sodium nitrate?
6. What volume (standard conditions) of nitrous oxide can be prepared from 100 g. of ammonium nitrate?
7. What volume of concentrated nitric acid could be prepared by the Ostwald process from 10 (standard) liters of ammonia? Assume that 90 per cent of the ammonia is oxidized and that all other reactions are complete.
8. Identify the following: laughing gas, N_2O_5, nitrogen tetroxide, nitrous acid, pyroxylin, aqua regia, amitol, KCN, $(CN)_2$, $Ca(CN)_2$, nitrosyl chloride, nitroglycerine, picric acid, $C_6H_2(NO_2)_3CH_3$.
9. Show by equations two ways in which nitric acid may react with certain organic compounds, using glycerine and benzene as the substances that react with the acid.
10. Assuming that a yield of 100 per cent can be obtained, what weight of pure hydrogen nitrate can be produced from 10 liters of liquid ammonia (sp. gr., 0.62) by the Ostwald process? If this nitric acid is dissolved in water, what volume of concentrated nitric acid can be produced?
11. What is the weight of nitric acid in one liter of 6 N solution?
12. One of the oxides of nitrogen contains 63.64 per cent of nitrogen. Which of the oxides is it?
13. What (standard) volume of nitric oxide can be produced by the reaction of an excess of nitric acid upon 127.14 g. of copper?
14. Balance the following equations: (Water may be formed.)
   (*a*) $(H^+ + NO_3^-) + S \longrightarrow (2\ H^+ + SO_4^{=}) + NO$
   (*b*) $(H^+ + NO_3^-) + P \longrightarrow (3\ H^+ + PO_4^{\equiv}) + NO$
   (*c*) $(H^+ + NO_3^-) + Fe \longrightarrow (Fe^{+++} + 3\ NO_3^-) + NO$
   (*d*) $(H^+ + NO_3^-) + SO_2 \longrightarrow (2\ H^+ + SO_4^{=}) + NO_2$
   (*e*) $(H^+ + NO_3^-) + Al \longrightarrow (Al^{+++} + 3\ NO_3^-) + (NH_4^+ + NO_3^-) + H_2O.$
15. Summarize all the steps involved in the production of nitric acid from air and water. Write equations for all the reactions used in the different steps.

REFERENCES FOR FURTHER READING

Riegel, E. R., *Industrial Chemistry.*
Nitric Acid: *Ind. and Eng. Chem.*, **19,** 789 (1927); **23,** 456, 860 (1931); **26,** 1287 (1934); *Chem. and Met. Eng.*, **36,** 614 (1930); **37,** 604 (1930); **39,** 430 (1932); **43,** 282 (1936).
Nitrates: *Ind. and Eng. Chem.*, **23,** 456 (1931).

29

THE SULFUR FAMILY

1. Introduction

Oxygen, sulfur, selenium, and tellurium constitute one of the well-known families of elements. The physical properties of oxygen and sulfur are very different — oxygen is a colorless gas and sulfur is a yellow solid — but their family relationships are prominently revealed when we study their chemical properties and those of the compounds that they form. The following list of the compounds of sulfur and oxygen shows some of the likenesses of these compounds, at least with regard to composition and formulas. In many instances, the corresponding compounds have, also, similar chemical properties.

H_2S Na_2S CS_2 As_2S_3 CuS Cu_2S NaSH
H_2O Na_2O CO_2 As_2O_3 CuO Cu_2O NaOH

SULFUR

2. History and Occurrence

Sulfur was used in medicine and as a fumigant as early as 1000 B.C. To the alchemists of the early and middle ages, it was a substance of great importance and many uses. In its early history, it was commonly called *brimstone* or burning stone. It is found in the free state in regions where volcanoes are active or where they were once active: Sicily, Mexico, and Japan. Deposits in Louisiana and Texas now supply a large part of the sulfur used in the world. These deposits were probably produced by the reduction of *gypsum*, $CaSO_4.2\ H_2O$, to free sulfur.

Compounds of sulfur are more abundant in nature than the free element. These include sulfates, the most important of which are sodium sulfate, potassium sulfate, magnesium sulfate, *gypsum* and *barite* ($BaSO_4$); and sulfides of the metals, such as *galena* (PbS), *cinnabar* (HgS), and *zinc blende* (ZnS), *iron pyrites* (FeS_2), and several ores of copper, gold, and other metals. The element is also found in many organic compounds. The albumen of the egg, for example, contains about 1 per cent of sulfur. It is also present in many vegetable oils, such as those of garlic and mustard.

3. The Production of Sulfur

Most of the world's sulfur supply, at one time, came from Sicily. This is still a source of the element, but the United States, before the outbreak of the second World War, produced about 80 per cent of the world's output.

The sulfur deposits of Louisiana and Texas are covered by several hundred feet of material, of which a part is quicksand. The deposits are 400–600 feet thick and several thousand feet in diameter. Sulfur is recovered from them by a process developed by Frasch about 1900 (Figure 217).

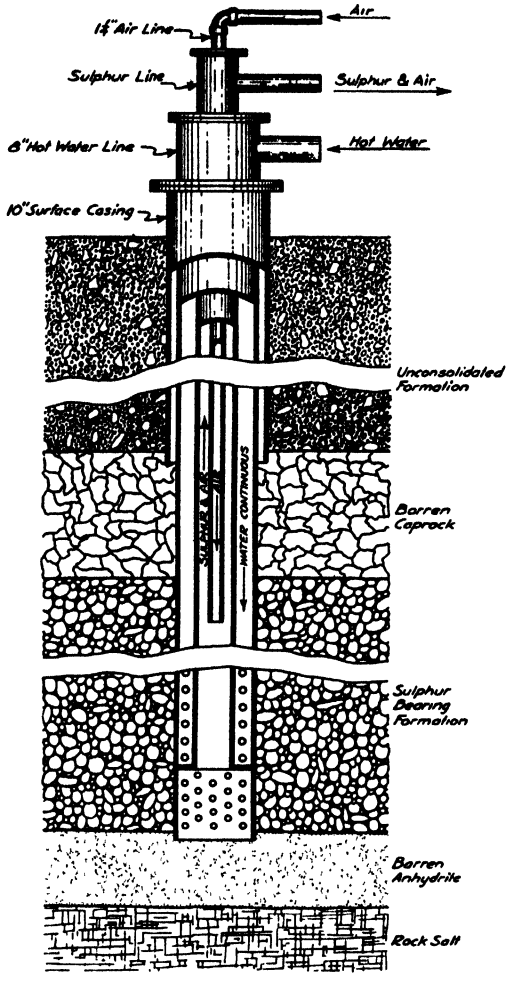


Figure 217. Sulfur Well
(Courtesy of Freeport Sulfur Co.)

Water is heated to about 170° (under pressure) and forced down the outside pipe; this melts the sulfur. Hot air is forced through the smallest pipe. This mixes with the melted sulfur and the water to form a mixture of low density, which is forced to the surface through the middle pipe by the pressure of the air and water. Almost pure sulfur (99.5 per cent) is produced by this process.

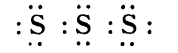
The annual production varies greatly, because the quantity of sulfur produced is determined by the demand of the industries using the sulfur itself or its most important compound, sulfuric acid (page 365). The annual production of sulfur in the United States is about 4,800,000 tons.

4. Physical Properties

Sulfur exists as crystals of *monoclinic* and *rhombic* forms (Figure 219 and 220). The transition temperature from the rhombic to the monoclinic form is 96°. At ordinary temperatures, therefore, rhombic sulfur is the stable form. The monoclinic form may be prepared by allowing melted sulfur to crystallize above 96°. Both crystalline forms are readily soluble in carbon disulfide but not in water.

Sulfur is an odorless, tasteless, brittle, yellow solid. The densities of the rhombic and monoclinic forms are 2.07 and 1.96 g. per cc., respectively at 20°, and the melting points are 112.8° and 119°. The boiling temperature is 444.6°. When sulfur melts, it forms several liquid forms having different molecular arrangements of its atoms. If the melting proceeds slowly, the different forms of the liquid attain equilibrium with one another and with the solid, at 114.5°; and hence, this temperature is regarded as the melting point of the element.

At a temperature slightly above the boiling point, sulfur vapor consists chiefly of molecules of S_8 with, perhaps, some smaller molecules of S and S_2. At higher temperatures diatomic and monatomic molecules predominate. The molecules are formed by sulfur atoms that share electrons with one another:



In the S_8 molecule eight atoms, it is believed, form a ring:

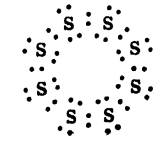




Figure 218. Sulfur Storage Pile
(*Courtesy of Freeport Sulfur Co.*)

At higher temperatures, the ring structures break, forming chains, and at still higher temperatures, these chains break up into shorter lengths.

Sulfur melts to form a pale yellow, very mobile liquid. When this liquid is heated, the color changes to dark brown, and the liquid becomes stiff and viscous. These differences in the properties of the liquid indicate different forms of molecules of liquid sulfur. The first form probably consists of ring molecules. The more viscous form is probably one that consists of large chain molecules, which are formed when the rings break, and the eight-atom chains thus formed combine to form very long chains, which become entangled and make the liquid more viscous. The viscosity reaches its maximum between 200°–260°, and then decreases at higher temperature, as the long chain-molecules presumably are broken up into shorter lengths.

If liquid sulfur which has been heated almost to the boiling point is cooled rapidly by pouring it into water, it is converted into a soft, amorphous, pliable mass, somewhat like rubber. This is called *plastic* sulfur. This form is probably composed of long chain-molecules that do not have time, as they are cooled, to reform the ring-molecules that are more stable at low temperatures. The plasticity of this form is probably the result of the presence of these chains, which can be pulled and extended. Upon standing plastic sulfur changes slowly into small rhombic crystals.

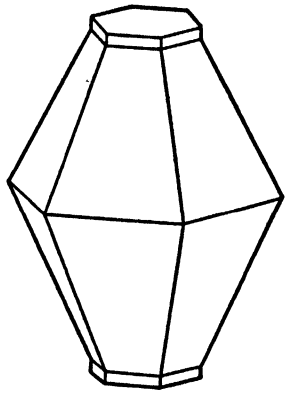


Figure 219. Rhombic Sulfur

5. Chemical Properties

Just as oxygen forms oxides, sulfur combines directly with many elements to form sulfides. Most of the metals form sulfides when heated with sulfur. It combines with oxygen at elevated temperatures to form sulfur dioxide, SO_2. The following are representatives of its compounds with other non-metals: H_2S, CS_2, S_2Cl_2, SCl_3, P_4S_3. Sulfur is converted by oxidizing agents, such as nitric acid, into SO_2, and upon further oxidation, into SO_3.

Like oxygen and the other members of the family, the sulfur atom has six valence electrons, and may acquire, therefore, two electrons to complete the octet. If it acquires these electrons from an electropositive element, its oxidation number is -2. This gives the sulfide ion, $S^=$. The sulfur atom shares electrons to give it the oxidation numbers of $+4$ and $+6$.

6. Uses

The principal use of sulfur is the manufacture of sulfuric acid. Another important use is in the vulcanization of rubber. Mixed with lime it is used to form *lime-sulfur sprays* that are used as fungicides. Some is used in making black gunpowder, as a fumigant, and in the manufacture of many useful compounds, including sulfur dioxide, carbon disulfide, sodium thiosulfate, and the sulfide of phosphorus, P_4S_3. It is used to some extent as an electrical insulator. Mixed with sand and heated, it gives an acid-proof cement. A substitute for slate is made from sulfur, cement, and asbestos. In organic chemistry it has many uses, but the most important is probably in the manufacture of certain dyes and drugs. Medicinally, sulfur is used in treating certain diseases of the skin. The early "friction" matches always contained sulfur and were often called "sulfur matches."

HYDROGEN SULFIDE

7. Occurrence

Since many organic materials contain sulfur, usually as a constituent of certain proteins, the decay or destructive distillation of these substances usually results in the liberation of hydrogen sulfide (H_2S). It is present in the gases which are evolved when coal is distilled, in gases escaping from volcanoes, and in sewer gas. It is the substance which is largely responsible for the odor of rotten eggs. The waters from "sulfur springs" also contain hydrogen sulfide.

8. Preparation

Hydrogen sulfide is formed directly from the elements when hydrogen is passed into boiling sulfur. It is usually prepared, how-

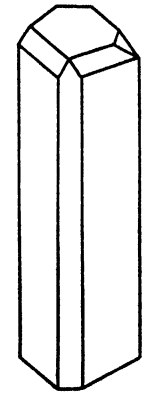


Figure 220. Monoclinic Sulfur

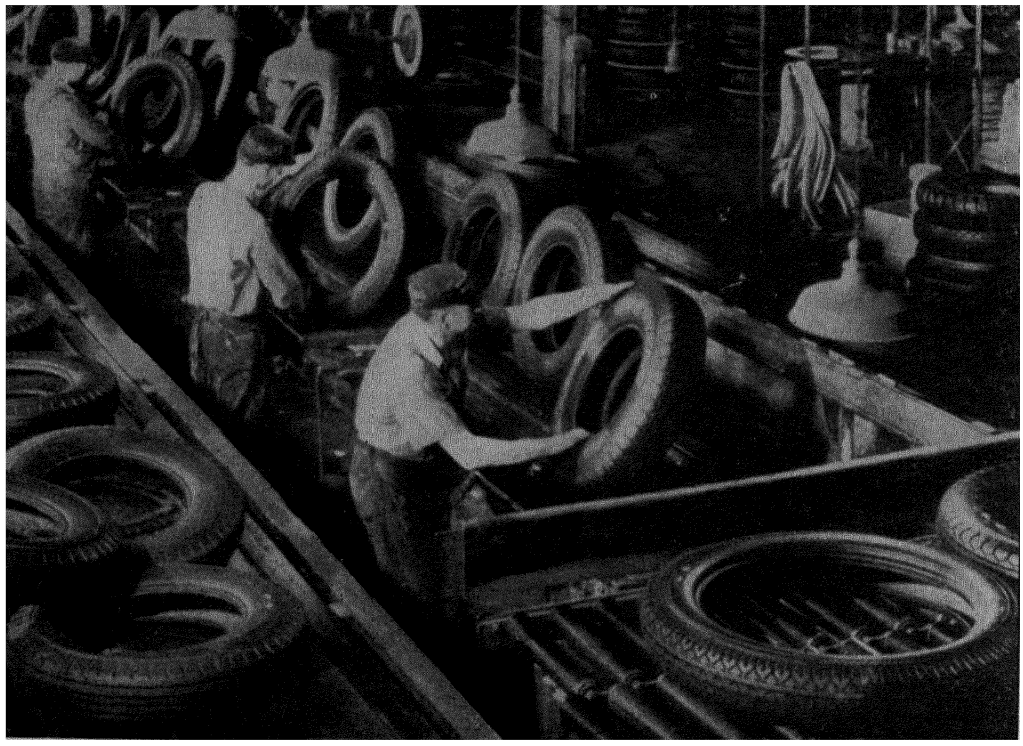


Figure 221. Vulcanization of Tires
(Courtesy of Freeport Sulfur Company)

ever, by the action of dilute hydrochloric acid upon ferrous sulfide in a Kipp generator (page 72).

$$FeS + 2\,(H^+ + Cl^-) \longrightarrow (Fe^{++} + 2\,Cl^-) + H_2S\uparrow\ .$$

Hydrogen sulfide is also prepared by heating solid hydrocarbons (paraffin) with sulfur, which reacts with the hydrogen of the hydrocarbon to form H_2S. A residue of carbon is left.

9. Properties

Hydrogen sulfide is a colorless gas. It has a sweet, disagreeable taste and a very foul odor. The density of the gas is 1.18, as compared with air; its boiling point is $-59.6°$; and its freezing point is $-83°$. At 15°, one volume of water dissolves a little more than three volumes of hydrogen sulfide. It is very poisonous. Continued inhalation of a very dilute mixture with air produces headache and nausea, and one part in 200 parts of air may prove fatal to persons and animals breathing the mixture. A little chlorine, largely diluted with air, may be breathed as an antidote.

Chemically, hydrogen sulfide is characterized by the following properties:

(1) It is not very stable. When heated it decomposes into the elements:

$$H_2S \rightleftarrows H_2 + S.$$

If a cold porcelain dish is held in a flame of burning hydrogen sulfide, a deposit of sulfur condenses upon the surface of the dish. The gas decomposes into hydrogen and sulfur, but the cold dish lowers the temperature of the mixture to a point below the kindling temperature of sulfur.

(2) The gas burns in the air with a blue flame and produces water and sulfur dioxide:

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

If the supply of oxygen is limited, the hydrogen is converted into water, and the sulfur is set free:

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

The second reaction occurs slowly when a solution of hydrogen sulfide is exposed to the air; the hydrogen is converted into water, and the sulfur precipitates as a finely divided solid, called *milk of sulfur.*

(3) Hydrogen sulfide is a reducing agent. The following equations show its behavior in this respect:

$$H_2S + I_2 \longrightarrow 2\ (H^+ + I^-) + S.$$

$$2\ (Fe^{+++} + 3\ Cl^-) + 3\ H_2S \longrightarrow S\downarrow + 2\ FeS\downarrow + 6\ (H^+ + Cl^-)$$

$$3\ H_2S + 2\ (H^+ + NO_3^-) \longrightarrow 2\ NO + 3\ S\downarrow + 4\ H_2O.$$

(4) Hydrogen sulfide resembles water in its action upon metals. When the gas is passed over heated iron filings, hydrogen and Fe_3S_4 (compare with Fe_3O_4) are produced:

$$3\ Fe + 4\ H_2S \rightleftarrows Fe_3S_4 + 4\ H_2.$$

All of the metals in the electromotive series down to and including silver readily react with hydrogen sulfide. The black tarnish on silver is caused by the interaction of the metal with this substance.

(5) The aqueous solution of hydrogen sulfide acts as a very weak dibasic (or diprotic) acid (page 323) and ionizes to form hydrogen, sulfide ($S^=$), and hydrosulfide (SH^-) ions. As an acid it is known as *hydrosulfuric* acid. It neutralizes bases to form sulfides and hydrosulfides ($2\ Na^+S^=$ and Na^+SH^-). Both the $S^=$ and the SH^- ions are strongly basic and, therefore, they react with water:

$$S^= + H_2O \rightleftarrows SH^- + OH^-$$

$$SH^- + H_2O \rightleftarrows H_2S + OH^-.$$

Therefore, both sulfides and hydrosulfides hydrolyse considerably, if they are soluble in water.

10. Sulfides

Many of the sulfides of the metals occur naturally and are important ores of the metals. In the laboratory, the metallic sulfides are prepared by the following methods: (1) By the neutralization of a base with hydrosulfuric acid; (2) by heating the metals with sulfur; and (3) by the reaction of ions of the metals with sulfide ion in solutions containing salts of the metals and hydrogen sulfide. The third method is usually employed to form sulfides that are not readily soluble in water. The sulfides of the alkali metals and of the alkaline earth metals (barium, strontium, calcium, and magnesium) cannot be produced in this manner, because they are soluble and, also, because they are hydrolyzed to produce the hydroxides of the metals and hydrogen sulfide.

Because of differences in the behavior of their sulfides, metals may be divided into three groups:

(1) Metals whose sulfides are precipitated in acid solution.

(2) Metals whose sulfides or hydroxides precipitate in a neutral or alkaline solution but not in an acid solution of H_2S.

(3) Metals which are not precipitated by hydrogen sulfide. These are sodium, potassium, ammonium, calcium, magnesium, barium, and strontium.

This is the principle which underlies the most commonly used method of separating the cations into small groups for analytical purposes.

11. Polysulfides

When aqueous solutions of the hydroxides or sulfides of calcium, ammonium, sodium, and potassium are heated with sulfur, the sulfur dissolves to form polysulfides of the metals or of ammonium ion. The composition of these compounds resembles that of the peroxides (page 191). The lime-sulfur sprays contain

polysulfides of calcium, probably CaS_4 and CaS_5. Ammonium polysulfide, sometimes called "yellow ammonium sulfide," is usually represented as $(NH_4)_2S_x$ and contains $(NH_4)_2S_2$, $(NH_4)_2S_3$, $(NH_4)_2S_4$, and $(NH_4)_2S_5$.

SULFUR DIOXIDE AND SULFUROUS ACID

12. Sulfur Dioxide: Its Production

Sulfur dioxide occurs in the gases that escape from volcanoes and in the gases from the combustion of coal, which usually contains some sulfur. It is produced by the following general methods:

(1) By burning sulfur or by roasting metallic sulfides in the air:

$$S + O_2 \longrightarrow SO_2$$
$$2\ CuS + 3\ O_2 \longrightarrow 2\ CuO + 2\ SO_2.$$

(2) Small quantities of pure sulfur dioxide can be prepared by treating a sulfite with an acid. Sulfurous acid (H_2SO_3) is first formed and decomposes into water and sulfur dioxide:

$$(2\ Na^+ + SO_3^=) + 2\ (H^+ + Cl^-) \longrightarrow SO_2 + H_2O + 2\ (Na^+ + Cl^-).$$

(3) By the reduction of sulfuric acid. Concentrated sulfuric acid reacts with copper, certain other metals, carbon, and even sulfur itself to produce sulfur dioxide.

$$Cu + 2\ (2\ H^+ + SO_4^=) \longrightarrow (Cu^{++} + SO_4^=) + SO_2 + 2\ H_2O.$$

13. Properties of Sulfur Dioxide

Sulfur dioxide is a colorless gas, 2.26 times as heavy as air, and possessing a sharp, irritating odor. The gas is very easily liquefied in a freezing mixture of ice and salt at atmospheric pressure. The boiling point of the liquid is about $-10°$, and the freezing point is about $-73°$. It is very soluble in water; at one atmosphere and at 0°, 1 volume of water dissolves approximately 80 volumes of the gas. Sulfur dioxide is sold in the liquid form in steel cylinders and even in tankcars.

The electronic formula of sulfur dioxide is probably best expressed as

$$:\ddot{O}:S::\dot{O}\cdot,$$

but the double bond (double pair of electrons) may be considered as resonating between the two O—S positions.

The chemical properties of sulfur dioxide may be summarized as follows:

(1) It acts as an oxidizing agent. This is a property of minor importance and is illustrated by the action of SO_2 upon H_2S:

$$SO_2 + 2\ H_2S \longrightarrow 2\ H_2O + 3\ S.$$

(2) Sulfur dioxide is an active reducing agent. It is oxidized by such substances as $KMnO_4$, $K_2Cr_2O_7$, HNO_3, and even oxygen, itself, to sulfur trioxide, or sulfuric acid.

(3) Sulfur dioxide is useful in bleaching certain organic materials, such as silk, wool, paper, and straw. Sulfur dioxide, or sulfurous acid, in acting as a bleaching agent, may combine directly with the colored substances to form colorless, unstable *addition compounds*. These substances slowly decompose and change back to the original colored materials, especially in sunlight; and hence, a newspaper made from wood pulp that has been bleached with sulfur dioxide turns yellow after it has been allowed to lie in the sunlight for a short time. The same change may occur in straw hats if the straw is bleached in the same manner.

14. Sulfurous Acid

A solution of sulfur dioxide in water is weakly acidic owing to the presence of sulfurous acid, which forms H^+, HSO_3^- and $SO_3^=$ ions:

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$
$$HSO_3^- \rightleftarrows H^+ + SO_3^=.$$

The acid is known only in solution, because it is unstable and cannot be obtained in the pure state.

15. The Uses of Sulfur Dioxide, Sulfurous Acid, and the Sulfites

The most important use of the gas is in the manufacture of sulfuric acid and the sulfites. Large quantities of SO_2, or sulfurous acid, are used in bleaching straw and papermaking materials, also silk and wool, which cannot be bleached with chlorine. Corn to be canned, molasses, wine, and other products are sometimes treated with sulfur dioxide which acts as a preservative. The discoloration of fruits as they are dried may be prevented by the bleaching action of sulfur dioxide, which also kills fungi, molds, and other organisms which cause fermentation and decay. It is also used in electric refrigerators in the same manner as ammonia (page 345). In earlier times, the dioxide was used as a disinfectant, but it has been largely replaced by formaldehyde.

Calcium bisulfite, $Ca(HSO_3)_2$, is extensively used as a bleaching agent in the preparation of wood-pulp for the manufacture of paper. This substance is prepared by the action of sulfur dioxide upon calcium hydroxide or upon limestone or dolomite. Its use in the preparation of wood-pulp depends upon its ability to react with and to dissolve *lignin*, a substance which holds together the wood fibers. The removal of this cementing material allows the fibers to be separated and, finally, to be arranged as a tangled mass of interlacing threads in the sheet of paper. Sodium bisulfite can be used for the same purpose.

SULFURIC ACID

16. Sulfur Trioxide

This substance is a white solid which exists in several different forms, one of which melts at 17°. Liquid sulfur trioxide boils at 45°.

Sulfur trioxide acts as an oxidizing agent but only with very vigorous reducing agents. It is the anhydride of sulfuric acid. In the air it fumes strongly; the white fumes consist of tiny droplets of sulfuric acid. It reacts vigorously with water to form the acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4 + 21{,}360 \text{ calories.}$$

For this reason, SO_3 is a powerful dehydrating agent. It dissolves in 100 per cent sulfuric acid to form *pyrosulfuric*, or *fuming sulfuric*, acid:

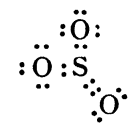
$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7.$$

Sulfur trioxide is produced by the reaction of sulfur dioxide with oxygen:

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3 + 45{,}000 \text{ calories.}$$

The reaction is reversible, and since it is strongly exothermic, it is not favored by high temperatures. It is also very slow unless catalyzed by finely divided platinum or some other material. This reaction is the fundamental one in the manufacture of sulfuric acid.

The electronic structure of sulfur trioxide is



17. Sulfuric Acid

Sulfuric acid is by far the most widely used acid. The annual consumption in the United States is around 11,000,000 tons of 100 per cent acid. So important is this substance, that the quantity produced from year to year is a good index of industrial prosperity.

18. Physical Properties

The anhydrous (100 per cent) sulfuric acid (or hydrogen sulfate) is a colorless, heavy, "oily" liquid, freezing at 10.5° C. It is sometimes called *oil of vitriol*. The density of 100 per cent H_2SO_4 is 1.85 g. per cc. at 20°. The constant boiling acid, obtained by distillation, contains 98.5

per cent, and the ordinary concentrated acid of commerce about 95 per cent, of H_2SO_4. The latter has a specific gravity of 1.83. Both the pure acid and its concentrated solution evolve sulfur trioxide when heated to moderately high temperatures (about 150°). Hydrogen sulfate mixes with water in all proportions. When the concentrated acid is poured into water, considerable heat is liberated, indicating that water combines with the acid to form hydrates.

19. Production of Sulfuric Acid by the Lead-Chamber Process

This process is shown in Figure 222. The materials used consist of the following substances; sulfur or pyrites (FeS_2), which is burned to form sulfur dioxide; the oxides of nitrogen, $N_2O_3 \rightleftarrows NO + NO_2$; air which supplies oxygen; and water or steam.

The basic reactions of the process can be summarized as follows:

$$S + O_2 \longrightarrow SO_2$$
$$2\,NO + O_2 \longrightarrow 2\,NO_2$$
$$NO_2 + SO_2 \longrightarrow SO_3 + NO$$
$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

The actual reactions are much more complex. The different steps in the process are described below, and for each step the reactions, as they are thought to occur, are stated.

20. Steps in the Lead-Chamber Process

The different parts of a lead-chamber plant and the reactions that occur in each of them are described as follows:

(1) *The Sulfur Burners.* Iron pyrites or sulfur is burned in the furnace, kiln, or burner. A large excess of air is used to provide oxygen not only to form sulfur dioxide but to leave a surplus for later reactions in the lead chambers.

(2) The sulfur dioxide and the excess of air next pass over the "niter pot" where nitric acid is made by the reaction of H_2SO_4 upon $NaNO_3$. The nitric acid is reduced by the sulfur dioxide, forming NO and NO_2:

$$2\,HNO_3 + 2\,SO_2 + H_2O \longrightarrow 2\,H_2SO_4 + NO + NO_2.$$

The oxides of nitrogen may be, and now usually are, produced by oxidizing ammonia catalytically; these oxides may be introduced directly into the lead chambers. The mixture of gases next passes through a dust remover, where the oxides of iron and arsenic and other materials are desposited. More air may be admitted here if necessary.

(3) The gases next pass through the *Glover tower* in which the oxides of nitrogen that have already been used are added once again to the system. See (6) below.

(4) *The Lead Chambers.* The mixture containing sulfur dioxide, air, and the oxides of nitrogen enter the lead chambers, and water or steam is added. The chambers are lined with sheet lead and are approximately $100 \times 40 \times 40$ feet in size. From three to five chambers may be used in a plant, the first in the series is usually the largest. In the recently constructed plants

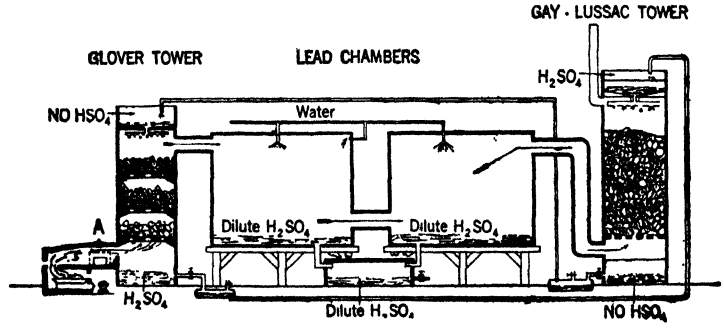


Figure 222. Lead-Chamber Plant for the Production of Sulfuric Acid
A is the "niter pot."

smaller chambers are built, and in some, circular towers are used instead of the lead rooms. The following reactions occur in the lead chambers.

$$(1)\ 2\,SO_2 + NO + NO_2 + O_2 + H_2O \longrightarrow 2\,[SO_2(OH)(NO_2)].$$

The product of this reaction is *nitrosyl* sulfuric acid. In the presence of water, the second reaction occurs, forming sulfuric acid, and liberating the oxides of nitrogen:

$$2\,[SO_2(OH)(NO_2)] + H_2O \rightleftarrows 2\,H_2SO_4 + NO + NO_2.$$

The oxides of nitrogen pass out of the chambers into the *Gay-Lussac tower*. The sulfuric acid solution (60–70 per cent) collects in the bottom of the chambers and is drained into a reservoir.

(5) *The Gay-Lussac Tower.* One function of this tower is that of a chimney, which helps to move the gases through the chambers, but its most important purpose is the recovery of the oxides of nitrogen. The gases escaping from the lead chambers pass in at the bottom of this tower, and move upward through tile or flint chips, over which concentrated sulfuric acid is sprayed. As the acid comes into contact with the escaping gases, the following reaction occurs:

$$2\,H_2SO_4 + NO + NO_2 \rightleftarrows [SO_2(OH)(NO_2)] + H_2O.$$

The concentrated acid, containing also nitrosyl sulfuric acid, is drained from the bottom of the Gay-Lussac tower into a reservoir. From here it is forced (under air pressure) to the top of the Glover tower.

(6) *The Glover Tower.* The acid from the Gay-Lussac tower is sprayed over tile, which fills the Glover tower, and as it descends it meets the hot ascending gas from the sulfur burners. It is also diluted by the addition of dilute sulfuric acid from the lead chambers. The reaction that occurs in the Gay-Lussac tower is reversed, and the oxides of nitrogen are set free once again to begin a new trip through the lead chambers. While passing over the heated tile of the Glover tower, the acid is concentrated. It is this acid, from the bottom of the Glover tower, that is forced to the top of the Gay-Lussac tower, there to be used in absorbing once again the oxides of nitrogen.

21. Concentration of Chamber Acid

To prepare the more concentrated solutions required in certain industries, chamber acid (60–70 per cent) must be evaporated. This process may be carried out in lead pans placed on top of the sulfur burners. The concentration in lead cannot be carried beyond 77 per cent of H_2SO_4, since stronger acid dissolves the layer of lead sulfate which forms on the pans and protects them against the action of the acid. The solution can be further concentrated (to about 94 per cent) in vessels made of glass, porcelain, platinum, silica, or acid-resisting Duriron (iron-silicon). The acid may also be concentrated by allowing it to flow over the bricks or tile of a tower in which hot gases are passed upward. Commercial concentrated acid is distilled from glass containers to give the chemically pure acid (about 98 per cent).

22. The Contact Process

The different parts of the plant used in manufacturing sulfuric acid by the contact process are shown in Figure 224. The reaction involved is:

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3 + 45{,}000 \text{ calories.}$$

Because this reaction is extremely slow, it must be catalyzed. High temperatures must be avoided because the reaction is exothermic. The catalyst first used was finely divided platinum deposited upon crystals of magnesium sulfate or upon asbestos. Ferric oxide, with which cupric oxide is mixed, and mixtures containing vanadium pentoxide (V_2O_5) have been found to be very effective. The sulfur dioxide is very carefully purified, and special precautions are taken to remove arsenic and its compounds, which act as "poisons" to the catalyst.

After purification in dust removers, scrubbers, and arsenic purifiers, the mixture of sulfur dioxide and air is heated to a temperature of about 400°–470° in a heat-

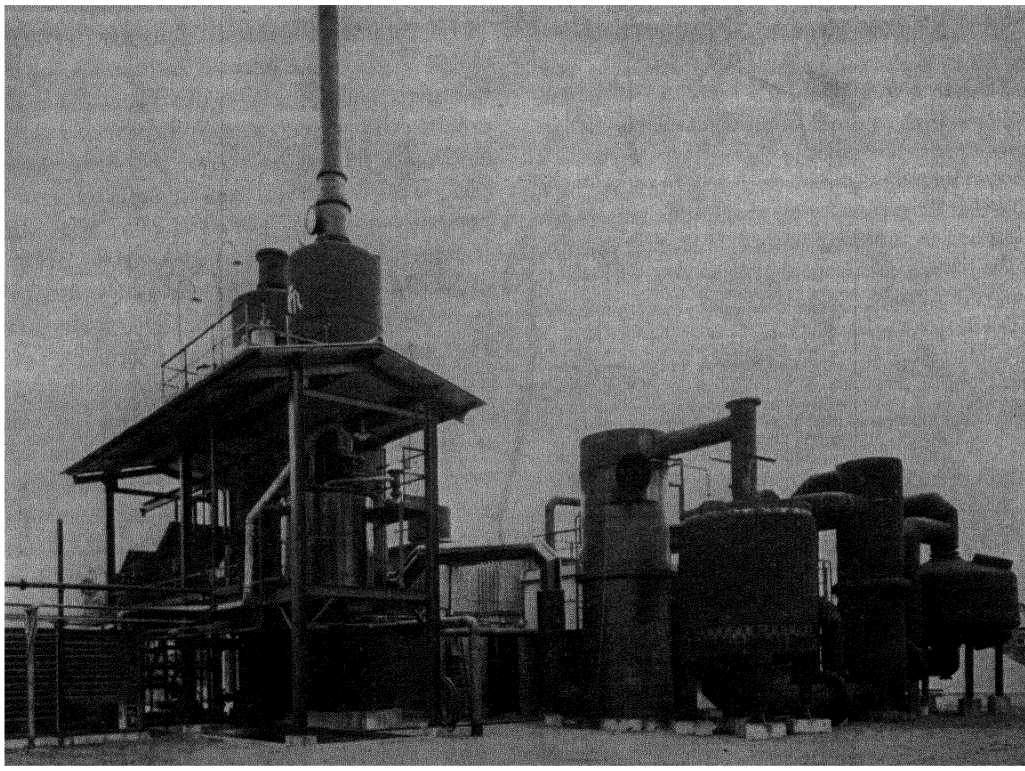


Figure 223. Contact Sulfuric Acid Plant
(Courtesy of Chemical Construction Company)

exchanger, in which the cold gases on their way to the catalytic chamber are heated by the hot gases that likewise pass through the heater on their way from the catalytic chamber to the absorber in which sulfur trioxide is converted into sulfuric acid. The gases then pass over the catalyst, and, because of the heat liberated in the reaction, the temperature rises to about 600°. At this temperature the reaction is only about 75 per cent completed. Sometimes, therefore, the gases are cooled and passed into a second catalytic chamber, where additional sulfur trioxide is produced. The gases from this chamber then pass through a second heat exchanger and into the absorber.

The sulfur trioxide is absorbed in concentrated sulfuric acid (97–98 per cent). Unless the mixture is diluted, this results in the formation of *oleum* or fuming sulfuric acid. The concentration of the acid which absorbs the trioxide can be regulated by allowing water to mix with it as the trioxide is absorbed. Sulfur trioxide cannot be absorbed in water, because it forms a fog of small droplets that pass through water without dissolving.

23. Comparison of the Contact and Lead-Chamber Processes

The contact process produces any concentration of sulfuric acid from oleum to a very dilute solution. Chamber acid, on the other hand, must be concentrated to give the stronger solution by a difficult and tedious process of evaporation. The acid from a lead-chamber plant usually contains more

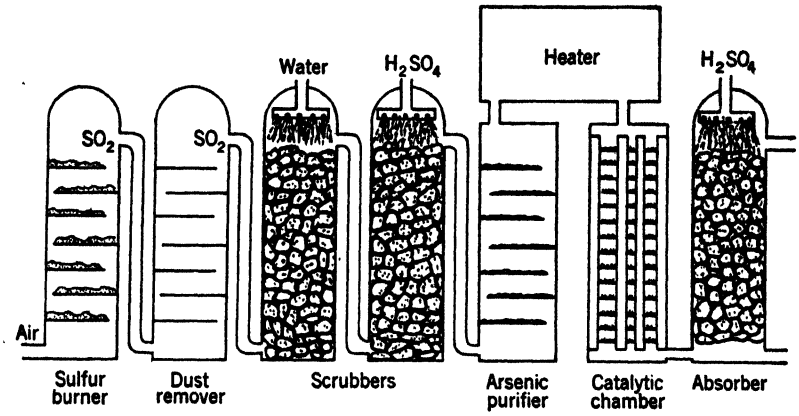


Figure 224. Diagram of a Contact Plant for the Manufacture of Sulfuric Acid

impurities in the form of dissolved lead sulfate, oxides of nitrogen, and compounds of iron, arsenic, and other metals than contact acid. Nevertheless, the former is still used extensively, just as it comes from the lead chambers, to manufacture ammonium sulfate and phosphate-fertilizers, into which goes almost one-third of the acid produced annually in the United States. The disadvantage of the contact process arises from the poisoning of the catalyst, which requires frequent renewal or regeneration. This was particularly true in the earlier days of the contact process when platinum was used as the catalyst. For this reason, the contact process requires very pure sulfur dioxide. The lead-chamber process can use, as a source of sulfur dioxide, iron pyrites and sulfide ores, which contain substances that would easily poison a contact catalyst.

24. The Chemical Properties of Sulfuric Acid

(1) An aqueous solution of sulfuric acid has the properties of a moderately strong, dibasic (diprotic) acid. It reacts with metals above hydrogen in the electrochemical series to liberate hydrogen; is a good conductor of the electric current; liberates carbon dioxide from carbonates, sulfur dioxide from sulfites, and hydrogen sulfide from sulfides; and reacts with the oxides and hydroxides of metals to form normal sulfates or bisulfates.

(2) The concentrated acid is an active oxidizing agent when heated. The reactions with carbon, sulfur, and copper (page 364) and with HI (page 278) illustrate this property.

(3) The action of the acid in liberating volatile acids from their salts has been illustrated in the manufacture of hydrochloric (page 277) and nitric (page 350) acids. Its use for this purpose depends upon its low volatility.

(4) Because of its vigorous reaction with water to form hydrates, concentrated sulfuric acid is an efficient drying agent for gases that do not react with it. It also removes the elements of water (hydrogen and oxygen) from compounds containing them. This effect is especially pronounced if the compounds contain the two elements in the same proportion as water. Paper, cotton, and wood, which consist essentially of cellulose, $(C_6H_{10}O_5)_x$, are charred by sulfuric acid because they are dehydrated by it. Sugar, $C_{12}H_{22}O_{11}$, is likewise dehydrated, leaving a charred mass of carbon.

25. Uses of Sulfuric Acid

Many industries use vast quantities of



Figure 225. Stainless Steel Drums Used for Shipping Sulfuric and Nitric Acids
These drums are replacing the glass carboys used formerly.

sulfuric acid. Its most important uses are enumerated below.

(1) Fertilizer manufacture. The acid is used to produce ammonium sulfate and soluble phosphate fertilizers.

(2) Refining of petroleum. The acid is used to remove dark colored substances, or substances that become dark when they are exposed to the air, and other undesirable substances from petroleum products.

(3) Manufacture of chemicals. This includes the production of hydrochloric, nitric, and phosphoric acids; sulfates of the metals, such as aluminum sulfate, alum, cupric sulfate, and ferrous sulfate; and many other substances, such as ether.

(4) Manufacture of dyes and drugs. These products include different substances made from coal and coal tar products.

(5) Pickling of steel. Before steel is coated with enamel, tin, or zinc (galvanized), the surface is cleaned of iron rust by dipping the metal into a "pickling bath" of acid.

(6) Metallurgical uses. Certain metals, such as zinc and copper, are produced or purified by the electrolysis of solutions of their sulfates. To purify crude copper an impure anode and a pure copper cathode are placed in a bath of sulfuric acid, and an electric current passed through them.

(7) Paints and pigments.

(8) Explosives. Sulfuric acid is used to take up the water resulting from the reaction between nitric acid and glycerine, cellulose, toluene, phenol, or other organic compounds.

(9) Nitrocellulose products, textiles, storage batteries, and other uses.

THE SODIUM SALTS OF SOME OF THE SULFUR ACIDS

26. Sodium Sulfate (Na_2SO_4)

Sodium sulfate occurs naturally in deposits located in Canada and in the southwestern portion of the United States. It is also present in several mineral waters and in the water of certain lakes in Siberia. It is produced as a by-product in the manufacture of hydrochloric acid. It crystallizes from solutions at temperatures below 32.4° as the decahydrate, $Na_2SO_4.10\ H_2O$, called Glauber's salt, after the alchemist Glauber, who used the salt as a medicine in the seventeenth century. The anhydrous salt may be formed by evaporating a solution of the substance at temperatures above 32.4°, the transition point. The hydrate loses moisture to dry, warm air because of its high dissociation pressure. Sodium sulfate is used in manufacturing glass and paper. In the manufacture of cheap glass, it serves as a substitute for sodium carbonate. In paper making, it is used in the preparation of wood pulp from southern pine and certain other woods. The acid sulfate ($NaHSO_4$) is not very useful, except in the manufacture of hydrochloric acid from salt (page 277).

27. Sodium Sulfite (Na_2SO_3) and Bisulfite ($NaHSO_3$)

When sulfur dioxide is passed into a solution of sodium carbonate, it first reacts with water to form sulfurous acid, H_2SO_3, which then reacts with sodium carbonate to form the acid sulfite (bisulfite):

$$(2\ Na^+ + CO_3^=) + 2\ H_2SO_3 \longrightarrow 2\ (Na^+ + HSO_3^-) + H_2O + CO_2.$$

If the saturated solution of the bisulfite is then treated with a fresh solution containing the same quantity of sodium carbonate that was used in making the bisulfite, the normal sulfite will be formed:

$$2\ (Na^+ + HSO_3^-) + 2\ Na^+ + CO_3^=) \longrightarrow 2\ (2\ Na^+ + SO_3^=) + H_2O + CO_2 \uparrow$$

Both the normal and the acid sulfite are reducing agents. They are used to some extent as bleaching agents, as preservatives, and in photography. Sodium sulfite is used to remove the excess of chlorine in the bleaching of textiles by that substance. When used for this purpose, the sulfite is called an *antichlor*. It reacts with the excess of chlorine according to the following reaction:

$$(2\ Na^+ + SO_3^=) + Cl_2 + H_2O \longrightarrow (2\ Na^+ + SO_4^=) + 2\ (H^+ + Cl^-)$$

The bisulfite is used in making paper, in tanning leather, in manufacturing some dyes, and as an antichlor.

28. Sodium Thiosulfate ($Na_2S_2O_3$)

This is the substance which is familiar to photographers as "hypo." Its use in photography depends upon its ability to dissolve silver salts from plates, films, or printing paper after these have been developed. The developing process reduces the silver salt which has been affected by light to metallic silver. In the "fixing" bath, which consists of a solution of sodium thiosulfate, the undeveloped silver salts that have not been affected by light are removed, so that they will not be converted into metallic silver when the "negative" or "positive" is exposed to the light.

Sodium thiosulfate is formed by treating a boiling solution of sodium sulfite with sulfur:

$$(2\ Na^+ + SO_3^=) + S \longrightarrow (2\ Na^+ + S_2O_3^=).$$

When the resulting solution is evaporated, the thiosulfate crystallizes out as the pentahydrate, $Na_2S_2O_3.5\ H_2O$. This is the substance commonly called *hypo* or *hyposulfite* of soda. The name hyposulfite is erroneous, however, since the substance is really a sulfate. Sulfur is oxidized in the reaction which produces the thiosulfate from an oxidation number of + 4 in Na_2SO_3 to + 6 in $Na_2S_2O_3$. We may think of the second

sulfur atom as playing the same role as the fourth oxygen atom does in $SO_4^{=}$.

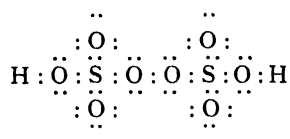
When an acid is added to a solution of the thiosulfate, the free acid, *thiosulfuric*, is liberated, and, being unstable, immediately decomposes into free sulfur and sulfurous acid, which is also unstable.

$$(2\ Na^+ + S_2O_3^{=}) + 2\ (H^+ + Cl^-) \longrightarrow 2\ (Na^+ + Cl^-) + H_2S_2O_3.$$

$$H_2S_2O_3 \longrightarrow SO_2 \uparrow + S \downarrow + H_2O.$$

29. The Peroxysulfuric Acids and Their Salts

The peroxysulfuric acids, H_2SO_5 and $H_2S_2O_8$, contain the peroxy, $-O-O-$, group, which we first encountered in the peroxides (page 191). They are called *peroxymonosulfuric* and *peroxydisulfuric acids*, respectively. The structure of the latter is



The acids are made by the electrolysis of a solution of sulfuric acid or a bisulfate. They are vigorous oxidizing agents. When they so act, the oxidation number of sulfur remains at + 6, but the number of oxygen in the O_2 group changes to − 2 from − 1. The salts of the acids are called peroxysulfates, or simply *persulfates*. They, too, are oxidizing agents.

30. Sodium Sulfide (Na_2S)

This compound of sodium is prepared by treating a solution of sodium hydroxide with hydrogen sulfide. Sodium hydrosulfide (NaHS) is first formed, but if the solution is then mixed with a volume of fresh sodium hydroxide solution equal to the volume first saturated with hydrogen sulfide, normal sodium sulfide is produced:

$$(Na^+ + OH^-) + H_2S \longrightarrow (Na^+ + HS^-) + H_2O$$

$$(Na^+ + HS^-) + (Na^+ + OH^-) \longrightarrow (2\ Na^+ + S^{=}) + H_2O.$$

Commercially, sodium sulfide is produced by reducing sodium sulfate with carbon at a temperature of about 900°. It is a white crystalline solid, which is very soluble. Its aqueous solutions are strongly alkaline in reaction because of the hydrolysis of the salt:

$$(2\ Na^+ + S^{=}) + HOH \longrightarrow (Na^+ + HS^-) + (Na^+ + OH^-)$$

$$(Na^+ + HS^-) + HOH \longrightarrow H_2S + (Na^+ + OH^-).$$

It is used in dyeing cotton with the "sulfur dyes," in manufacturing some dyes, and in removing hair from hides in the preparation of leather.

SELENIUM AND TELLURIUM

31. Selenium

Selenium was discovered by Berzelius in 1817. The name of the element was derived from a Greek word meaning *the moon*. It is found as the free element and in compounds occurring with free sulfur, iron pyrites, and certain sulfides. A common source is the dust that collects in the flues of pyrite-burners. It is also obtained in the electrolytic purification of copper, lead, and other metals from their sulfide ores. Its most familiar allotropic forms are red (amorphous) and gray (metallic) selenium. It is used to make colorless glass, which otherwise would have a slight green color produced by ferrous (Fe^{++}) compounds. It may also be used in larger amounts to make red glass. Gray selenium is used in some types of photoelectric cells, because the electrical conductivity of selenium varies with the intensity of the light to which it is exposed. It is also used to make current rectifiers, certain pigments, ceramics, rubber articles, alloys of copper, and stainless steels.

32. Tellurium

Tellurium was discovered by Reichen-

stein and Kloproth about 1800. It occurs in small amounts in nature as the free element and in the combined state. The most widely distributed compounds of tellurium are those in which the element is combined with gold, lead, and silver. The compounds are called *tellurides*. The name of the element signifies "the earth."

Tellurium is usually obtained in the sludge which collects at the anode when copper and lead are purified electrolytically. It is much more metallic in appearance than either sulfur or selenium. It is used to make easily machined alloys of copper; to increase the resistance of lead to the action of acids; to improve the physical properties of rubber; and to make cast iron more resistant to wear.

The relationships of sulfur, selenium, and tellurium are best seen by a comparison of their compounds of which we list a few: H_2S, H_2Se, H_2Te; SO_2, SeO_2, TeO_2; H_2SO_4, H_2SeO_4, H_2TeO_4. The compounds of tellurium are more like those of metals than the compounds of either sulfur or selenium.

REVIEW EXERCISES

1. How was the molecular formula of sulfur vapor shown to be S_8?
2. Compare and contrast sulfur and oxygen as members of the same family of elements.
3. Suggest a method of preparing sulfur from each of the following: Hydrogen sulfide; sulfuric acid; sodium sulfite; sodium sulfate.
4. Write equations which show the ionization of hydrosulfuric acid in two steps. Write equations which show other properties of hydrogen sulfide.
5. Write equations for the following reactions. If any other materials are required, add them in the equations.
   Nitric acid + Hydrogen sulfide $\longrightarrow$
   Nitric acid + Sodium sulfite $\longrightarrow$
   Hydrogen sulfide + Ferric chloride $\longrightarrow$
6. Suggest a reason for using chlorine as an antidote for hydrogen sulfide in cases of poisoning produced by the latter.
7. Write an equation to show the oxidation of H_2S in a solution containing HCl and $K_2Cr_2O_7$. Chromium is reduced to Cr^{+++} and sulfur is oxidized to S.
8. How many liters of SO_2 under standard conditions can be prepared by burning the hydrogen sulfide produced by the reaction of 100 g. of FeS with HCl?
9. How many cubic milliliters of H_2S (under standard conditions) will be required to precipitate completely the copper in 100 ml. of 1 N cupric sulfate solution?
10. For what reasons is sulfur classed as a nonmetallic element?
11. Summarize the principal occurrences, physical forms, and uses of sulfur.
12. Starting with a sample of galena (PbS) show how you would prepare in succession the following substances: Sulfur dioxide, sodium sulfite, sodium sulfate.
13. How would you prepare a solution of calcium bisulfite? Show by an equation how this substance would react with hydrochloric acid.
14. Write equations to show how dilute sulfuric acid solution would react with the following substances: Sodium sulfide, sodium carbonate, aluminum, sodium hydroxide.
15. Compare the properties of sulfurous and sulfuric acids.
16. What weight of sulfur must be burned to form 10 liters of 1 N sulfuric acid solution?
17. Explain the function of each part of a lead-chamber sulfuric acid plant.
18. What conditions are most desirable in carrying out the following reaction?

    $$2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 + 45{,}000 \text{ calories.}$$

    What would be the advantage and the disadvantages of using pure oxygen instead of air?
19. Explain the nature of the reactions which occur in each of the following cases: (1) When sulfuric acid is used as a dehydrating agent; (2) when concentrated sulfuric acid acts upon carbon; (3) when concentrated sulfuric acid is dissolved in water; (4) when concentrated sulfuric acid reacts with sodium nitrate; (5) when a dilute sulfuric acid solution has added to it a solution of barium chloride.
20. Starting with sulfur state how you would

prepare the following substances in succession: Ferrous sulfide, hydrogen sulfide, sulfur dioxide, sulfuric acid, sodium bisulfate, sodium sulfate.

21. Ten grams of commercial sulfuric acid and water were mixed to give 500 ml. of solution. A 25 ml. sample of this solution was titrated against 0.1 N NaOH solution, and 50 ml. of the solution of the base was required to neutralize it. What was the percentage of H_2SO_4 in the original sample?
22. How is sulfuric acid used in the fertilizer industry?
23. How is sulfuric acid used in the manufacture of explosives? What properties of the substance make it suitable for this use?
24. Why is sulfuric acid used, instead of some other acid, in liberating HCl from chlorides and HNO_3 from nitrates?
25. Gypsum is a very abundant substance in nature. Why is it not used in the production of sulfuric acid? Suggest a scheme which might be used to convert gypsum into sulfuric acid.
26. How would you determine whether a sample of a given substance was sodium sulfite or sodium sulfate?
27. Identify the following: Pyrosulfuric acid, oil of vitriol, nitrosyl sulfuric acid, plastic sulfur, brimstone, H_2Te, H_2SeO_4, H_2TeO_4.
28. Ten grams of sulfur is converted into ferrous sulfide, which is then treated with hydrochloric acid. What volume of hydrogen sulfide can be produced under standard conditions? Is it necessary to know or to calculate the weight of iron or of ferrous sulfide? Explain.
29. What is the maximum weight of sulfur that can be produced from 64 g. of sulfur dioxide and 68 g. of hydrogen sulfide when these two substances react to form sulfur and water?
30. Approximately what standard volume of air is required to produce one ton of sulfuric acid from sulfur by the contact process?

REFERENCES FOR FURTHER READING

Clarke, *Marvels of Modern Chemistry.*

Cushman, A. S., *Chemistry and Civilization.*

U.S. Bureau of Mines, *Sulfur,* Information Circular 6329, Washington, D.C.

Selenium and Tellurium: *Ind. and Eng. Chem.*, **34,** 899 (1942); *J. Chem. Ed.*, **9,** 474 (1932); **12,** 403 (1935).

Sulfur: *Ind. and Eng. Chem.*, **4,** 131 (1912); **16,** 1026 (1924); **30,** 740, 746 (1938); *Chem. and Met. Eng.*, **28,** 459 (1923); **31,** 144 (1924); **32,** 82; 365, 917 (1925); **37,** 668 (1930); **39,** 392 (1932), **40,** 454 (1933); **41,** 116 (1934); **48,** 104 (1941); *J. Chem. Ed.*, **6,** 129, 138 (1929); **7,** 1384 (1930); **8,** 1631 (1931); **12,** 17, 83, 121 (1935); **17,** 473 (1940).

Sulfur Dioxide: *Ind. and Eng. Chem.*, **24,** 626, 862 (1932); **27,** 587 (1935); **29,** 1396 (1937); **32,** 73, 910 (1940); **34,** 1017 (1942).

Sulfuric Acid: *Ind. and Eng. Chem.*, **10,** 751 (1918); **14,** 498 (1922); **21,** 417 (1929); **24,** 717 (1932); *Chem. and Met. Eng.*, **18,** 83 (1917); **19,** 404 (1918); **29,** 755, 885 (1923); **30,** 829 (1924); **38,** 330 (1931); **43,** 301 (1936); **44,** 376 (1937); **45,** 22, (1938); **46,** 478 (1939); *J. Chem. Ed.*, **3,** 1083 (1926); **6,** 129 (1929).

30

OTHER ELEMENTS OF THE NITROGEN FAMILY

1. Introduction

The family of elements of which nitrogen is the lightest element occurs in the B division of group five. These elements, in addition to nitrogen, are phosphorus, arsenic, antimony, and bismuth. The atoms of each element have five electrons in their outermost group and, consequently, exhibit a maximum positive oxidation number of five. The negative oxidation number is three. The metallic properties increase toward bismuth, which is more like a metal than a non-metal. The similarities and also some of the differences between the members of this family are shown in Table 17.

From top to bottom of the different columns in Table 17 the following variations occur:

(1) The hydroxides and oxides become less acidic and more basic in character.

(2) The hydrides become less stable.

(3) The chlorides are less hydrolysed. Nitrogen trichloride is very unstable.

PHOSPHORUS

2. History

This element was discovered by Brand, in 1669, during his attempts to find the philosopher's stone. It was isolated by the reduction of phosphates crystallized from urine. Because of its peculiar properties, especially its tendency to glow in the dark, Brand was convinced that his search was ended. The method of producing phosphorus was rediscovered by Robert Boyle.

3. Occurrence

Phosphorus does not occur free in nature. The most widely and abundantly distributed compound is calcium phosphate,

TABLE 17. COMPOUNDS OF ELEMENTS OF GROUP FIVE

Hydrides	Chlorides	Trioxide	Properties of trioxide	Pentoxide	Properties of pentoxide
NH_3	NCl_3	N_2O_3	Acidic	N_2O_5	Acidic
PH_3	PCl_3, PCl_5	P_4O_6 *	Acidic	P_4O_{10} *	Acidic
AsH_3	$AsCl_3$, $AsCl_5$	As_4O_6 * †	Weakly acidic, but slightly amphoteric	As_4O_{10} * †	Acidic
SbH_3	$SbCl_3$, $SbCl_5$	Sb_4O_6* †	Amphoteric	Sb_4O_{10} * †	Acidic
BiH_3	$BiCl_3$	Bi_2O_3	Basic	Bi_2O_5	Weakly acidic

* These oxides are frequently represented by the formulas P_2O_3, P_2O_5, As_2O_3, As_2O_5, Sb_2O_3 and Sb_2O_5, but the real formulas appear to be those shown in the table.

† These oxides are very slightly soluble in water. However, As_4O_6 does dissolve slightly, and its solution shows the presence of an acid.

$Ca_3(PO_4)_2$ which occurs as *phosphorite*, $Ca_3(PO_4)_2$, or *apatite*, $3\ Ca_3(PO_4)_2.CaF_2$, minerals commonly called *phosphate rock*. This material is mined in Tennessee, Florida, Wyoming, Idaho, and Montana for use in producing phosphate fertilizers. The production in 1948 was 8,700,000 short tons.

Calcium phosphate is present in all soils, unless the supply has been depleted by the continued growth of crops. From this source, plants obtain the phosphorus which is found, as various organic phosphorus compounds and as phosphates, in their structures and products, particularly in the germs of seeds. About one per cent of the weight of man's body consists of this element. Bones are composed, largely, of calcium phosphate, and other compounds containing phosphorus are found in the brain, muscles, nerves, blood, urine, and in other fluids of the body.

4. Yellow, or White, Phosphorus

Phosphorus has three allotropic modifications: *Yellow* (or white), *red* (or violet), and *black*.

Yellow phosphorus possesses the properties usually associated with the element. It is semi-transparent, soft, and wax-like. It melts at 44° and boils at about 280°. It does not dissolve in water but is readily soluble in carbon disulfide, olive oil, and certain other oils and organic solvents. The vapor consists of molecules of P_4 (Figure 226). Yellow phosphorus is very poisonous. Chemically it is very active.

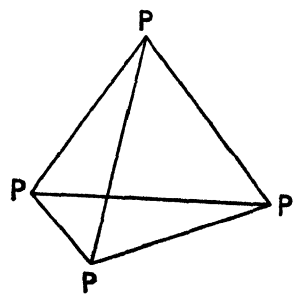


Figure 226. The Phosphorus Molecule

It combines readily with oxygen and ignites at about 30°. The oxides, P_4O_6 and P_4O_{10}, are produced by this reaction. It is preserved under water. The glowing of phosphorus in the dark is due to light which is emitted by changes that occur during slow oxidation. The name phosphorus comes from this *phosphorescence* of the substance.

5. Red Phosphorus

When yellow phosphorus is heated in the absence of air, it is changed into red phosphorus. At ordinary temperatures, the conversion is very slow, but at 250°–300° it is very rapid. This reaction is catalyzed by iodine and greatly accelerated by light. The properties of red phosphorus are very much different from those of the white, or yellow, form. It ignites only when heated to about 240°. It does not dissolve in carbon disulfide and it is not poisonous. It melts at about 600° under increased pressure, has no odor, and is slightly more dense than white phosphorus — 2.1 as compared with 1.82 g. per cc.

Black phosphorus is prepared by subjecting other forms of the element to about 4000 atmospheres at an elevated temperature.

6. Production of Phosphorus

The element is produced by reducing the phosphorus in mineral calcium phosphate or bone ash with carbon in an electric furnace (Figure 227). Sand (silica, SiO_2) is added to react with the calcium phosphate to form calcium silicate:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 \longrightarrow 6\ CaSiO_3 + P_4O_{10}.$$

Calcium silicate is the *slag*, and sand acts as a *flux*. The melted slag is drawn off through the outlet (S) at the bottom of the furnace. The carbon reduces phosphorus pentoxide:

$$P_4O_{10} + 10\ C \longrightarrow 10\ CO + P_4.$$

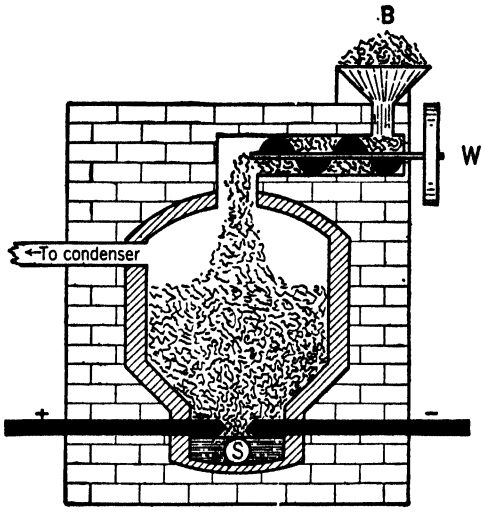


Figure 227. An Electric Furnace in Which Phosphorus Is Produced

The charge, consisting of phosphate rock, coke, and sand, is fed into the furnace from B by means of the screw W. The volatilized phosphorus passes out of the furnace through the tube leading to the condenser.

Vaporized phosphorus escapes through an outlet at the top, and is condensed. The liquid phosphorus is then run into molds and cast into sticks.

7. Uses of Phosphorus

Phosphorus forms dense clouds of P_4O_6 and P_4O_{10} when it burns, and because of this property it is sometimes used in the production of smoke screens. It is also used in making incendiary bombs, shells, and grenades. The use of phosphorus and its compounds in the manufacture of matches was introduced about 1825. The element is also used in producing phosphor-bronzes and in manufacturing certain compounds of phosphorus, such as the chlorides, PCl_3 and PCl_5, and the sulfide, P_4S_3.

8. Matches

The ordinary friction match depends upon the ease with which red phosphorus or compounds of phosphorus can be ignited. The first matches of this kind contained yellow phosphorus, but its use was later prohibited universally, because it is a source of great fire hazards and because it is dangerous to the health of workers in the match-factory; it produces very serious necrosis — decay — of the bones of the jaw.

The match which is "struck" by rubbing it upon almost any type of surface (the more friction the better) contains the following materials in its head: A layer of paraffin on the "head-end" of the stick; an oxidizing agent, such as potassium chlorate; and combustible substances, such as paraffin and sulfur. The head also contains glue to act as a binding agent; some filler such as clay, starch, or plaster of Paris; and, sometimes, an abrasive material, such as fine sand or ground glass. The tip on the head of the match contains, in addition to the substances in the rest of the head, phosphorus sesquisulfide, P_4S_3. This substance is ignited when it is heated by the friction produced when the match is rubbed against some object. The combustion of this substance then starts the reaction between sulfur (or some other combustible material) and the oxidizing agent ($KClO_3$). This, in turn, ignites the paraffin, and eventually the wood, itself, begins to burn.

The *safety match* is "struck" by rubbing it on the side of the box. The head of the match contains an oxidizing agent, such as potassium chlorate, and a readily combustible substance, usually antimony sulfide, Sb_2S_3. The side of the box is coated with a mixture of glue, an abrasive, red phosphorus, and an oxidizing agent.

COMPOUNDS OF PHOSPHORUS

9. Phosphine

The best known hydride of phosphorus is *phosphine* (PH_3), which corresponds to ammonia (NH_3). Like the latter, phosphine reacts with HI and HCl to form *phosphonium* iodide and chloride, PH_4I and PH_4Cl, but these do not produce PH_4^+ ions in aqueous solution; instead, PH_3 is released. Phosphine also forms a hydrate $PH_3.H_2O$, corresponding to NH_4OH.

Phosphine is a very poisonous gas and possesses an offensive odor. It is usually prepared by heating a solution of concentrated sodium hydroxide in which small particles of yellow phosphorus are suspended (Figure 228). Air must first be removed from the flask and tube by passing

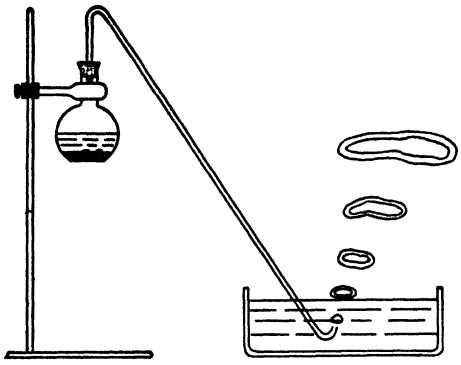


Figure 228. The Production of Phosphine and Its Spontaneous Combustion in the Air

a stream of illuminating gas through the apparatus. Phosphine[1] ignites spontaneously as bubbles of it escape into the air, and the oxides formed float away as smoke rings. The reaction is

$$3\,(Na^+ + OH^-) + 3\,H_2O + P_4 \longrightarrow 3\,(Na^+ + H_2PO_2^-) + PH_3.$$

The compound NaH_2PO_2 is *sodium hypophosphite.* Phosphine is also prepared by allowing water to act upon calcium phosphide:

$$Ca_3P_2 + 6\,H_2O \longrightarrow 2\,PH_3 + 3\,(Ca^{++} + 2\,OH^-).$$

10. Chlorides and Other Halides

The chlorides, PCl_3 and PCl_5, are representative of the compounds which phosphorus forms by direct combination with all of the halogens. Phosphorus triiodide, for example, is formed by grinding red phosphorus and iodine together in a mortar. The trichloride is a fuming, colorless liquid; the pentachloride is a yellow solid. They are used in the preparation of certain compounds in organic chemistry. Both the trichloride and pentachloride are almost completely hydrolyzed:

$$PCl_3 + 3\,HOH \longrightarrow 3\,(H^+ + Cl^-) + H_3PO_3$$
$$PCl_5 + 4\,HOH \longrightarrow 5\,(H^+ + Cl^-) + H_3PO_4$$

[1] The compound that starts the combustion is thought to be P_2H_4, which is produced as an impurity in the phosphine.

or, if hydrolysis is only partially completed, the oxychloride is formed:

$$PCl_5 + HOH \longrightarrow 2\,(H^+ + Cl^-) + POCl_3.$$

A similar reaction of PBr_3 and PI_3 with water will be recalled as a method of preparing pure hydrobromic and hydriodic acids (page 278).

11. Oxides

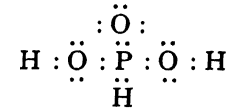
The two best-known oxides of phosphorus are the trioxide (P_4O_6) and the pentoxide (P_4O_{10}), both of which are white solids. The simplest formulas are P_2O_3 and P_2O_5, and these are frequently used, but the actual molecular formulas appear, from measurements of the densities of the vapors, to be P_4O_6 and P_4O_{10}, respectively. The latter is produced by burning phosphorus in an excess of oxygen; the trioxide is produced, usually with some P_4O_{10}, if the supply of oxygen is limited. The trioxide is the anhydride of phosphorous acid; the pentoxide is the anhydride of phosphoric acid. The trioxide is a reducing agent, but the pentoxide is very stable and ordinarily exhibits neither oxidizing nor reducing properties. Because of the pronounced tendency of P_4O_{10} to react with water, this oxide is a powerful drying agent. There is also a tetroxide of phosphorus, P_2O_4.

12. Phosphorous Acids

Phosphorus trioxide reacts with cold water to form *orthophosphorous acid:*

$$P_4O_6 + 6\,H_2O \longrightarrow 4\,H_3PO_3.$$

The acid is usually prepared, however, by the hydrolysis of PCl_3. It is an active reducing agent and a fairly strong, *dibasic* acid:



Only the atoms of hydrogen that are parts of hydroxyl groups of oxygen acids can be

given up to other substances as protons; and hence, phosphorous acid is dibasic (diprotic) because it can give up only two protons per molecule. Its sodium salts — sodium phosphites — are NaH_2PO_3 and Na_2HPO_3, which are vigorous reducing agents and are used to some extent as antiseptics. The acid itself crystallizes as a white, very deliquescent solid, which melts at about 70° and decomposes at 200°. *Pyrophosphorous acid*, $H_4P_2O_5$, and *metaphosphorous acid*, HPO_2, may be formed when the trioxide is placed in limited quantities of water.

The salt, NaH_2PO_2, which is made in the preparation of phosphine (page 377) is a salt of *hypophosphorous acid*, H_3PO_2. This acid is monobasic, because two of the atoms of hydrogen in the molecule are attached directly to phosphorus. Both the acid and its salts are reducing agents, and the salts, called *hypophosphites*, are used in medicine as tonics and in the treating of certain bone diseases.

13. Phosphoric Acids

There are three acids of which the pentoxide is the anhydride, and which, therefore, may be called phosphoric acids:

$$P_4O_{10} + 2\ H_2O \longrightarrow 4\ HPO_3,$$ *metaphosphoric acid*,

$$P_4O_{10} + 4\ H_2O \longrightarrow 2\ H_4P_2O_7,$$ *pyrophosphoric acid*,

$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4,$$ *orthophosphoric acid*.

14. Pyrophosphoric and Metaphosphoric Acids

The prefix *pyro* refers to the formation of pyrophosphoric acid by *heating* orthophosphoric acid to 200–250°:

$$2\ H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O\uparrow\ .$$

If the ortho acid is heated to a higher temperature (400–500°), metaphosphoric acid is produced:

$$H_3PO_4 \longrightarrow HPO_3 + H_2O\uparrow\ .$$

The empirical formula for metaphosphoric acid is HPO_3, but there appear to be several acids corresponding to this simple formula, all differing in the number of HPO_3 units in the real molecule. *Hexametaphosphoric acid*, for example, is $(HPO_3)_6$, salts of which are known. Both of these acids are white, crystalline compounds. Metaphosphoric acid can be melted, and the liquid upon cooling forms a glass-like solid, sometimes called *glacial* phosphoric acid. Metaphosphoric acid is used in some dental cements.

15. Hypophosphoric Acid

This acid has the formula $H_4P_2O_6$, and its anhydride is P_2O_4. The acid and its salts, the hypophosphates, are among the less important compounds of phosphorus.

16. Orthophosphoric Acid

This is the most important of the three phosphoric acids. Anhydrous orthophosphoric acid (hydrogen phosphate) is a colorless, crystalline substance (m.p. 42°). It is best known as a syrupy solution containing about 85 per cent of H_3PO_4. This acid is usually prepared by the oxidation of phosphorus in air (followed by the addition of water) or by the action of concentrated sulfuric acid upon calcium phosphate:

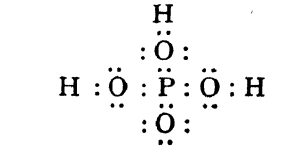
$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 3\ CaSO_4\downarrow + 2\ H_3PO_4.$$

The acid can also be prepared by oxidizing red phosphorus with nitric acid.

Orthophosphoric acid is tribasic (page 323):

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^=$$
$$HPO_4^= \rightleftarrows H^+ + PO_4^{\equiv}$$

The electronic formula of orthophosphoric acid is



17. Phosphates

Corresponding to its three stages of ionization, the acid forms three series of salts. The sodium salts and the names commonly applied to them are:

NaH_2PO_4, *primary* or *monosodium phosphate*
Na_2HPO, *secondary* or *disodium phosphate*
Na_3PO_4, *tertiary* or *trisodium phosphate.*

When normal calcium phosphate ($Ca_3(PO_4)_2$) is treated with sulfuric acid, the primary (calcium) phosphate is produced:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4.$$

The normal calcium phosphate is very slightly soluble, while the primary salt, commonly called *superphosphate of lime,* is much more soluble. If the normal salt is used as a fertilizer, it is not readily available as a plant food. It is for this reason that phosphate rock is treated with sulfuric acid or with a mixture of sulfuric and phosphoric acids, (page 370) in the manufacture of fertilizers. The primary salt is more readily soluble and is therefore more available for plant use.

Salts of pyrophosphoric and metaphosphoric acids are prepared by heating acid salts of orthophosphoric acid:

$$2\ Na_2HPO_4 \longrightarrow Na_4P_2O_7 + H_2O.$$
$$NaH_2PO_4 \longrightarrow NaPO_3 + H_2O.$$

18. Uses of Phosphoric Acid and Its Salts

Phosphoric acid is used in soft drinks and in making certain fertilizers, such as ammonium phosphate. Its salts are used as fertilizers, in baking powders (page 246), in softening water, as a cleansing agent, in fireproofing fabrics, in weighting silk, yeast making, and clarifying sugar solutions.

Sodium hexametaphosphate, $Na_6P_6O_{18}$, ($6\ NaPO_3$), is produced by heating sodium acid pyrophosphate, $Na_2H_2P_2O_7$, to about 700°. It is used as a water softener and as a cleansing agent.

19. The Hydrolysis of Phosphates

A solution of trisodium phosphate is rather strongly alkaline because of the following reaction:

$$PO_4^{\equiv} + HOH \rightleftarrows HPO_4^{=} + OH^-.$$

The secondary phosphate gives a slightly alkaline solution because it, also, reacts with water to liberate hydroxyl ions:

$$HPO_4^{=} + HOH \rightleftarrows H_2PO_4^- + OH^-.$$

It also ionizes to a small extent to form hydrogen ions:

$$HPO_4^{=} \longrightarrow H^+ + PO_4^{\equiv},$$

but the $HPO_4^{=}$ ion has a slightly greater tendency to combine with H^+ than it has to liberate this ion, and hence, the solution of the secondary phosphate of sodium is slightly alkaline.

Primary sodium phosphate ionizes to form, principally, $H_2PO_4^-$ ion, but this further ionizes to some extent to produce $HPO_4^{=}$, $PO_4^{\equiv}$, and H^+ ions. The first stage of the ionization of phosphoric acid is fairly strong. Hence, there is no pronounced tendency for the $H_2PO_4^-$ ion to combine with the hydrogen ions of water. The tendency of this ion to further dissociate, producing H^+, is greater than its tendency to combine with hydrogen ions. A solution of the primary phosphate is, consequently, slightly acid in reaction.

ARSENIC

20. Occurrence

Arsenic compounds have long been known. The alchemists were acquainted with the oxide, and brightly colored arsenic sulfides were used by the Greeks and Romans as pigments.

Small quantities of arsenic occur in the free state, but the principal sources are the sulfur compounds: *orpiment* (As_2S_3); *realgar* (As_2S_2); and *arsenopyrite* (FeAsS). Most of the arsenic produced in America comes

from the dust that collects in the flues of smelters using copper, lead, and gold ores. When the sulfides of these metals are roasted, preparatory to their reduction to the metals, arsenic sulfide is converted into the oxide, As_4O_6, which is volatile and condenses in the dust that collects in the flues of the furnaces.

21. Preparation and Properties

The element is prepared by reducing the trioxide (As_4O_6) with carbon:

$$As_4O_6 + 6\,C \longrightarrow 6\,CO + 4\,As.$$

Arsenic is a dark gray, brittle, crystalline solid. It sublimes at about 600°, forming a yellow, poisonous vapor, which possesses the odor of garlic. It has two allotropic forms of which *gray*, or metallic, arsenic is the most stable and the only one of any importance. *Yellow* arsenic is soft, volatile, and unstable, changing rapidly to the gray form.

Chemically, arsenic resembles phosphorus in many ways. The main difference between them consists of the slightly greater tendency of arsenic to act as a metal. This is by no means a pronounced tendency. It is best illustrated by the fact that in solutions containing trivalent arsenic compounds there are some As^{+++} ions. This fact is evidenced by the precipitation of As_2S_3 from such solutions, when sulfide ion is added and the solutions are acidified.

Arsenic oxidizes slowly at ordinary temperature, but it ignites at about 180°, forming the trioxide. It burns in chlorine to form the trichloride, $AsCl_3$, and combines with the other halogens to form similar compounds. It also reacts directly with sulfur. With the metals it forms *arsenides*, e.g., Na_3As. It is a reducing agent; nitric acid, for example, oxidizes it to arsenic acid (H_3AsO_4). The density of the vapor at about 650° indicates that the molecular formula is As_4 for the free element.

22. Uses

Free arsenic is used in manufacturing certain bronzes and other alloys, lead shot, and compounds of the element. In making shot, arsenic is added to form harder and more nearly spherical drops of lead. Shot is made by pouring melted lead through a screen which breaks up the liquid into a great many small drops. When arsenic has been added, the drops solidify more slowly, allowing more time for the small masses of liquid lead to attain spherical form. Its presence in other alloys increases the luster, strength, hardness, fluidity, and resistance to certain chemical actions. Only about 2000 tons of arsenic are produced annually.

23. Arsine

The compound of arsenic corresponding to phosphine and ammonia is *arsine* (AsH_3). This substance is an extremely poisonous gas with a garlic-like odor. Unlike ammonia, it does not react with water to form AsH_4^+ ions, and it does not form any salts similar to the ammonium salts. It is unstable and decomposes into the elements when only moderately heated:

$$2\,AsH_3 \longrightarrow 3\,H_2 + 2\,As.$$

It burns with a slightly blue flame to form water and free arsenic, if the supply of oxygen is limited, but in an excess of air the arsenic is oxidized to As_4O_6. Arsine is produced by the action of atomic hydrogen upon the compounds of arsenic.

$$H_3AsO_3 + 6\,(H) \longrightarrow AsH_3 + 3\,H_2O.$$

The atomic hydrogen is supplied, usually, by the reaction of an acid with a metal, such as zinc, in the presence of the arsenic compound. This reaction is the basis of *Marsh's test* for arsenic (Figure 229). The arsine produced in the flask is dried by passing through a tube filled with calcium chloride and then decomposes forming a mirror of metallic arsenic at the point where the outlet tube is heated. The

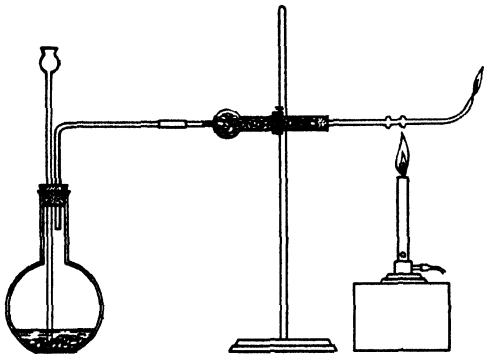


Figure 229. Diagram of Apparatus Used in the Marsh Test for Arsenic

arsenic mirror is further identified by its insolubility in a solution containing ClO^-, which dissolves deposits of other elements, such as antimony, which may form at the same time.

24. Oxides

Arsenic trioxide, As_4O_6, but frequently referred to as As_2O_3, is the substance known as *white arsenic* and to the general public is "arsenic." Most of the compounds of arsenic are produced from this oxide. It has a sweet taste and is extremely poisonous. Its chief use is in the preparation of insecticides used in sprays for fruit trees and vegetables, in animal dips, to kill the boll weevil in cotton fields, etc. It is also used to preserve furs, stuffed birds, and other skins; in preparing poisons for rats and ants; preservatives for wood; mordants for dyeing; weed killers; etc. Some is also used in decolorizing glass and in making enamels and opaque glass. Some of the compounds made from it are used in medicine. The best known of these compounds is *salvarsan*, a specific remedy for syphilis.

Arsenic pentoxide cannot be prepared by burning arsenic in an excess of air. It is made by heating arsenic acid until the water is expelled:

$$4\ H_3AsO_4 \longrightarrow 6\ H_2O + As_4O_{10}.$$

Like the trioxide it is a white crystalline substance.

25. Arsenious Acid and the Arsenites

Arsenic trioxide is not very soluble in water, but its solution is acidic because of the presence of some arsenious acid H_3AsO_3. Only the salts of this acid are known in the pure state. The usual sodium or potassium salts correspond to the meta form of the acid and are, therefore, *metaarsenites* ($KAsO_2$ and $NaAsO_2$). The heavy metals form *orthoarsenites*, such as $Pb_3(AsO_3)_2$, Ag_3AsO_3, etc. The most important salts of arsenious acid are those of copper:

Scheele's green — $CuHAsO_3$
Paris green — $Cu_2(C_2H_3O_2)(AsO_2)_3$.

These compounds are used as pigments and insecticides. The oxide is also slightly basic as shown by the fact that it dissolves in solutions of acids to a greater extent than in pure water.

26. Arsenic Acids and the Arsenates

Arsenic pentoxide is the anhydride of arsenic acid (H_3AsO_4). Salts corresponding to *ortho*, *pyro*, and *meta arsenic acids* are known: Na_3AsO_4, $Na_4As_2O_7$, and $NaAsO_3$. *Calcium orthoarsenate* ($Ca_3(AsO_4)_2$) is one of the most important of the salts; it is used as an insecticide to kill boll weevil in the cotton fields. The lead salts of arsenic acid ($Pb_3(AsO_4)_2$ and $PbHAsO_4$) are also important insecticides. Arsenic acid is produced by the oxidation of the trioxide with nitric acid. When the resulting solution is evaporated, crystals of $H_3AsO_4.H_2O$ are obtained.

27. Sulfides

In solutions containing hydrochloric acid, compounds of trivalent arsenic react with hydrogen sulfide to form a precipitate of yellow arsenic trisulfide, As_2S_3:

$$2\ (H^+ + Cl^-) + 2\ (Na^+ + AsO_2^-) + 3\ H_2S \longrightarrow As_2S_3\downarrow + 2\ (Na^+ + Cl^-) + 4\ H_2O.$$

The hydrochloric acid prevents arsenic trisulfide from forming the colloidal state (page 228).

The pentasulfide, As_2S_5, is precipitated by hydrogen sulfide from a solution containing the arsenate ion and an acid, usually hydrochloric acid. Some trisulfide is usually formed at the same time, because some of the arsenate ion is reduced to arsenite by hydrogen sulfide:

$$2\,(3\,Na^+ + AsO_4^{-3}) + 6\,(H^+ + Cl^-) + 5\,H_2S \longrightarrow As_2S_5\downarrow + 6\,(Na^+ + Cl^-) + 8\,H_2O.$$

The sulfides also possess acid properties and react with the sulfides of certain metals and with ammonium sulfide to form *thiosalts*. Thus, As_2S_3 reacts with sodium sulfide to form soluble *sodium thioarsenite*:

$$As_2S_3 + 3\,(2\,Na^+ + S^=) \longrightarrow 2\,(3\,Na^+ + AsS_3^{-3}),$$
or $$As_2S_3 + (2\,Na^+ + S^=) \longrightarrow 2\,(Na^+ + AsS_2^-).$$

The pentasulfide reacts with these basic sulfides to form *thioarsenates*:

$$As_2S_5 + 3\,(2\,NH_4^+ + S^=) \longrightarrow 2\,(3\,NH_4^+ + AsS_4^{-3}).$$

When solutions of the thio salts are acidified, the corresponding thio acids (H_3AsS_3 and H_3AsS_4) are probably first produced, but these decompose immediately into the sulfides and hydrogen sulfide:

$$6\,(H^+ + Cl^-) + 2\,(3\,Na^+ + AsS_4^{-3}) \longrightarrow As_2S_5\downarrow + 3\,H_2S + 6\,(Na^+ + Cl^-).$$

These reactions are used in analytical chemistry to separate the sulfide of arsenic from the sulfides of metals, such as CuS and FeS, that are not soluble in sodium or ammonium sulfide.

ANTIMONY

28. Occurrence and Preparation

Antimony occurs in the earth, principally as the mineral *stibnite* (Sb_2S_3). Some of the element occurs in the free state. The principal producing regions of the world are China, Mexico, and Bolivia, and the annual production is normally 30,000–40,000 tons.

Antimony sulfide is melted by heating the ore to about 600°. The liquid sulfide is drained away from the rock of the ore and heated with iron:

$$Sb_2S_3 + 3\,Fe \longrightarrow 2\,Sb + 3\,FeS.$$

Liquid antimony is heavier than the ferrous sulfide which is also melted; the latter floats on top and is easily removed. The sulfide can also be changed to the free element by first roasting the ore in air, and then reducing the oxide with carbon:

$$Sb_2O_3 + 3\,C \longrightarrow 3\,CO + 2\,Sb.$$

29. Properties and Uses

There are two forms of antimony: A very unstable yellow form and the more important and common metallic variety.

Antimony is much more metallic in appearance and in properties than either phosphorus or arsenic. The element has a silver white, brilliant luster; is very brittle; has a density of 6.8 g. per cc.; melts at 630°; and crystallizes from the molten state, with a slight expansion, to form large, beautiful crystals. Antimony combines directly with the halogens, phosphorus, arsenic, and sulfur. It does not displace hydrogen from HCl, but dissolves in nitric acid to form oxides, which are slightly soluble, and, therefore, slightly basic at best.

More than one half of the antimony used in the United States is consumed in the manufacture of bearing metal and storage battery plates for use in the automobile industry. Lead containing about 12 per cent of antimony is much harder than ordinary lead and is used in making bullets, shrapnel, etc. Antimonial lead is also resistant to the action of acids. Because it tends to expand when it solidifies, an alloy containing from 14–30 per cent of antimony is used as type metal. The expansion of the metal gives a sharp outline and a clear, distinct imprint of the type. Alloys containing antimony are also used in pewter and antifriction metals (Babbitt metal), as coatings for copper telephone cables, and other purposes.

30. The Compounds of Antimony

Stibine, SbH_3, is produced by the action

of atomic hydrogen upon compounds of antimony. It is a poisonous gas and resembles arsine but is less stable. If present, it produces a mirror like that of arsenic in the Marsh test but, unlike arsenic, the deposit of antimony is soluble in a solution containing the ClO^- ion. The oxides of antimony are Sb_4O_6, Sb_4O_{10} and Sb_2O_4. The latter is probably antimonous antimonate, $SbSbO_4$. The trioxide displays some basic properties in forming salts with acids. Thus, nitric and sulfuric acids added in excess react with the trioxide to form $Sb(NO_3)_3$ and $Sb_2(SO_4)_3$, but if an excess of the acid is not added, the basic salts $SbONO_3$ and $(SbO)_2SO_4$ are produced.

Antimony chloride, $SbCl_3$, can be produced by the direct action of antimony and chlorine. It hydrolyses to form the basic chloride, which then decomposes to form *antimony oxy-chloride:*

$$SbCl_3 + 2\,HOH \rightleftarrows Sb(OH)_2Cl + 2\,(H^+ + Cl^-)$$
$$Sb(OH)_2Cl \longrightarrow H_2O + SbOCl\downarrow$$

The white trioxide is produced by oxidizing the element with nitric acid, and the pentoxide by heating antimonic acid. The trioxide is amphoteric. Thus, it reacts with alkali hydroxides, such as NaOH, to form antimonites:

$$Sb_4O_6 + 4\,(Na^+ + OH^-) + 6\,H_2O \longrightarrow 4\,(Na^+ + Sb(OH)_4^-).$$

The antimony compound produced in this reaction is *sodium metaantimonite*, and its formula may also be written as $NaSbO_2 \cdot 2\,H_2O$. The pentoxide exhibits only acidic properties. When antimony trioxide is further oxidized by nitric acid a white, very slightly soluble substance is produced. This is called *antimonic* acid and it corresponds roughly to the formula $HSb(OH)_6$. This compound may be regarded as a hydrated antimony pentoxide or as $HSbO_3 \cdot 3\,H_2O$. It reacts with potassium hydroxide to form $KSb(OH)_6$ or $KSbO_3.3\,H_2O$, which is potassium antimonate.

Antimony trisulfide is an orange-red colored compound which precipitates when hydrogen sulfide is passed into a solution of the trichloride or slightly acidified solutions of antimonites and other compounds of trivalent antimony. The *pentasulfide*, Sb_2S_5, is formed in a similar manner from compounds of pentavalent antimony. Like the sulfides of arsenic, both sulfides of antimony dissolve in solutions of the alkali or ammonium sulfides and polysulfides, forming *thioantimonites* and *thioantimonates*. Thus, with ammonium sulfide, $(NH_4)_3SbS_3$ and $(NH_4)_3SbS_4$ are formed from Sb_2S_3 and Sb_2S_5, respectively. When solutions containing the thio salts are acidified, antimony trisulfide is precipitated. The trisulfide is used in manufacturing red rubber and matches.

Tartar emetic, a basic potassium antimony tartrate, $K(SbO)C_4H_4O_6$, is used in medicine and as a mordant in dyeing.

BISMUTH

31. Occurrence

Bismuth occurs most abundantly in nature as the free element. It also occurs as the oxide ($Bi_2O_3.H_2O$), called *bismite*, and as the sulfide (Bi_2S_3), called *bismuthenite*. Some bismuth is produced in the United States as a by-product of lead smelters and refineries. The chief sources of the element and its compounds are in the United States, Bolivia, Peru, Canada, and Spain. The metal is recovered from ores containing free bismuth by melting and separating the molten metal from the earthy portion of the ore. The sulfide ore is roasted to form the oxide, which is then reduced by carbon.

32. Properties

Bismuth is a silvery gray metal with a reddish tint. It occurs in one form, which is crystalline, lustrous, hard, and brittle. Its specific gravity is 9.8; it melts at 271° and boils at 1450°.

Bismuth burns in air or oxygen to form the oxide, Bi_2O_3. It combines directly, but not very vigorously, with the halogens and with sulfur. It dissolves readily in nitric acid to form the nitrate ($Bi(NO_3)_3$). The formation of the nitrate by bismuth shows its decided metallic character in contrast to the non-metallic nature of the other members of its family. The element also dissolves in concentrated sulfuric acid, in much the same manner that copper does, to form the sulfate, $Bi_2(SO_4)_3$.

33. Compounds

In practically all its compounds, bismuth acts as a trivalent metal, forming simple salts, such as $BiCl_3$ and $Bi(NO_3)_3$. Its hydride, *bismuthine* (BiH_3) is an extremely unstable compound and very little is known about it. The most familiar oxide is Bi_2O_3, which forms when the metal is heated in the air. The *monoxide*, BiO, and the *pentoxide*, Bi_2O_5, are also known.

The *trioxide* is a yellow solid. It does not react with alkalies, such as NaOH, and, therefore, has no acid properties. It dissolves in acids and when the solutions are evaporated, normal salts, such as the chloride, nitrate, or sulfate, are obtained as crystals. These salts hydrolyze readily, when water is added, to form basic salts; for example, *basic bismuth chloride* is formed by the hydrolysis of bismuth chloride:

$$BiCl_3 + 2\ HOH \rightleftarrows Bi(OH)_2Cl + 2\ (H^+ + Cl^-)$$

$$Bi(OH)_2Cl \longrightarrow BiOCl + H_2O.$$

The basic salt, however, decomposes immediately and forms *bismuth oxychloride*, BiOCl. The oxychloride is also known as *pearl white*. It is used as a white paint pigment and in face powders. The basic nitrate, best known as *bismuth subnitrate*, is used in medicine in treating intestinal inflammations, ulcers, and skin diseases. It is also used in face powders.

The salts of bismuth react in solutions with sodium hydroxide to form white, slightly soluble bismuthyl hydroxide, BiO(OH), which is soluble in acids but not in alkalies.

The *pentoxide* reacts, however, with very concentrated solutions of sodium hydroxide to form *sodium bismuthate*, $NaBiO_3$, which hydrolyzes in water, or reacts when an acid is added, to form the very weak *bismuthic acid*, $HBiO_3$. This acid and its salts correspond to nitric acid and the nitrates and show that, in its highest oxidation state, bismuth possesses, to a slight degree, the non-metallic and acid-forming properties of the other members of the family.

Bismuth trisulfide, Bi_2S_3, is precipitated as a brown compound, when hydrogen sulfide is passed into a solution containing a bismuth salt. Like the trioxide, it has no acid properties and consequently does not dissolve in solutions of sodium or ammonium sulfide to form thio-salts. The separation of bismuth from arsenic and antimony in analytical chemistry depends upon this difference in the behavior of the sulfides of the elements.

34. Uses of Metallic Bismuth

Metallic bismuth is used to produce many alloys. The presence of bismuth in these alloys gives low melting points and prevents shrinkage upon solidification, since bismuth expands upon cooling. Examples of two of these alloys and their composition are given below:

	Bi	Pb	Sn	Cd	Melting Point
			(Parts)		
Wood's metal	50	25	12.5	12.5	71°
Rose's metal	50	25	25		94°

These low-melting alloys are used for many purposes: Electric fuses; automatic fire alarms; automatic sprinkler systems; releases on automatic fire-doors; and safety plugs for boilers. When slightly heated, the bismuth alloy melts, releasing water from the sprinkling systems, closing an electric circuit which rings a bell, or automatically removing the stops that hold open fire-doors. Bismuth alloys are also used as antifriction metals to some extent.

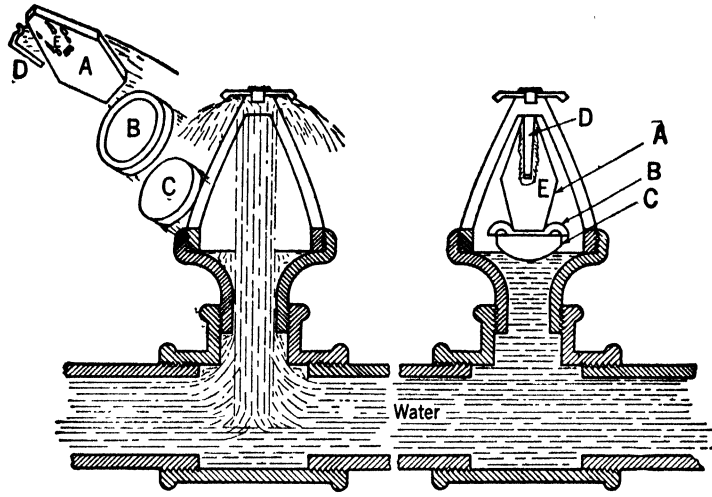


Figure 230. Automatic Sprinkler

D is made of the low-melting alloy solder; it holds the strut composed of A, B, and C in place. When D melts, the pressure of the water throws A, B, and C out of the way, and the water escapes through the opened valve.

REVIEW EXERCISES

1. Compare and contrast the properties of the elements of the nitrogen family.
2. If a sample of rock phosphate contains 80 per cent of $Ca_3(PO_4)_2$, how much of this material would be required for the production of one ton of superphosphate (including the calcium sulfate produced)?
3. What weight of (1) phosphorus and (2) of phosphoric acid could be produced from the weight of rock phosphate calculated above?
4. Show why a solution of primary sodium phosphate is slightly acid while a solution of secondary sodium phosphate is alkaline.
5. Which should have a higher *p*H, a solution of primary sodium phosphate or primary ammonium phosphate? Why?
6. Starting with rock phosphate outline a series of reactions which could be used to prepare the salt $NaPO_3$.
7. How would you proceed to bring about the transformations indicated below?
   $Sb_2S_3 \longrightarrow Sb$; $Sb \longrightarrow SbOCl$; $Na_2HPO_4 \longrightarrow Na_4P_2O_7$; $Bi \longrightarrow Bi_2(SO_4)_3$; $As \longrightarrow H_3AsO_4$; $H_3AsO_3 \longrightarrow AsH_3$; $H_3AsO_3 \longrightarrow As_2S_3$.
8. Explain the meaning of the term *amphoteric hydroxide*. What hydroxides of the members of this family are amphoteric and which are not? Illustrate the reactions, with acids and bases, of one of the amphoteric hydroxides.
9. Identify: Arsine, bismuth subnitrate, Wood's metal, tertiary sodium phosphate, sodium hexametaphosphate, bismuth oxy-chloride, bismuthic acid, Marsh's test, Paris green, white arsenic, ammonium thioarsenite, and arsenopyrite.
10. Show the relationships between the three phosphoric acids and their anhydride.
11. Write equations for the following reactions. (Show all soluble ionic compounds in the usual manner.)

    (1) $BiCl_3 + NaOH \longrightarrow$
    (2) $Na_2HPO_4 + CuCl_2 \longrightarrow$
    (3) $P + HNO_3 \longrightarrow$
    (4) $BiOCl + H_2S \longrightarrow$
    (5) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow$
    (6) Na_2HPO_4 (heat) $\longrightarrow$
    (7) $H_3AsO_3 + (H) \longrightarrow$
    (8) $Na_3PO_4 + H_2O \longrightarrow$

12. Account for the natural occurrence of bismuth and antimony in the free state. Why is phosphorus not found in the free state?
13. Given a sample which may be phosphorus, bismuth, arsenic, or antimony. What physical appearances, or other properties, would you look for as means of identification? How would you proceed by chemical methods to determine which of the elements is present, assuming that the sample contains only one of the four?

14. Why is antimony sulfide not hydrolyzed while antimony chloride is?
15. Suggest two methods of separating bismuth from arsenic, starting with a solution which contains $BiCl_3$ and $NaAsO_2$. Write equations for all necessary reactions.
16. In using the Marsh test, the mirror of arsenic produced in the tube of the apparatus weighed 10 mg. The material tested weighed 10 g. and contained As_4O_6. What weight of the oxide was present per 100 g. of the material tested?
17. What reactions can be used to produce the following changes in the order indicated: $As_4O_6 \longrightarrow As_2S_3 \longrightarrow Na_3AsS_3 \longrightarrow As_2S_3$?
18. Starting with 10 g. of As_4O_6, what weight of As_2S_3 should one obtain by the series of reactions in 17, assuming that there are no losses?
19. What weight of primary sodium phosphate can be produced from the phosphoric acid made by the oxidation of 10 g. of phosphorus with nitric acid?
20. To one liter of 0.1 N solution of orthophosphoric acid sufficient calcium chloride is added to precipitate the phosphate ion almost completely. What weight of $Ca_3(PO_4)_2$ can be produced by this procedure?
21. Name the compounds corresponding to the following formulas: $NaBiO_3$, SbOCl, $NaSbO_2$, $(NH_4)_3AsS_4$, $Pb_3(AsO_4)_2$, $CaHPO_4$, K_2HPO_4, $NaPO_3$, $H_4P_2O_7$, and Cu_3P_2.
22. How does PH_4^+ react with water?
23. Why does phosphorous acid, H_3PO_3, form no sodium salt having the formula Na_3PO_3?
24. What changes, if any, in the oxidation numbers of phosphorus occur in each of the following conversions:

    H_3PO_4 into $H_4P_2O_7$
    H_3PO_4 into HPO_3
    P into $H_2PO_2^-$
    P_4O_{10} into P_4O_6
    Ca_3P_2 into PH_3.

25. In each of the solutions described below a compound of phosphorus, arsenic, antimony or bismuth is present. Identify the element from the information given.
    (*a*) Hydrogen sulfide forms a brown precipitate which does not dissolve in a solution of sodium or ammonium sulfide.
    (*b*) The addition of sodium hydroxide produces a white precipitate which dissolves when an excess of NaOH is added.
    (*c*) The addition of sodium hydroxide produces a white precipitate that does not dissolve in an excess of NaOH.
    (*d*) When hydrogen sulfide is passed into a solution that has been acidified with HCl, a yellow precipitate is formed. This is soluble in ammonium polysulfide.

REFERENCES FOR FURTHER READING

Roush, G. A., and A. Butts, *Mineral Industry*, New York: McGraw-Hill Book Company, published annually.

Arsenic: *Chem. and Met. Eng.*, **23,** 957 (1921); **24,** 527 (1921); **27,** 1141, 1191, 1195, 1201, 1234, 1241 (1922).

Bismuth (alloys): *Ind. and Eng. Chem.*, **27,** 1464 (1935).

Insecticides: *J. Chem. Ed.*, **6,** 1100, 1243 (1929); **7,** 2301 (1930).

Matches: *J. Chem. Ed.*, **6,** 1359 (1929); **17,** 515 (1940); **18,** 116, 277, 380, 428 (1941).

Phosphate Rock and Fertilizers: *Chem. and Met. Eng.*, **29,** 393 (1923); *Ind. and Eng. Chem.*, **23,** 14 (1931); **34,** 13 (1942); *J. Chem. Ed.*, **3,** 655 (1926); **6,** 899 (1929); **11,** 477 (1934); **23,** 529 (1946).

Phosphorus: *J. Chem. Ed.*, **4,** 1105 (1927).

Superphosphate: *Ind. and Eng. Chem.*, **28,** 1182 (1936).

31

SILICON AND RELATED ELEMENTS

SILICON

1. Occurrence

Silicon does not occur in nature as the free element. Its compounds, however, are very abundant, forming about 87 per cent of the solid crust of the earth. One of the most abundant compounds of silicon is the oxide called *silica*, SiO_2, which occurs most abundantly in sand, sandstone, and quartz. It also occurs in many variously colored crystalline forms, among which are *rose quartz*, *amethyst*, *rock crystal*, *chalcedony*, *carnelian*, *onyx*, *agate*, *flint*, *jasper*, and *opal*. Other minerals containing silicates of different kinds include granite, shale, clay, marl, micas, feldspars, asbestos, tourmaline, and topaz.

2. Preparation of the Element

Small samples of silicon can be prepared by reducing silica (SiO_2) by means of powdered aluminum or magnesium. Commercially, silicon is produced by reducing the oxide with carbon in an electric furnace. If a mixture of silica and ferric oxide is reduced by carbon, an alloy of iron and silicon, called *ferrosilicon*, is produced. Since the principal use of silicon is in the preparation of steels of special properties, ferrosilicon, instead of pure silicon, is most often produced.

3. Properties

Amorphous silicon is a brown powder, which probably consists of very small crystals. The crystalline variety is gray in color and hard enough to scratch glass; has a density of 2.4 g. per cc.; melts at 1427°; boils at about 2300°; and is a fair conductor of electricity.

The element reacts readily with the halogens to form SiF_4, $SiCl_4$, $SiBr_4$, and SiI_4. With fluorine the element reacts spontaneously and is ignited by the heat liberated in the reaction. Silicon burns when heated in the presence of oxygen. It does not liberate hydrogen from acids. When heated, it reacts with sulfur (SiS_2), carbon (SiC), nitrogen (Si_3N_4), and with some metals. The compounds with the metals are called *silicides*. Typical silicides are Li_3Si, Mg_2Si, FeSi (ferrosilicon) and $CoSi_3$.

4. Uses

Although one of the most abundant of the elements, silicon in its free state has few uses. It is, however, an essential substance in the steel industry. Ferrosilicon is added during the production of steel to combine with and remove dissolved oxygen, which weakens the finished product. Silicon steel contains up to 5 per cent of silicon. This variety of steel has desirable magnetic properties and, therefore, is used in making the cores of transformers and electromag-

nets. If 15–16 per cent of silicon is added, the steel produced is very hard and resistant to corrosion and the attack of acids. *Duriron* and *Tantiron* are alloy steels of this kind. The steel used in making springs contains manganese and silicon, and an alloy of aluminum and silicon is used in automobiles.

5. Halides

The halides of silicon have the general formula SiX_4. They can be prepared by the direct combination of silicon and the halogens, but only the fluoride is formed at ordinary temperatures. Silicon tetrafluoride (SiF_4) is usually made by allowing hydrofluoric acid to act upon silica or a silicate:

$$SiO_2 + 4\ HF \longrightarrow 2\ H_2O + SiF_4\uparrow$$
$$CaSiO_3 + 6\ HF \longrightarrow CaF_2 + SiF_4\uparrow + 3\ H_2O.$$

It is a colorless, non-combustible gas, which fumes in most air. With water it hydrolyzes to some extent as follows:

$$SiF_4 + 4\ HOH \longrightarrow H_4SiO_4 + 4\ HF.$$

A portion of the *silicic acid*, H_4SiO_4, precipitates, and a part reacts with HF to form *fluosilicic acid*, H_2SiF_6:

$$H_4SiO_4 + 6\ HF \longrightarrow (2\ H^+ + SiF_6^=) + 4\ H_2O.$$

Fluosilicic acid is a moderately strong acid.

Silicon tetrachloride, $SiCl_4$, is produced by the action of chlorine upon a heated mixture of silica and carbon or by the reaction of chlorine and silicon carbide, SiC. The tetrachloride hydrolyzes readily and fumes strongly in moist air, forming a dense cloud consisting of droplets of hydrochloric acid and small particles of silicic acid:

$$SiCl_4 + 4\ HOH \longrightarrow 4\ (H^+ + Cl^-) + H_4SiO_4.$$

If ammonia is present, the smoke is still more dense, because of the formation of ammonium chloride. A mixture of this kind is used to make smoke screens.

6. Oxides; Silica

Silicon forms two oxides, the monoxide, SiO, and the dioxide, SiO_2. The monoxide is yellow-brown in color and relatively unimportant.

The dioxide, commonly called *silica*, occurs as beautiful, colorless crystals of *quartz*, which is also called *rock crystal*. Small amounts of impurities are sometimes present, and these give crystals of characteristic colors. The *amethyst* is quartz plus a trace of an oxide of manganese. Small air bubbles are responsible for the appearance of *milk quartz*. *Rose quartz*, *onyx*, *jasper*, *agate*, *flint*, *opal*, *petrified wood*, and *chalcedony* are other forms of impure silica. The dioxide constitutes most of the material in sand and sandstone. Silica is present in some forms of animal and plant life, such as bamboo, rushes, straw, feathers of certain birds, and sponges. Small aquatic organisms, called *diatoms*, have skeletons of silica. Collections of these skeletons form deposits of *diatomaceous earth* or *kieselguhr*, which is widely used to adsorb colored substances from oils and other liquids. It is also used in soaps and in metal polishes as a mild scouring powder.

7. Fused Quartz

When heated to temperatures above 1700°, quartz gradually softens, and eventually forms a thick liquid. Vessels made of fused quartz are expensive but have many desirable properties. They are not likely to break when heated and suddenly cooled, because of the small coefficient of expansion of quartz. Quartz also resists the chemical action of practically all reagents, except strongly alkaline solutions or fused alkalies, and is less soluble in water than glass. The alkalies react with quartz, of course, because it is an acidic oxide. Quartz allows ultra-violet light to pass through it, while ordinary glass does not.

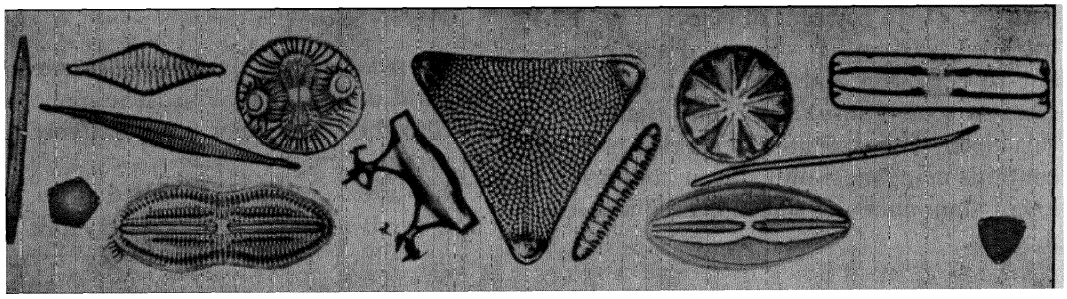


Figure 231. Diatoms

Diatomaceous earth is composed of diatoms, such as these, which are skeletons of small aquatic organisms. *(Courtesy of Johns-Manville Company)*

If quartz is heated until it softens, bubbles of air and other gases make the quartz opaque. This form, called *vitreous quartz*, is used in the manufacture of many articles, such as large quartz tubes and evaporating dishes. Clear quartz is made by reducing the pressure in the furnace in which the quartz is melted. The decreased pressure causes most of the bubbles of gas to escape. The pressure is increased as the mass hardens so that the bubbles remaining will be made small.

8. Chemical Properties of Silica

Silica does not dissolve in water, and since it has no basic properties it is also insoluble in acids (except hydrofluoric). It is an acidic oxide and, consequently, reacts with (fused) alkalies, such as NaOH or KOH, to form silicates. When heated with certain oxygen salts, whose acid anhydrides are volatile, it forms silicates and releases the oxide of the non-metal of the salt:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$
$$Na_2SO_4 + SiO_2 \longrightarrow Na_2SiO_3 + SO_3 \uparrow$$
$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2 \uparrow .$$

These reactions are important in the manufacture of glass.

9. Silicic Acid

Silicic acid is usually prepared by adding an acid, such as HCl, to a solution of sodium silicate:

$$H_2O + (2\,Na^+ + SiO_3^{=}) + 2\,(H^+ + Cl^-) \longrightarrow 2\,(Na^+ + Cl^-) + H_4SiO_4 \downarrow .$$

The compound, H_4SiO_4, is called *orthosilicic* acid, which corresponds to the formula of the hypothetical hydroxide $Si(OH)_4$, and *metasilicic acid* is H_2SiO_3. Actually both of these formulas are hypothetical and are used only because salts corresponding to these formulas of the acids are known. The compounds really formed when a solution of sodium silicate is acidified may contain different quantities of water and are probably hydrous oxides, $xSiO_2.nH_2O$.

Many silicate minerals may be regarded as salts of orthosilicic acids:

Mica	$KH_2Al_3(SiO_4)_3$
Willemite	Zn_2SiO_4
Zircon	$ZrSiO_4$
Forsterite	Mg_2SiO_4
Pyrope	$Mg_3Al_2(SiO_4)_3$
Andalusite	$(AlO)AlSiO_4$.

When hydrochloric acid is added to a solution of sodium silicate, the substances produced are first in a colloidally suspended state, but after a short time they are changed to a gelatinous precipitate or jelly (page 230), unless an excess of hydrochloric acid which stabilizes the suspension is added. When this jelly is heated, the silicic acid loses water, and, if the dehydration is continued, only the dioxide eventually remains. Several intermediate stages in the dehydration occur, however,

and these result in the formation of different compounds. Thus, if orthosilicic acid loses one molecule of water, metasilicic acid is produced:

$$H_4SiO_4 \longrightarrow H_2SiO_3 + H_2O.$$

Further loss of water results in the formation of other compounds:

$$2\ H_4SiO_4 - H_2O \longrightarrow H_6Si_2O_7$$
$$2\ H_4SiO_4 - 2\ H_2O \longrightarrow H_4Si_2O_6$$
$$2\ H_4SiO_4 - 3\ H_2O \longrightarrow H_2Si_2O_5$$
$$3\ H_4SiO_4 - 4\ H_2O \longrightarrow H_4Si_3O_8.$$

These compounds and others of a similar nature are called *polysilicic*, or *condensed silicic*, acids. They may be looked upon as derivations of two or more molecules of H_4SiO_4. All of them are purely hypothetical acids, the formulas of which correspond to the compositions of many silicates found in minerals. There is no evidence that pure acids corresponding to these formulas exist.

Some of the silicates that may be regarded as salts of these acids and which are found in minerals are: *Orthoclase*, $KAlSi_3O_8$; *beryl*, $Be_3Al_2(SiO_3)_6$; *albite*, $NaAlSi_3O_8$; and *natrolite*, $Na_2Al_2Si_3O_{10}$. *Talc*, $H_2Mg_3(SiO_3)_4$, and *asbestos*, $Mg_3Ca(SiO_3)_4$, are salts of metasilicic acid.

The unit of structure in the silicate minerals is the SiO_4^{-4} group in which the silicon atom is at the center of a tetrahedron, and the oxygen atoms are located at the four points of the tetrahedron.

In other silicates two or more SiO_4^{-4} groups may be united by having an oxygen atom occupy points in two tetrahedra. A combination of two tetrahedra, with one atom of oxygen in common, for example, gives the $Si_2O_7^{-6}$ group. Three SiO_4^{-4} tetrahedra, in which each of two oxygen atoms belong to two different tetrahedra, give the $Si_3O_{10}^{-8}$ group.

10. Silica Gel

When silicic acid jelly is dehydrated by

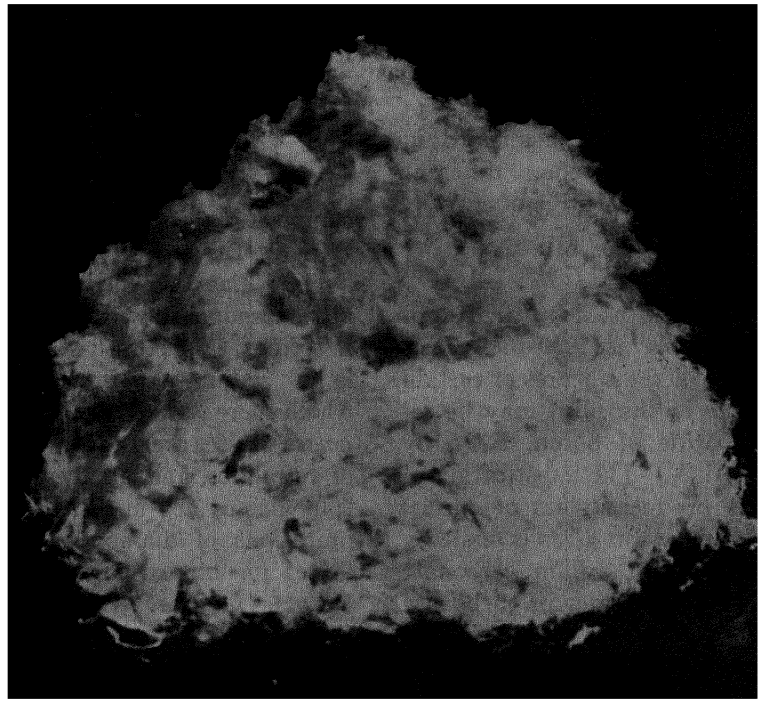


Figure 232. Asbestos Fibers
(Courtesy of Johns-Manville Company)

heating it at 300° under reduced pressure until it contains about 5 per cent of water, the product is called *silica gel*. This substance adsorbs many gases, such as sulfur dioxide, nitrogen dioxide, and the vapors of many volatile organic liquids, e.g., benzene. It is used, therefore, to separate substances that it adsorbs from those that it does not adsorb. When the gel has adsorbed its full capacity, it is heated to release the adsorbed material. Because of its capacity to act as an adsorbent, silica gel also serves as a contact catalyst in several reactions.

11. Sodium Silicate

Sodium silicate (Na_2SiO_3) is made by heating silica (sand) with sodium hydroxide or sodium carbonate (page 390). It is usually marketed as a concentrated, viscous solution and is commonly known as *water glass*. As the solution is heated, it becomes more viscous and finally gives a hard glass-like mass. Since it is the salt of a strong base and a weak acid, sodium silicate hydrolyzes in water to give strongly alkaline solutions. It is used in some soaps and washing powders; in cement; as an adhesive in making boxes of pasteboard; in fireproofing and waterproofing different materials; and as a preservative of eggs.

12. Glass

Glass was made and used by the Egyptians at least as early as 5000 B.C. It is usually a mixture of the silicates of certain metals, but some of the silica may be replaced by the oxide of boron, B_2O_3, by As_4O_6, and by Al_2O_3. The substitution of other materials produces glass of special properties. Ordinary soft glass is made by heating together sand, sodium carbonate or sodium sulfate, and calcium carbonate (page 390). The product is a clear, brittle, and amorphous solid; at least, it has some of the physical characteristics of a solid. When it is heated, it has no definite melting point but softens gradually; and hence, it is looked upon, not as a true solid, but as a supercooled liquid.

Melted glass, as it comes from the pots of the glass-making furnace, is worked into different articles by means of a blowpipe, or the objects are blown in molds by means of machines and with the help of compressed air. The latter practice has largely replaced the glass-blower. Glass for window panes is first made into long cylinders, or it is drawn out into flat ribbons. The cylinders are cracked and softened in a furnace until they flatten out to form sheets of glass, which are then rolled while still soft to the desired thickness. Plate glass is made by rolling a mass of softened glass. All articles made of glass must be *annealed* by passing them through a long, heated chamber or a furnace that has a high temperature at the entrance and a low temperature at the exit. Annealing prevents the formation of strains in the glass by rapid cooling.

13. Varieties of Glass

Common or soda-lime glass is a mixture of sodium and calcium silicates. It is used for window panes, bottles, dishes, and many other articles. The approximate compositions of different kinds of glass are given in Table 18.

Hard glass, which must be heated to a higher temperature than soda glass before it softens, is a potash glass. *Pyrex* brand is a sodium-aluminum borosilicate, in which there is an excess of silica. The *lead-potash* glasses are soft but have a high index of refraction and are very brilliant. The lead glasses are used as paste in making imitations of diamonds and other gems, lenses for optical instruments, and some cut glass articles.

The non-shattering glass, now used in automobiles, bullet-proof windows, etc., is made by placing sheets of cellulose acetate or some other plastic between layers of sheet glass. Recently, inexpensive com-

TABLE 18. THE COMPOSITION OF GLASS

	SiO_2	Na_2O	CaO	K_2O	PbO	B_2O_3	As_4O_6	Al_2O_3
Soda Glass	75	15	8					2
Optical Glass	71	5	10	13			0.8	0.2
Pyrex Brand	80.6	3.8	0.4	0.6		11.3		2
Potash Glass	80	0.6	7	12				0.4
Lead Glass	55			11	33			1

mercial glasses have been produced for use in hospitals and elsewhere as a substitute for quartz. This glass transmits ultra-violet light. A strong, flexible plate glass, which crumbles when it is broken, is made by suddenly cooling (tempering) the surface of the plate glass in a stream of cold air.

Glass bricks are used in constructing walls of buildings, thus making windows unnecessary. This use of glass is important in air-conditioned buildings. Spun glass, or glass fiber, consists of filaments made by drawing out softened glass through dies. These filaments can be woven into fabrics, which are used, for example, in making window curtains. Spun glass is also used as a means of heat insulation and as a filter for gases and liquids. Invisible glass can be produced by coating the surface with a thin layer of certain kinds of soaps or of sodium fluoride. Glass is visible because of the light that it reflects. The layer on the surface of invisible glass interferes with reflection.

14. Color of Glass

Common glass is often slightly green in color because of the presence of small amounts of ferrous silicate. This color is changed to the less noticeable yellow of ferric silicate by adding manganese dioxide as an oxidizing agent during the manufacture of the glass. Blue glass is made by adding cobalt to form cobalt silicate. Colloidal dispersions of copper and gold produce red or ruby glass. Selenium decolorizes green glass and is also used to make red glass. Violet glass contains manganese, and green glass, chromium or copper. Opaque or white glasses are produced by adding substances such as stannic oxide, calcium fluoride, and boric acid, which are suspended in the glass, or which melt without reacting with the other constituents.

15. Uses of Silicates

In addition to the manufacture of glass, silica or silicates are essential raw materials in the cement industry and in the manufacture of brick, tile, porcelain, terra cotta, and other *ceramics*. Many of the natural silicates are used in large quantities for various purposes. *Mica* is used as an electric insulator; as a decorative material ("snow"), in paints, and in the windows of stoves. *Asbestos* is used as an insulating material around hot water, hot air, and steam pipes and in the manufacture of fireproof shingles. *Talc* is used in soap, paint, rubber, and paper. *Soapstone* is used for switchboards, table tops, and sinks. Manufactured *zeolites* ($NaAlSiO_4$) are used in softening water. Silica is used as a flux, as in the production of phosphorus from rock phosphate. It reacts with calcium oxide to form the easily fused calcium silicate (slag). Since it is the oxide of a nonmetal, silica is an acid-flux and is added when a basic material is to be converted into slag. Conversely, when silica is the impurity which is to be removed from an ore, a basic-flux, such as calcium oxide or limestone, is added. *Rock wool* is made by blowing out into fine threads thin streams of fused natural silicates or blast furnace slag, which is largely composed of silicates.

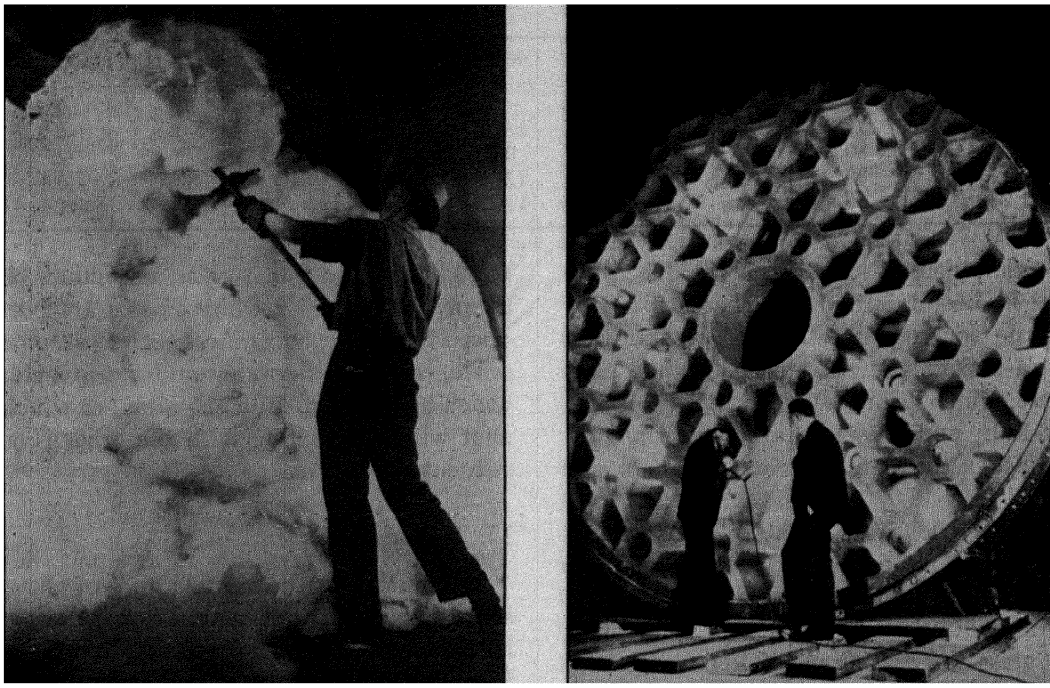
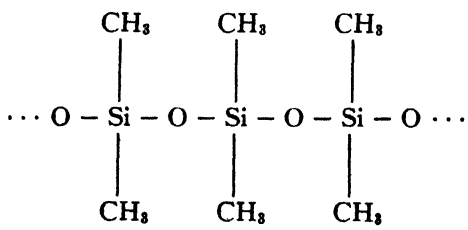


Figure 233. *Left* **Glass wool.** *Right* **The 200-inch glass disc in the telescope mirror, Mt. Palomar Observatory.** (*Courtesy of Corning Glass Company*)

16. Silicones

These interesting compounds have recently received considerable attention. Their structures consist of SiO_2 groups linked together in the form of chains or rings. In addition to oxygen atoms, organic radicals, such as CH_3 or C_2H_5, are also attached to the atoms of silicon. A simple silicone may be represented as follows:



There are several types of silicones. Those that have a chain structure are usually oily liquids and are used as lubricants in airplane motors. Other silicones resemble rubber, resins and other plastic materials. They are used for electrical insulation on wire, as waterproof coatings on cotton and wood, and for several other purposes.

BORON

17. Occurrence

Boron is not an abundant element; it constitutes about 0.001 per cent of the earth's crust. It occurs as *boric acid*, H_3BO_3, and as salts of condensed boric acids, such as $H_2B_4O_7$, which is called *tetraboric acid*. The Stassfurt deposits contain magnesium borate. Deposits in the desert regions of California contain *ulexite*, $NaCaB_5O_9.8\,H_2O$; *colemanite*, $Ca_2B_6O_{11}.5\,H_2O$; *rasorite*, $Na_2B_4O_7.4\,H_2O$; and *borax*, $Na_2B_4O_7.$-

10 H_2O. The normal annual production of borax in the United States is about 300,000 tons.

18. Preparation and Properties

Boron oxide is difficult to reduce, but the reduction can be accomplished by heating the oxide with magnesium:

$$B_2O_3 + 3\ Mg \longrightarrow 3\ MgO + 2\ B.$$

The boron produced by this reaction is an amorphous, brown powder. This melts at about 2300°, and the product which solidifies upon cooling is very hard and brittle. The element burns with a green flame and oxidizes slowly at lower temperatures. It ignites spontaneously in fluorine and combines with the other halogens at elevated temperature. Its halide compounds, BF_3, BCl_3, BBr_3, and BI_3, resemble the halides of the non-metals, such as CCl_4 and PCl_3; they are covalent. It forms a sulfide (B_2S_3) when heated with sulfur, and a nitride (BN) with nitrogen. It does not dissolve in acids but does dissolve in melted alkalies, such as KOH, to form borates (K_3BO_3). When heated with certain metals it forms borides (Mg_3B_2). In general, therefore, boron displays the chemical properties of a non-metal.

19. Boric Acid

Orthoboric acid is usually prepared by heating a solution of borax with sulfuric acid:

$$(2\ Na^+ + B_4O_7^=) + (2\ H^+ + SO_4^=) \longrightarrow (2\ Na^+ + SO_4^=) + H_2B_4O_7$$

$$H_2B_4O_7 + 5\ H_2O \longrightarrow 4\ H_3BO_3.$$

Since it is not readily soluble, boric acid precipitates as thin flakes, which are pearl-like in color, and which are oily to the touch. It is commonly known as *boracic acid*, and is used as an antiseptic, a preservative, and as a glaze for some kinds of pottery. It is a weak acid. When heated moderately, boric acid loses a molecule of water and forms *metaboric acid:*

$$H_3BO_3 \longrightarrow HBO_2 + H_2O.$$

The *tetraboric acid* is formed upon further heating:

$$4\ HBO_2 \longrightarrow H_2B_4O_7 + H_2O.$$

20. Borax

Neutralization of boric acid by sodium hydroxide yields sodium tetraborate, $Na_2B_4O_7$. The hydrate, $Na_2B_4O_7.10\ H_2O$, which crystallizes from solutions at temperatures below 60°, is called *borax*. This substance is found in the Mohave Desert of California and in Searles Lake (page 248).

Borax is used in making certain kinds of glass, enamels, and glazes. Its solution is alkaline, since boric acid is very weak, and for this reason it is used as a milk alkali to soften water; in soaps; as an antiseptic; and as a preservative. Melted borax forms a glass-like substance upon cooling. This glass dissolves the oxides of certain metals, because it contains an excess of the acid anhydride, B_2O_3, which reacts with the oxides of the metals to form metaborates. Thus, cobalt is converted into *cobalt metaborate*, which is blue:

$$Na_2B_4O_7 \longrightarrow 2\ NaBO_2 + B_2O_3$$

$$B_2O_3 + CoO \longrightarrow Co(BO_2)_2.$$

For this reason borax is sometimes used to free metallic surfaces from coats of oxides before welding or soldering. Since the borates formed by this reaction have different colors, the borax-glass beads formed by heating mixtures of borax and compounds of the metal on a platinum wire are used to detect certain metals in materials that are analyzed in the laboratory.

21. Other Compounds

Sodium perborate, $NaBO_3.H_2O$, sometimes assigned the formula $NaBO_2.H_2O_2$, is a vigorous oxidizing agent. It is used in

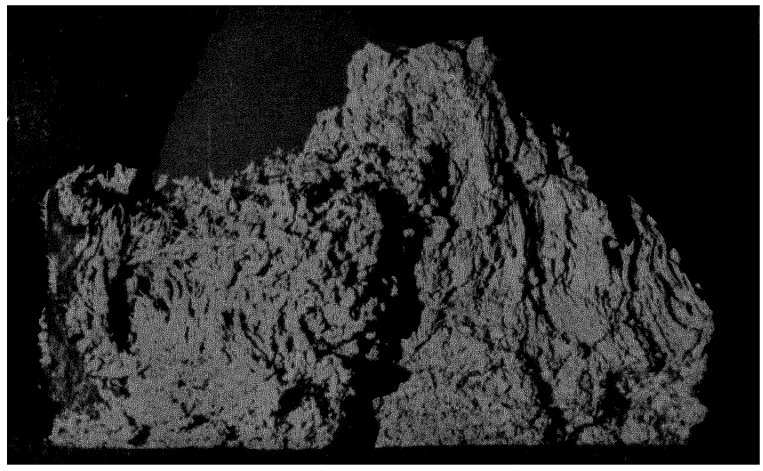


Figure 234. Titanium Metal Sponge
(Courtesy of National Lead Co.)

bleaching and as an antiseptic. It is made by the action of hydrogen peroxide upon sodium borate. The *carbide* of boron, B_6C, is almost as hard as diamond and is used for cutting hard materials.

OTHER ELEMENTS OF THE SILICON FAMILY

22. Occurrence and Preparation of Titanium

Titanium occurs in the soil and in many natural silicates in which it replaces a part of the silicon, which it resembles very closely. It occurs as *rutile* (TiO_2) and as *ilmenite*, an iron ore ($FeTiO_3$). These minerals are obtained in this country from Virginia, California, and Florida. It is a rather plentiful element as shown by ore resources equivalent to 5,500,000 tons of the element.

Titanium is produced by reducing the oxide (TiO_2) by means of carbon in an electric furnace, or by reducing the chloride ($TiCl_4$) with sodium. An alloy, known as *ferrotitanium* and analogous to ferrosilicon, is produced when titanium-bearing iron ores are reduced with carbon. This alloy is used in making titanium steel; the titanium removes impurities and gives a steel of great strength and possessing the ability to withstand sudden stresses or shocks.

23. Properties and Compounds

Titanium is silvery-white in appearance; its specific gravity is 4.5; and its melting point is about 1800°. Unlike silicon, it shows the properties of a metal in some of its compounds and those of a non-metal in others. The dioxide (TiO_2) is amphoteric. It reacts with concentrated sulfuric acid, for example, to form *titanyl sulfate*, $(TiO)SO_4$. When a solution of this compound is treated with a solution of sodium hydroxide, a white, gelatinous precipitate is formed; this may be regarded as $Ti(OH)_4$, although it is more likely that we should think of it as the hydrous oxide. The precipitate dissolves in both acids and alkalies, forming titanium salts in acids and titanates in alkalies. With sodium hydroxide it forms sodium titanate, Na_2TiO_3. As in the case of silicic acid and its salts there are several titanates corresponding to different theoretical titanic acids. Ilmenite, $FeTiO_3$, for example, is a ferrous salt of metatitanic acid, H_2TiO_3.

Besides the dioxide, the monoxide (TiO) and the trioxide (Ti_2O_3) are known. These

are basic in character. Hence, titanium forms salts in which the element acts as a trivalent or a divalent metal. Examples of these compounds are the chlorides, $TiCl_3$ and $TiCl_2$, and the sulfate, $Ti_2(SO_4)_3$. Since titanium acts normally as a non-metal and forms stable compounds, such as TiO_2, in which its oxidation number is + 4, these salts are vigorous reducing agents.

The tetrachloride, $TiCl_4$, is a covalent compound. This substance hydrolyzes in moist air, producing dense clouds and, for this reason, is used in making smoke-screens.

The dioxide, TiO_2, which is white, is used as a pigment in paints, porcelain, and other ceramic products. Marketed under various trade names, titanium pigments can be secured in the form of lead titanate, the pure dioxide, or the dioxide mixed with barium, calcium, and magnesium pigments. These pigments are extensively used in the manufacture of paints.

24. Zirconium and Hafnium

Zirconium occurs in nature as ZrO_2 and the silicate $ZrSiO_4$, called *zircon*. The element forms an alloy with iron called *ferrozirconium* which is analogous to ferrosilicon.

Zirconium is much more metallic in character than silicon and titanium. It forms the dioxide and also probably the oxides, ZrO and Zr_2O_3. The hydroxide corresponding to ZrO_2 dissolves in both acids and bases, and is, therefore, amphoteric. It readily dissolves in acids to form salts, such as $ZrCl_4$, and in bases, zirconates, such as Na_2ZrO_3, are formed.

The most important compound of zirconium is the oxide, ZrO_2, which is used in making brick for lining furnaces, crucibles, and other utensils or articles which must withstand high temperature without melting.

Hafnium is one of the more recently discovered elements (1922). It is somewhat more metallic in chemical behavior than zirconium, as might be expected from its position in the Periodic Table.

REVIEW EXERCISES

1. Compare and contrast the properties of carbon and silicon, and of their chlorides, dioxides, and acids.
2. What is silica gel? For what purposes is it used?
3. Identify: Water glass; quartz; borax; $CaSiO_3$; rock crystal; ferrosilicon; diatomaceous earth; orthoclase; H_2TiO_3; asbestos; hafnium.
4. Why are solutions of sodium silicate and borax alkaline?
5. Why is borax used in soap and in cleaning metallic surfaces? Why should borax react with oxides of metals?
6. What is the chemical nature of glass? What is the difference in composition between soft and hard glass? How does the composition of Pyrex glass differ from that of ordinary soft glass?
7. Why is calcium carbonate added to the charge of blast furnaces in which iron ores are reduced to metallic iron?
8. In what respects are boron and its compounds similar to silicon and its compounds and in what respects are they different?
9. How does the abundance of silicon and its compounds in nature compare with the abundance of carbon and its compounds?
10. What is a flux? With what kinds of substances do boron trioxide and silicon dioxide act as fluxes?
11. Write an equation to show how boric acid, H_3BO_3 can be prepared from borax.
12. What is the general method of preparing the free elements boron, silicon, titanium, zirconium, phosphorus, arsenic, antimony, and bismuth from their oxides?
13. How would you proceed to prepare the following substances in succession, starting with silica? Na_2SiO_3; SiF_4; and H_2SiO_3.
14. For what purposes is ferrosilicon added to iron in making steel? What are the composition and general properties of Duriron?
15. Using the percentages given in Table 18, calculate the weights of SiO_2, Na_2CO_3, and $CaCO_3$ required to make one ton of soda glass.

16. What weight of aluminum is required to produce a ton of silicon by the reduction of silica?
17. What is the percentage of silicon in beryl?
18. A certain silicate-mineral was found to contain 17.48 per cent of magnesium, 9.6 per cent of calcium, and 26.89 per cent of silicon. The remainder was found to be oxygen. What is the simplest formula of the silicate?
19. Outline a method involving a series of reactions that can be used to produce silica gel from sand.
20. An iron ore contains 3 per cent of silica. What weight of calcium carbonate (limestone) is required as a flux for each ton of ore?
21. A standard solution of sodium hydroxide should not be stored in a glass bottle. Why?
22. Write an equation to show how $Na_2B_4O_7$ can be produced from H_3BO_3 and NaOH.
23. How do "soda" and "potash" glasses differ in composition and properties?
24. Why is glass regarded as a supercooled liquid rather than as a true solid?

REFERENCES FOR FURTHER READING

Roush, G. A., and A. Butts, *Mineral Industry.*

Abrasives: *Ind. and Eng. Chem.*, **30,** 232 (1938).

Borax: *J. Chem. Ed.*, **8,** 2113 (1931); **9,** 1319 (1932).

Boron: *J. Chem. Ed.*, **5,** 1235 (1928); **6,** 550 (1929); **8,** 2112 (1931).

Ceramics: *J. Chem. Ed.*, **9,** 795 (1932).

Diatomaceous Earth: Calvert, R., *Diatomaceous Earth,* New York: Reinhold Publishing Company, 1930. *J. Chem. Ed.*, **7,** 2829 (1930); *Chem. and Met. Eng.*, **42,** 420 (1935); **45,** 28 (1938); *Ind. and Eng. Chem.*, **26,** 688 (1934).

Gems and Semi-precious Stones: *J. Chem. Ed.*, **8,** 613, 1015 (1931); **10,** 67, 713 (1933) **12,** 153, (1935).

Glass: *Chem. and Met. Eng.*, **37,** 418 (1930); **39,** 266, 601 (1932); **49,** 1 (1942); *Ind. and Eng. Chem.*, **23,** 505 (1931); **25,** 742, 1189, 1192 (1933); **27,** 1291 (1935); **28,** 267 (1936); **30,** 891 (1938); **32,** 1176, 1415 (1940); *J. Chem. Ed.*, **8,** 421 (1931); **19,** 287 (1942).

Rock Wool: *Chem. and Met. Eng.*, **42,** 550 (1935); *Ind. and Eng. Chem.*, **27,** 1298 (1935).

Sodium Silicate: *J. Chem. Ed.*, **10,** 418 (1933); *Chem. and Met. Eng.*, **37,** 736 (1930); **43,** 606 (1936); *Ind. and Eng. Chem.*, **22,** 972 (1930); **34,** 737 (1942).

Structure of Silicates: *J. Chem. Ed.*, **10,** 667 (1933).

32

ORGANIC CHEMISTRY: THE HYDROCARBONS

1. Introduction

In 1828, Wöhler converted an inorganic compound, *ammonium cyanate*, NH_4CNO, into the organic compound, *urea*, $CO(NH_2)_2$. Most of the nitrogen eliminated from the bodies of animals as a result of the oxidation of nitrogenous materials is found in the urine as urea. Wöhler's synthesis, therefore, produced an organic compound from a compound that is not associated in any way with living matter.

Wöhler's discovery marked the beginning of modern organic chemistry, and since 1828 many thousands of organic compounds have been synthesized. Some of them are substances that can be obtained from plants or animals, but many others that are not associated directly in any way with living material have also been made. In all, the number of carbon compounds now known exceeds 400,000, and the end is not yet in sight.

The great number of compounds that carbon forms can be explained by the capacity of its atoms to share electrons with many other kinds of atoms and, also, by the capacity to share electrons with each other. Since carbon has four valence electrons per atom, the maximum valence number of the element is four. The oxidation number varies in different compounds between + 4 and − 4. Two carbon atoms may share one, two, or three pairs of electrons with each other, thus forming *single*, *double*, or *triple bonds* between them.

2. Hydrocarbons

The hydrocarbons are compounds containing only carbon and hydrogen. Their molecules contain carbon atoms that share electrons with one another and with atoms of hydrogen. Each group of hydrocarbons is called a *homologous series*. Each hydrocarbon in a series differs from the preceding member by containing one more carbon atom and two more hydrogen atoms (CH_2) per molecule. The members of each series have the same general formula and display the same general chemical behavior. Only the first members of each series are shown in Table 19.

The *aliphatic* hydrocarbons have molecular structures in which carbon atoms are joined one after another in "open" chains by covalent bonds. The *aromatic* hydrocarbons are composed of molecules in which the atoms of carbon are arranged in a ring; i.e., the chain is "closed" by the two ends of the chain tieing together to make a ring.

3. The Methane or Paraffin Series

These hydrocarbons are found in petroleum and its products — gasoline, kerosene, lubricating oils, and paraffin. Methane, itself, is the principal component of natural

TABLE 19. THE HYDROCARBONS

Methane Series	Ethylene Series	Acetylene Series	Benzene Series
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	C_nH_{2n-6}
Methane CH_4	Ethylene (Ethene) C_2H_4	Acetylene C_2H_2	Benzene C_6H_6
Ethane C_2H_6	Prophylene (Propene) C_3H_6	Propyne C_3H_4	Toluene C_7H_8
Propane C_3H_8	Butylene (Butene) C_4H_8	Butyne C_4H_6	Xylene C_8H_{10}
Butane C_4H_{10}	Amylene (Pentene) C_5H_{10}	Pentyne C_5H_8	
Pentane C_5H_{12}	Hexylene (Hexene) C_6H_{12}		
Hexane C_6H_{14}	Heptalene (Heptene) C_7H_{14}		
Heptane C_7H_{16}	Octalene (Octene) C_8H_{16}		
Octane C_8H_{18}			
Nonane C_9H_{20}			
Decane $C_{10}H_{22}$			

gas. These compounds are sometimes called the *paraffin hydrocarbons*. They are also called *saturated hydrocarbons*, because each of the valences of carbon consists of a single pair of electrons, that unites a carbon atom with hydrogen or another atom of carbon. The first four hydrocarbons of the methane series are gases at ordinary temperature; those from C_5H_{12} to $C_{15}H_{32}$ are liquids; and those above $C_{16}H_{34}$ are solids. The highest known member of the series is $C_{94}H_{190}$.

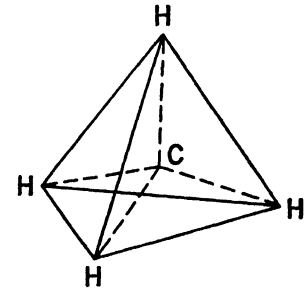
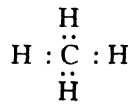


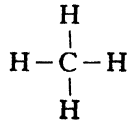
Figure 235. The Methane Molecule

4. Structural Formulas

The methane molecule has the following *structural* formula:



or if we represent each pair of shared electrons by a single line,



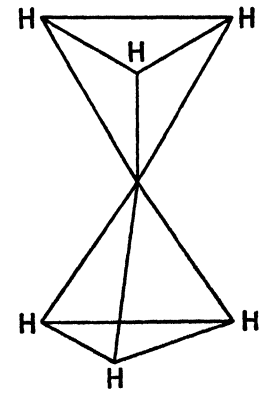
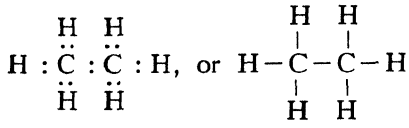


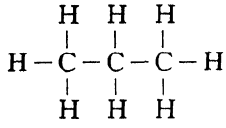
Figure 236. The Ethane Molecule

If we should represent the methane molecule in three dimensions instead of two, the carbon atom would be placed at the center of a tetrahedron with the four atoms of hydrogen at the corners of this structure.

In ethane, two carbon atoms share a pair of electrons; this link replaces one bond of each carbon atom with hydrogen.



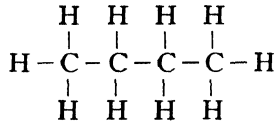
In *propane* one carbon atom shares electrons with two other atoms of carbon:



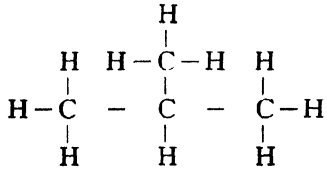
The formulas of these compounds are usually written as CH_4, $CH_3 - CH_3$, and $CH_3 - CH_2 - CH_3$.

5. Isomers

For none of the first three hydrocarbons of the methane series can we construct formulas showing linkages between the atoms that are different from those given above. But for *butane* it is possible to write formulas for two arrangements:



(normal butane)



(isobutane)

These have the same *empirical* formula, C_3H_{10}, but different *structural* formulas. Isobutane is called an *isomer* of normal butane. It is apparent that the difference in structure lies in the linkage of one carbon atom with three others in isobutane and with two in normal butane. We say that the carbon chain is branched in isobutane. The two butanes are different compounds; they have different properties. Butane, for example, boils at 1° C., and isobutane at − 17°. There are three isomers of *pentane*, and the number of possible isomers reaches an enormous value in the highest members of the series. We find, therefore, in the existence of isomers one more reason for the vast number of compounds of carbon.

6. Properties of the Methane Hydrocarbons

The members of the methane series are colorless gases, liquids, or solids. They are insoluble in water. They burn in the presence of oxygen to form water and carbon dioxide. They are relatively inactive substances; the name paraffin, *par(um) affin(itas)*, means "little affinity." They are unaffected by acids and bases and are only slightly affected by oxidizing agents at ordinary temperatures. Since the methane hydrocarbons are saturated, they can react with chlorine and other elements only by the *substitution* of chlorine for hydrogen, e.g., to form CH_3Cl (page 260).

When heated to the required temperatures all of the paraffin hydrocarbons burn, and in the vapor state they react with nitric acid to form nitroparaffins, which are used as solvents and in the production of other compounds.

7. Methane

Methane is sometimes called *marsh gas*, a name related to its production during the decay of vegetable matter in swamps, marshes, and ponds. In the laboratory it is produced by heating a mixture of sodium

acetate and sodium hydroxide in the absence of air:

$$NaOH + NaC_2H_3O_2 \longrightarrow CH_4 + Na_2CO_3.$$

Natural gas contains, usually, from 80 to 95 per cent of methane. A mixture of methane and air, called *fire damp*, sometimes collects in coal mines and is a source of considerable danger because of its inflammability.

8. Natural Gas

Natural gas is often encountered in drilling wells for petroleum and sometimes is found where petroleum is not present. The principal producing localities of the United States are in Pennsylvania, West Virginia, Oklahoma, Louisiana, Kansas, Texas, Ohio, Indiana, Kentucky, and California. Some of the gas produced in Texas contains only about 50 per cent of methane, but the natural gas of Ohio and Indiana contains about 94 per cent and that from Pennsylvania and West Virginia about 80 per cent. Ethane and other light paraffins are also present in natural gas. The annual production of gas is about 2,800,000,000,000 cu. ft.

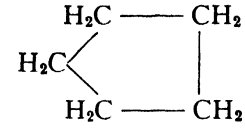
Natural gas is a valuable fuel, since it usually contains a very high percentage of methane, which has a high heat of combustion:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 210{,}800 \text{ calories.}$$

A considerable quantity is also used in the production of carbon black (page 296).

9. Petroleum

Petroleum is a solution of gaseous and solid hydrocarbons in a mixture of liquid hydrocarbons. Most of the readily volatile hydrocarbons belong to the methane series, but the portion of crude oil remaining after the removal of the volatile compounds may contain many other hydrocarbons. This residue, or "base," of some crude oils is composed largely of heavier paraffins, while others have an asphalt base. The latter contains saturated hydrocarbons in which carbon atoms are joined in closed rings and which are called cycloparaffins, e.g., cyclopentane is



The name petroleum is derived from two words *petra oleum* meaning rock or mineral oil.

The United States in normal times produces about 65–70 per cent of the petroleum supply of the world. Most of the remainder is produced in Venezuela, Russia, Persia, Rumania, Dutch East Indies, and Mexico. The principal oil producing states of this country, at the present time, are California, Oklahoma, and Texas, and fields with smaller outputs are located in Kansas, Louisiana, Arkansas, New Mexico, Pennsylvania, and several other states. The world's production of petroleum is normally around 2,800,000,000 barrels (42 gallons). The United States produces about 1,800,000,000 barrels.

10. The Refining of Petroleum

To obtain the products listed in Table 20 petroleum is fractionally distilled. A diagram of the old-fashioned refinery, which shows the principles involved, is shown in Figure 237. Modern practice uses the "bubble tower" to separate the oil into its different fractions (Figure 238). Petroleum under pressure is first heated by passing it through pipes in a furnace. The hot liquid is then passed into a "flash chamber" where, by reducing the pressure, it is converted into vapors. Some of the heavier portions of the oil do not vaporize and these are separated from other fractions at this point. The vapors then pass into the *bubble tower*, which consists of a great many

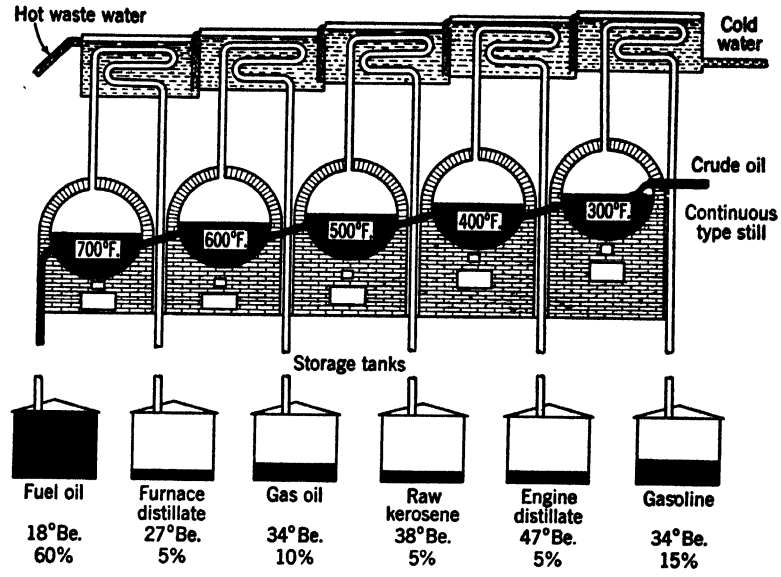


Figure 237. Diagram Showing the Fractional Distillation of Petroleum

The fuel oil can be further distilled with steam to give lubricating oils. Degrees Be refer to the densities of the different products.

sections, or pans, placed one above the other. As the vapors pass upward, the higher boiling oils condense, and the uncondensed gases bubble up through these liquids as they pass from one section to the next. The gasoline vapors pass through the tower and are then condensed by cooling. Kerosene is condensed in the upper portion of the tower, gas oil in the middle, and the heavier oils at the bottom. The heavier hydrocarbon fractions may be distilled by using superheated steam. The fraction containing the lubricating oils is again distilled with steam and is divided up into several portions — light, medium, and heavy motor oils. The paraffin is removed from these oils by chilling them, and the oils are usually filtered through fine clay (fuller's earth) to remove colored substances and materials formed by oxida-

TABLE 20. PETROLEUM PRODUCTS

Product	Composition	Boiling Point	Uses
Gases	Methane-butane		Fuel, manufacture of carbon black
Petroleum ether	Pentane-heptane	35°–90°	Solvent, dry-cleaning
Gasoline	Hexane-duodecane	up to 220°	Fuel, solvent
Kerosene	Duodecane-hexadecane	200°–315°	Illumination, fuel oil
Gas or fuel oil	C_{15} to C_{18}	up to 375°	Cracked to give gasoline; fuel for oil-burning furnaces; enrichment of water gas
Lubricating oil	C_{15} to C_{20}	350° up	Lubrication
Vaseline	C_{18} and up	semi-solid	Lubrication
Paraffin	C_{20} " "	melting point about 55°	Candles, water-proofing
Tar			Artificial asphalt
Petroleum coke			Fuel, electrodes

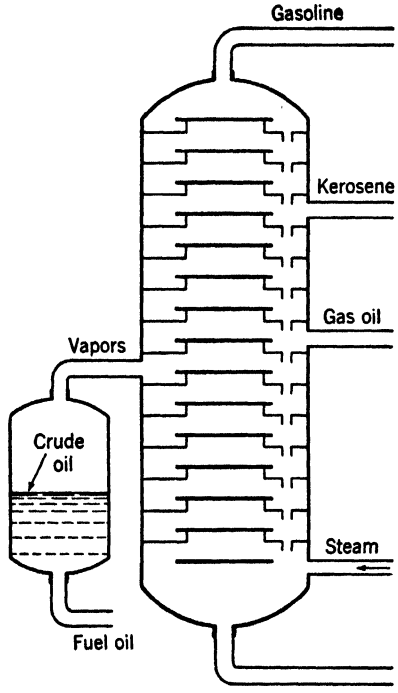


Figure 238. Bubble Tower

tion during refining; such materials, if not removed, would result in the formation of objectionable sludges in the oils used for lubrication.

The products of the petroleum refinery are usually treated with sulfuric acid to remove objectionable impurities, especially hydrocarbons containing double bonds which may, if not removed, produce gummy substances, tars, and resins. The acid is heavier than the oils and settles to the bottom of the treating tanks, where it is drawn off. The oils are then washed with a solution of sodium hydroxide or sodium carbonate to neutralize the acid. Recently, waxes, gums, asphalt, and other substances found especially in motor oils are removed by the use of solvents, such as liquid sulfur dioxide. This procedure is said to give lubricating oils of constant viscosity that do not form deposits of wax, gum, or carbon. Sulfur compounds are now removed by using a solution of litharge, PbO, in sodium hydroxide. Sulfuric acid is still used, however, in enormous quantities by the refineries.

A residue of tar, or of coke if carbonization is complete, is left after the complete distillation and removal of all the oil fractions. The tar is used in making roofing, sidewalks, and roads. Coke is used as a fuel, in metallurgy, and to make electrodes.

11. Gasoline

Gasoline is a mixture of low-boiling petroleum hydrocarbons, such as hexane, heptane, octane, and nonane. Ordinarily, the gasoline fraction of petroleum amounts to about 20 per cent of the crude oil, but this has been increased to almost 44 per cent by modifications of refinery practice.

Much of the increase in the production of gasoline has been accomplished through the use of a process called *cracking*, by which some of the less volatile hydrocarbons are broken up into lighter compounds that boil at lower temperatures. The decomposition of the heavier hydrocarbons is brought about by heating oil under pressure or by passing the hot oil-vapors over catalysts, such as anhydrous aluminum chloride. A typical cracking reaction is shown by the following equation:

$$C_{12}H_{26} \longrightarrow C_6H_{14} + C_5H_{12} + C$$
$$\searrow$$
$$C_6H_{14} + C_6H_{12}.$$

After the cracking treatment the oil is passed into a flash chamber from which the vapors enter the bubble tower.

Within fairly recent times, *polymerized* gasoline has also entered the field. This consists of molecules of gasoline-hydrocarbons that are built up by the combination of simpler molecules of ethylene, propylene, butylene, etc. The polymerization is accomplished by using high pressures, elevated temperatures, and suitable catalysts. Some of the gaseous constituents of petroleum, such as propane and butane, are first cracked and the products are then



Figure 239. Petroleum Refining

This picture shows a large refinery lighted for night operation. A catalytic unit is seen at the left and a unit for the recovery of volatile hydrocarbons in the foreground. (*Courtesy of Standard Oil Company of Indiana*)

polymerized to form gasoline. *Alkylation* is a still more recent development. It is based upon a reaction between isobutane and various unsaturated hydrocarbons, such as propylene, of the ethylene series, which are produced during cracking operations. Alkylation is carried out at high temperatures and pressures or at lower temperature when catalysts such as HF and H_2SO_4 are used.

Both of these processes — polymerization and alkylation — produce branched chain hydrocarbons (like isobutane, page 401), which give to gasoline a high octane rating.

The supply of gasoline is increased by recovering low-boiling hydrocarbons from natural gas, which is often saturated with the vapors of C_5H_{12}, C_6H_{14}, and C_7H_{16}, etc. About one tenth of the gasoline produced in the United States is obtained from this source. It is called *casing head gasoline.* The gasoline produced by cracking processes is blended with casing head gasoline

12. Anti-Knock Gasolines

The power obtainable by exploding a mixture of air and gasoline-vapor in the cylinders of an automobile engine depends upon the expansion occurring within the cylinder at the time of the explosion. If the mixture of gases is highly compressed before the explosion, greater expansion will occur and more power should, therefore, be produced. The automobile engineer has made use of this principle in the development of high compression motors, which are now widely used. But with ordinary gasoline, these high compression motors cannot operate without a rather serious "fuel knock." This knock is pro-

duced by a very sudden and complete explosion, which produces a sudden shove against the piston head of the cylinder.

Most of the gasoline used today is a mixture or blend of hydrocarbons obtained from different sources or in different ways — straight distillation, cracking, natural gas, etc. These blends are compounded in proportions designed to secure the most satisfactory anti-knock properties. Ordinary distilled gasoline, which produces pronounced knock, contains hydrocarbons consisting of straight chains of carbon atoms, i.e., normal hydrocarbons such as normal heptane. The cracked gasoline contains hydrocarbons consisting of branched chains of carbon atoms, e.g., iso-heptane and iso-octane (page 401), which do not cause much if any knock. The most familiar anti-knock gasoline, however, is that which contains small quantities of lead tetraethyl, $Pb(C_2H_5)_4$, ethylene dichloride and ethylene dibromide, $C_2H_4Cl_2$ and $C_2H_4Br_2$. The halogen compounds are added to form volatile compounds of lead so that this element is removed from the cylinders along with other products of combustion.

13. Anti-Knock Rating of Gasoline

The rating of gasoline with regard to its tendency to produce knocking is called the *octane number*. Pure iso-octane,

$$CH_3 - HC(CH_3) - CH_2 - C(CH_3)_2 - CH_3,$$

is given an octane number of 100, because it produces little or no knocking as compared with ordinary, straight-run gasoline. Normal heptane,

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3,$$

produces a very pronounced knock and is

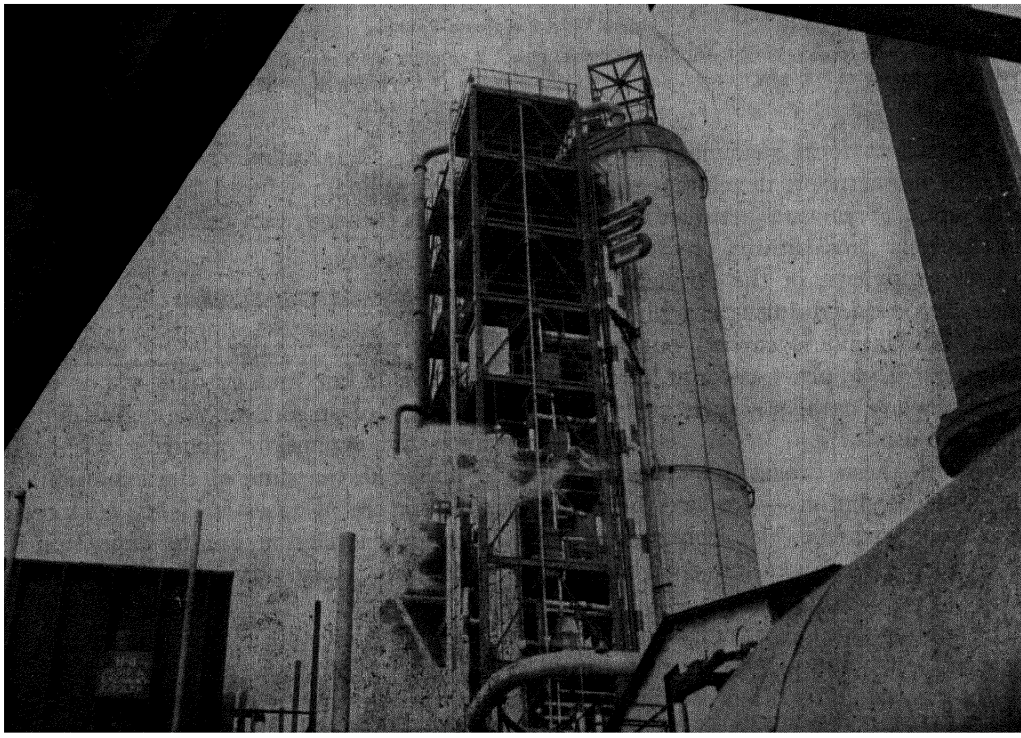


Figure 240. Pipe Still and Bubble Tower Used in Refining Lubricating Oils
(Courtesy of Standard Oil Company)

given the octane number of 0. To determine the rating of a certain fuel, the gasoline is used in a standard engine and its tendency to produce knocking is compared with different mixtures of the two hydrocarbons named above. If the gasoline produces the same intensity of knocking as a mixture containing 80 per cent of isooctane, its octane number is 80.

14. Motor Fuel for the Future

The Bergius process for the hydrogenation of coal has made available one more source of gasoline, kerosene, and lubricating oils (page 76).

The Fischer–Tropsch Process is probably more important as a possible future supply of petroleum products. This process is based upon a reaction of carbon monoxide and hydrogen at about 200°, under 10 atm. of pressure, and in the presence of a catalyst (cobalt, nickel, iron) to produce a petroleum-like mixture, which can be separated by distillation into high quality motor fuels, kerosene, fuel and lubricating oils, and paraffin.

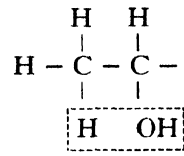
Certain shales contain organic compounds and when distilled produce an oil resembling petroleum. When the oil is fractionally distilled, the products obtained include gasoline, kerosene, lubricating oils, and similar substances.

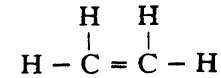
UNSATURATED HYDROCARBONS

15. The Ethylene, or Olefin, Series

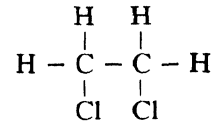
Another group of aliphatic hydrocarbons is called the olefin series. These hydrocarbons are unsaturated; i.e., their molecules contain two fewer atoms of hydrogen than are necessary to use all the valence numbers of the carbon atoms of the molecules.

Ethylene is the most important member of this series of hydrocarbons. Along with other unsaturated hydrocarbons it is produced in the cracking of petroleum. It is also produced by passing ethyl alcohol, C_2H_5OH, vapor over anhydrous aluminum silicate and by treating ethyl alcohol with concentrated sulfuric acid. In both of these reactions a molecule of water is removed from a molecule of the alcohol:



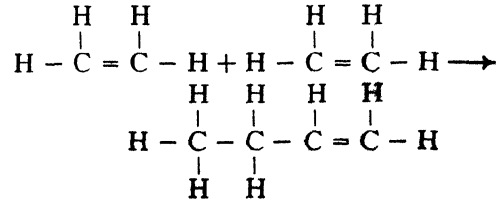


The removal of a hydrogen atom from one carbon atom and the removal of the hydroxyl radical from the other, leaves each carbon atom with one unused valence. To show that carbon has a valence of four, the organic chemist places this unused bond between the two carbon atoms, which are then said to be united by a *double bond.* Compounds containing double bonds are *unsaturated.* Their molecules form *addition* compounds by combining with atoms of active elements, such as chlorine and bromine, by means of the additional bond between the carbon atoms. Thus, two atoms of chlorine combine with a molecule of ethylene to form *dichloroethane*:



The unsaturated hydrocarbons also react, as methane does (page 401), with chlorine to form substitution compounds, in which chlorine replaces hydrogen, thus forming compounds such as $CHCl_2 - CHCl_2$.

Another important property of the olefins is their tendency to polymerize when aided by certain catalysts. Thus, ethylene polymerizes to form butylene:



Further polymerization may follow this first reaction. Reactions of this kind are important in building up heavier hydrocarbons, which are used in making synthetic rubber, plastics, and other organic compounds and materials.

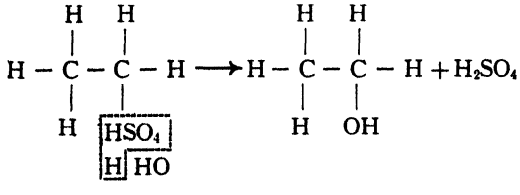
The unsaturated hydrocarbons are more readily decomposed by heat than the saturated hydrocarbons. The flame of a gaseous mixture of saturated hydrocarbons is nearly colorless in an excess of oxygen, because these hydrocarbons are converted directly in the flame into carbon dioxide and water. Unsaturated hydrocarbons decompose, at least partially, to form some free carbon, which becomes incandescent, or emits light, and adds color to the flame. Gas containing unsaturated hydrocarbons, therefore, is preferred for illuminating purposes.

Another series of hydrocarbons, called the *diolefins*, contain two double bonds in each molecule. They also are important in the synthesis of organic compounds, such as some kinds of synthetic rubber.

16. The Uses of Ethylene

Ethylene is an interesting compound. For example, it reacts with sulfur monochloride, S_2Cl_2, to form *mustard gas*, $(C_2H_4Cl)_2S$. An ethylene-oxygen mixture is used as an anesthetic in general surgical practice. Ethylene is also used to hasten the ripening of certain fruits.

If ethylene is treated with sulfuric acid, the two substances react to form $C_2H_5HSO_4$, which may then react with water to form ethyl alcohol:



This reaction is important as the simplest of several reactions, involving other unsaturated hydrocarbons, that can be used to produce higher alcohols and other organic compounds.

17. Acetylene Series

The only important member of this series is acetylene, C_2H_2, which is produced by allowing water to react upon calcium carbide (page 308):

$$CaC_2 + 2\ HOH \longrightarrow Ca(OH)_2 + C_2H_2.$$

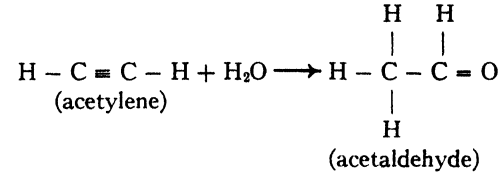
Structurally, the acetylene molecule differs from the molecules of ethane and ethylene in having a *triple bond*, or two additional pairs of electrons between its carbon atoms:

$$H - C \equiv C - H$$

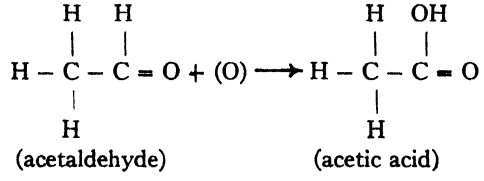
Pure acetylene is almost odorless, poisonous, dangerously unstable, burns with a very hot and yellow, smoky flame, and forms addition compounds with chlorine and other active elements.

It is a good illuminant, because of its highly unsaturated nature. When used for this purpose, it is usually dissolved under pressure in acetone, in which it is very soluble. The oxyacetylene blowpipe is used to produce high temperatures in the welding and cutting of metals.

Because of its unsaturated character, acetylene is the starting material in the production of many synthetic organic compounds, among which are acetic acid, one variety of synthetic rubber, plastics, and acetone. The following reactions illustrate one important application of this principle.



This reaction occurs in the presence of mercury salts, which act as catalysts. The acetaldehyde is then oxidized to acetic acid:

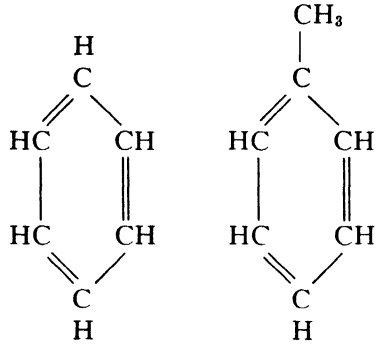


Many other unsaturated hydrocarbons, obtained as by-products of cracking and from other sources, are used in a similar manner to produce other products of commercial value.

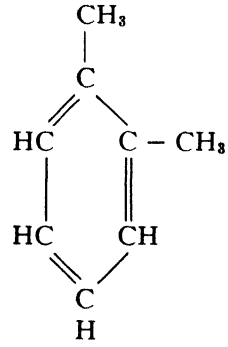
AROMATIC HYDROCARBONS

18. The Benzene Series and Related Hydrocarbons

Among the many valuable substances recovered from coal gas and from coal tar, both of which are products of the destructive distillation of coal, are certain hydrocarbons that differ greatly from the hydrocarbons found in petroleum and natural gas. The structural formulas of three of these hydrocarbons which are members of the benzene series, are shown below:



benzene or benzol — toluene or toluol

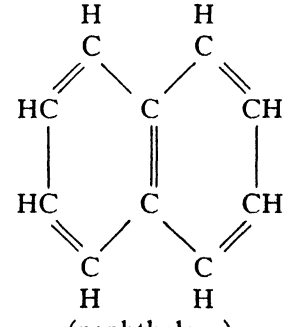


xylene or xylol

Three double bonds are placed in each molecule so that each carbon atom may show its normal valence number of 4. In the diagrams of molecular formulas shown above we have placed double bonds in fixed positions. There seems to be no reason, however, why we should not also expect to find the three double bonds in the three other positions in the molecule. It is thought that the molecule resonates (page 56) between the two possible arrangements; i.e., the locations of the double bonds are changing continuously within each molecule.

These hydrocarbons are used as solvents they are used in the manufacture of dyes drugs, and explosives; and benzene finds some use in motor fuel. They are commonly called the aromatic hydrocarbons to distinguish them from the open chain compounds of the aliphatic series.

Coal tar is also the source of other aromatic hydrocarbons, two of which are of special importance — *naphthalene* and *anthracene*. These substances are related to benzene, but they differ in the complexity of their ring structures. Two or more benzene nuclei, or units, are joined as follows:



(naphthalene)

Anthracene has three benzene units in its molecule. Naphthalene is used in moth balls, in the enriching of gas, and in the manufacture of dyes, such as indigo, and many other valuable organic compounds Anthracene is used in making dyes, particularly some of the important red dyes.

ILLUMINATING AND FUEL GAS

19. The Structure of Flames

Simple flames, consisting of two cones, one within the other, are produced when one gas burns by *combining* with another (Figure 241). Such flames are produced, with the ordinary Bunsen burner, when hydrogen or carbon monoxide burns in the air, or when hydrogen burns in chlorine. Combustion occurs only in the outer cone. The inner cone consists of uncombined gases, which can act as reducing agents; and hence, this portion of the flame is called the *reducing flame.* The outer portion in which there is an excess of oxygen is called the *oxidizing flame.*

If the gas contains hydrocarbons, a more complex flame (Figure 241) is produced. If the openings at the bottom of the burner are closed, the pure gas must burn in air, drawing from the surroundings the oxygen which is needed for the reaction. Under these conditions, the hydrocarbons in the interior of the flame are heated, but there is no oxygen to cause their combustion. The molecules are consequently decomposed (cracked), and particles of carbon which are liberated make the flame luminous. If the openings at the bottom of the burner are opened, air is mixed there with the gas, and a flame, such as the one shown in Figure 241 results.

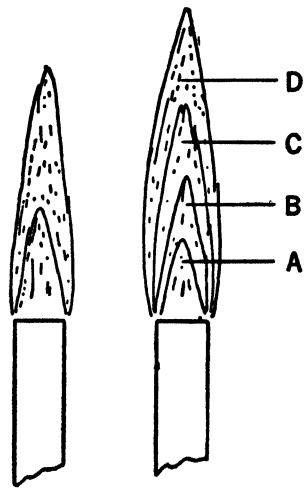


Figure 241. Simple and Complex Flames

The flame on the left is produced when one gas burns by directly combining with another. The flame on the right is produced by burning hydrocarbons.

Four cones can be detected in a flame of the Bunsen burner. The one at the center *A* contains unchanged gas, and the temperature is low. In the second cone *B*, which is bluish green in color, partial combustion results in the formation of hydrogen and carbon monoxide. In the third cone *C*, hydrogen and carbon monoxide are partially converted into water and carbon dioxide. Sufficient heat is liberated in this region to crack some of the unchanged hydrocarbon molecules (especially acetylene and ethylene), thus producing small particles of carbon, which make this cone luminous. The hottest part of the flame is just below the tip of this cone. The particles of carbon are completely burned in this cone; hence, the fourth cone is not luminous. In the fourth cone *D* the combustion of hydrogen and carbon monoxide is completed. This cone is most apparent as a blue, almost invisible region, near the base of the flame.

20. Gas Mantles

Water gas (H_2 and CO) and natural gas, which contains large amounts of methane but very little of the unsaturated hydrocarbons, burn with an almost colorless, non-luminous flame. If these gases are used for illumination, a gas mantle must be employed. Before the extensive use of electricity for lighting, the Welsbach gas mantle was an important illuminating device. These mantles consist of the oxide of thorium (99 per cent) and the oxide of cerium (1 per cent). When this mantle is suspended about a flame, it becomes incandescent and emits a brilliant light, which is much superior to the ordinary luminous gas flame.

21. Miners' Safety Lamp

Many of the disastrous explosions in coal mines result from the ignition of mixtures

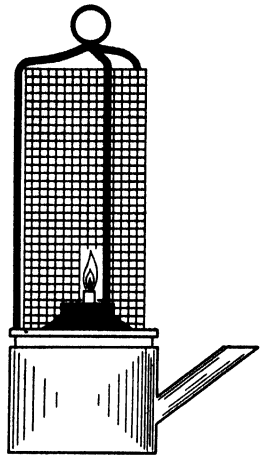


Figure 242. Miners' Safety Lamp

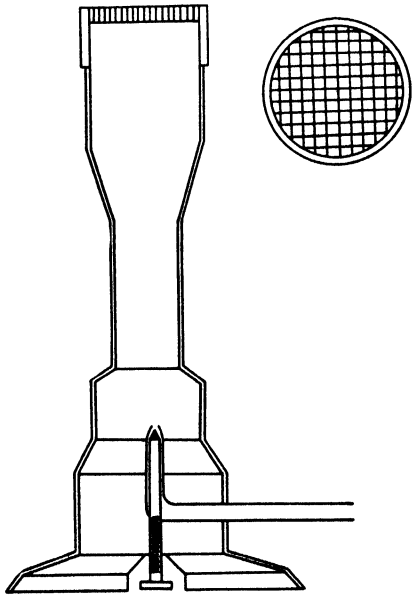


Figure 243. Meker Burner

of air and coal dust or methane (fire damp). Davy's safety lamp for miners (Figure 242) is based upon the principle that a flame is extinguished if the temperature of the burning gases becomes less than their ignition point. The ordinary glass chimney is replaced by a wire gauze or screen. If a mixture of methane and air, for example, starts to burn inside the screen, the flame travels out to the screen, which conducts away the heat so rapidly that the mixture on the outside does not reach the ignition temperature. The Meker burner (Figure 243) makes use of the same principle. The "striking back" of the flame — i.e., burning of the gas at the outlet in the base of the burner — is prevented by placing a screen at the top of the barrel of the burner. This screen prevents the gas in the barrel from becoming hot enough to ignite. The screen divides up the flame into a number of small cones, and very rapid combustion is secured by admitting an excess of air at the base of the burner. A temperature some 400° higher than that obtainable with an ordinary Bunsen burner may be produced by the Meker burner.

22. Coal Gas

When coal is heated in the absence of air, the gases which are evolved are combustible. In plants operated principally for the production of municipal gas supplies, bituminous coal is used, because it produces larger quantities of volatile substances per ton than anthracite coal. Coal gas is also a by-product of the modern coke ovens. A coal gas plant consists of the iron retorts, in which the coal is heated (Figure 244); the hydraulic main; condensers; water and oil scrubbers; a sulfur remover; and the gasholder. The gases which escape from the retorts bubble through the water seal in the hydraulic main. Here, and in the condenser, the tar, water, and other easily condensed and soluble substances are separated from the gas. The gas then passes into the first of the scrubbers, which is a tower filled with loose coke. Water is sprayed in at the top of the tower and, as it flows down over the coke, it dissolves ammonia and some of the hydrogen sulfide. In another scrubbing tower, heavy oil is used to dissolve benzene and toluene. The hydrogen sulfide is removed from the gas in the purifier, which contains quicklime or moist ferric oxide. The gas is then stored in the

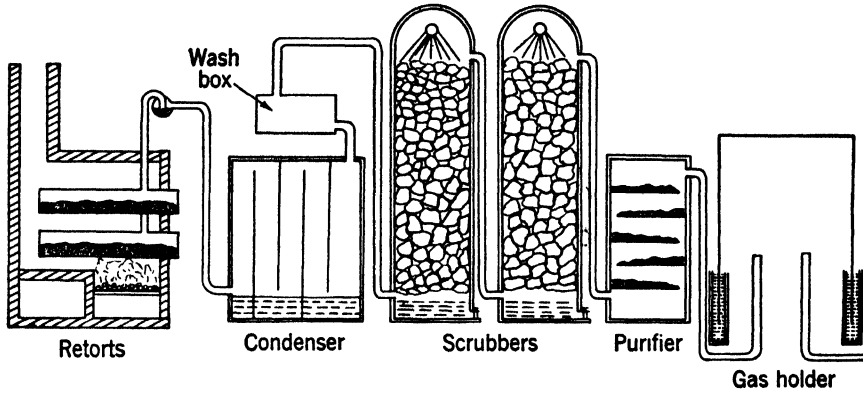


Figure 244. Coal Gas Plant

gas-holder, from which it is forced out into the city's mains.

One ton of soft coal produces about 1300 pounds of coke, 120 pounds of tar, and 12,000 cubic feet of gas. From the gas there may be recovered from 10–25 pounds of ammonium sulfate, 10 pounds of benzene, and about 3 pounds of toluene. The tar also gives many valuable products, such as phenol, naphthalene, anthracene, and pitch (see page 409). Coal gas contains about 20–35 per cent of methane, 10 per cent of carbon monoxide, 30–50 per cent of hydrogen, unsaturated hydrocarbons, such as ethylene and acetylene, and some vapors of benzene and toluene. The luminosity of the coal gas flame depends upon the percentage of unsaturated hydrocarbons in the mixture.

23. Water Gas

The production of water gas by passing steam through beds of red-hot coke has already been discussed (page 70). This gaseous mixture contains hydrogen and carbon monoxide. The flame of this gas is hot but non-luminous. It is often enriched by the addition of hydrocarbons from petroleum. These substances are added by passing hot water gas upward through a tower filled with brick over which oil is sprayed. The vapors from the oil, mixed with water gas, then pass into another heating chamber where the hydrocarbon molecules are cracked, forming lighter and more volatile compounds, also unsaturated hydrocarbons, and some free carbon, called gas carbon. Because of the presence of unsaturated hydrocarbons, enriched water gas burns with a luminous flame.

24. Producer Gas

A cheap fuel that is used rather widely in the industries is produced by blowing air through thick beds of hot coal. The carbon dioxide that is produced in the lower portions of the coal is reduced to carbon monoxide at the higher levels. Some steam is blown in along with the air, and this is reduced to hydrogen by the reaction with hot coal. Gases, such as methane, are distilled from the coal. Hence, the principal constituents of producer gas are hydrogen, carbon monoxide, methane and other hydrocarbons, carbon dioxide, and nitrogen.

25. Blast Furnace Gas

Iron ores are reduced to metallic iron by heating the ores, which are usually oxides, with coke in the blast furnace. The heat is supplied by burning some of the coke in a blast of air that is blown into the furnaces. The gases which escape contain carbon monoxide and some hydrogen, which comes from the reduction of the water that is

present in the ores. The gas also contains nitrogen and carbon dioxide. In general, it resembles producer gas, but it is of a lower quality because of its greater percentage of non-combustible components.

RUBBER

26. Natural Rubber

The world's supply of rubber comes from a tree which grows wild in certain tropical regions and which is also cultivated on rubber plantations. The trees are tapped by cutting through the bark, and from the cuts there flows a liquid called *latex*, which is a colloidal suspension of small rubber particles dispersed in water and stabilized by protective colloids. The addition of acetic acid precipitates the protective colloids, and causes the coagulation of the rubber. The rubber thus produced is dough-like, and white if pure.

The coagulated rubber consists, if pure, of a complex hydrocarbon, which is a polymerized form of *isoprene*, a diolefin hydrocarbon:

$$CH_2 = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - CH = CH_2 \quad (C_5H_8)$$

The polymer (rubber) is sometimes called *caoutchouc* and, since its exact molecular weight is unknown, it is represented by the formula $(C_5H_8)_x$. The rubber molecule has an elongated structure made up of a chain of isoprene units.

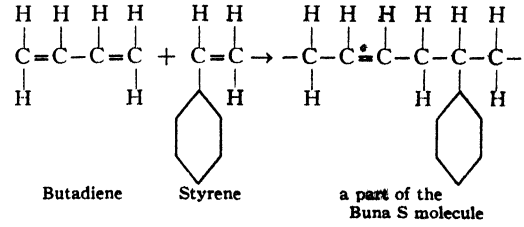
Pure rubber becomes brittle in cold weather and in warm weather is entirely too soft and sticky to be of any use in the manufacture of rubber articles. These difficulties are prevented by *vulcanizing* the rubber. This process consists of heating the raw rubber with small amounts of sulfur or sulfur monochloride, S_2Cl_2. From 5 to 30 per cent of sulfur is added. Small amounts are used in making soft and elastic rubber articles, while hard rubber or *ebonite* results when larger amounts of sulfur are added. When rubber is vulcanized, its long chain molecules are tied together by sulfur molecules. The latter, in the crystalline state, are composed of eight sulfur atoms each, arranged in a ring. Under the conditions employed in vulcanization, the sulfur rings break to make chains, and atoms of these chains combine with carbon atoms in different rubber chains at the double bonds, thus forming the links that bind rubber molecules together. Small percentages of certain organic compounds act catalytically to increase the speed of vulcanization. These substances are called *accelerators*.

Most rubber articles contain several substances in addition to rubber and sulfur. Red rubber contains antimony sulfide, and black rubber contains carbon black. Not only do these substances impart color to the finished product, but many of them increase the resiliency, strength, toughness, and resistance to wear. Zinc oxide is very often added to impart these qualities to the rubber used in the treads of automobile tires.

27. Synthetic Rubber

Synthetic rubbers are, in general, not real rubber but rubber-like materials that can be used for the same purposes as rubber.

Buna S, a general purpose rubber, is produced by the copolymerization of *butadiene*, $CH_2 = CH - CH = CH_2$, and *styrene*, $C_6H_5CH = CH_2$. The polymerization of these two compounds requires the use of a catalyst. The manner in which the two components unite is explained as follows:



Buna is widely used, and most of the synthetic rubber produced in the United States



Figure 245. Production of Automobile Tires
White walled tires contain titanium dioxide.
(Courtesy of National Lead Company)

during World War II was of this kind. The butadiene used to make Buna is produced from petroleum or ethyl alcohol, and the styrene from petroleum or coal.

Neoprene is produced by the polymerization of a chlorine derivative of isoprene, called *chloroprene*, $CH_2 = C(Cl) - CH = CH_2$, which is produced from acetylene and hydrogen chloride. The acetylene, in turn, is made from limestone, coke, and water. This rubber substitute possesses qualities that make it more desirable for some purposes than natural rubber; it is not disintegrated, for example, by oils. It can be used to produce many articles including tires, but it is expensive relatively.

Thiokol is a rubber substitute made from ethylene dichloride and a polysulfide of sodium.

Butyl rubber is a copolymer of isobutylene and butadiene. Isobutylene is one of the unsaturated hydrocarbons produced during the cracking of petroleum oils.

REVIEW EXERCISES

1. What are some of the reasons that account for the very large number of organic compounds?
2. What does the term *homologous series* mean as used in referring to hydrocarbons?
3. Give the name and structural formula of one member of each of the four series of hydrocarbons.
4. How are the unsaturated aliphatic hydrocarbons different in structure and in chemical properties from the saturated aliphatic hydrocarbons?
5. Define isomers. Illustrate by giving the structural formulas of the isomers that correspond to the empirical formula C_4H_{10}.
6. Suggest the structural formulas for as many different isomers as you can for the hydrocarbon that has the empirical formula C_5H_{12}.
7. What are the differences in the composition of gasoline, kerosene, and lubricating oils?
8. What does the term *cracking* mean as applied to the production of gasoline?
9. How is ethylene produced from grain alcohol (C_2H_5OH)? How is the same alcohol made from ethylene?
10. Calculate the densities in grams per liter of methane, ethylene, and acetylene (in their gaseous states and under standard conditions) from their formulas.
11. How many calories of heat are evolved during the combustion of 10 standard liters of methane?
12. Why is a high pressure favorable to the reactions involved in the Bergius process of "liquefying coal"?
13. From what source are benzene, toluene, and xylene obtained? How do the structures of these hydrocarbons differ?
14. Why is a flame of burning hydrogen not luminous? Why do unsaturated hydrocarbons produce flames that are more luminous than those produced by saturated hydrocarbons?

15. How is ethylene produced and what are its uses?
16. What is the meaning of the term *double bond* as applied to the linkage of two carbon atoms?
17. How could one determine whether or not a hydrocarbon contained carbon atoms joined by a double bond?
18. What is the chemical nature of petroleum? What are the principal petroleum products or fractions? Why are they spoken of as fractions? What are their uses?
19. What are the principal fuel gases? How is each produced, and what substances are found in each?
20. Define or identify: Isoprene, latex, vulcanized rubber, neoprene, butadiene, naphthalene, Davy's safety lamp, structural formula.
21. If water gas can be represented as an equal molecular mixture of hydrogen and carbon monoxide, what volume of air (21 per cent oxygen) will be required to burn completely 10 liters? Assume standard conditions in calculating the volume of air.
22. The octane number of a gasoline is 90. Explain.
23. Complete the simple, or empirical, formula of one hydrocarbon containing 8 carbon atoms (per molecule) in each of the four series of hydrocarbons.
24. Would you expect to obtain one, two, or more different compounds when chlorine reacts to replace *one* atom of hydrogen in the molecules of normal butane? Explain.
25. How do the aliphatic hydrocarbons differ in structure from the aromatic hydrocarbons?
26. What two isomeric compounds might be formed if a single hydrogen atom of a normal propane molecule were replaced by a chlorine atom?
27. What is the ratio of carbon and hydrogen atoms in all the hydrocarbons of the ethylene series? What is the ratio of the weights of carbon and hydrogen in the same compounds?
28. What substances would you expect to be produced by the cracking of n-pentane?
29. What is meant by the term *polymerization*? What is the relation of polymerization to natural rubber? To the production of gasoline? Give an example of co-polymerization.
30. Is Buna S a synthetic rubber or a substitute for rubber?

REFERENCES FOR FURTHER READING

Fisher, H. L., *Rubber and Its Use.* The Chemical Publishing Company, 1941.

Kalichevsky, N. A., *The Amazing Petroleum Industry.* New York: Reinhold Publishing Corporation, 1943.

Van Winkle, M., *Aviation Gasoline Manufacture.* New York: McGraw-Hill Book Company, 1944.

U.S. Bureau of Mines, *Origin of Petroleum*, Bulletin 220, Washington, D.C.

Cracking: *Chem. and Met. Eng.*, **35,** 610 (1928); **38,** 343 (1931); *Ind. and Eng. Chem.*, **20,** 1099 (1928); **21,** 643 (1929); **29,** 555 (1937); **35,** 768 (1943).

Ethylene: *Ind. and Eng. Chem.*, **10,** 339 (1924); **19,** 1135 (1927); **22,** 844 (1930); **23,** 1112 (1931); *J. Chem. Ed.*, **2,** 459, 1181 (1925).

Hydrogenation of Coal: *Ind. and Eng. Chem.*, **26,** 164 (1934); **29,** 1367 (1937).

Industrial Gases: *Ind. and Eng. Chem.*, **17,** 94 (1925); **18,** 1273 (1926); **22,** 502 (1930); *News Edition*, **20,** 62 (1942); **21,** 964 (1943); *Chem. and Met. Eng.*, **29,** 795 (1923); *J. Chem. Ed.*, **5,** 291 (1928); **6,** 738 (1929).

Petroleum and Hydrocarbons: *J. Chem. Ed.*, **3,** 683 (1926); **8,** 941, 1930 (1931); **10,** 524 (1933); **11,** 51 (1934); **18,** 582 (1941); *Ind. and Eng. Chem.*, **27,** 648 (1935); **28,** 860 (1936); **30,** 222 (1938); **33,** 324 (1941); **35,** 623 (1943); *News Edition*, **18,** 347 (1940); **21,** 939, 950 (1943); **22,** 248 (1944); *Chem. and Met. Eng.*, **49,** 1 (1942).

Polymerization: *Ind. and Eng. Chem.*, **27,** 933 (1935).

Rubber: *J. Chem. Ed.*, **2,** 1176 (1925); **3,** 253 (1926); **6,** 1286, 2235 (1929); **7,** 1788 (1930); **8,** 7 (1931); **9,** 975 (1932); **12,** 135 (1935); **19,** 522 (1942); *Nat. Geog. Mag.*, Feb. 1940.

Synthetic Rubber: *Ind. and Eng. Chem., News Edition*, **18,** 285, 374, 540 (1940); **21,** 490, 741, 864 (1943); *Ind. and Eng. Chem.*, **32,** 464, 1153 (1940); *Chem. and Met. Eng.*, **47,** 220, 561 (1940); *J. Chem. Ed.*, **21,** 15 (1944).

Tetraethyl Lead: *Ind. and Eng. Chem.*, **31,** 1439 (1939).

33

DERIVATIVES OF THE HYDROCARBONS

1. Alkyl Radicals

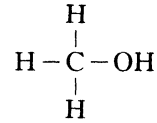
Many organic compounds can be considered as hydrocarbon derivatives in which various kinds of atoms and radicals are substituted for one or more of the hydrogen atoms of a hydrocarbon molecule. The portion of a hydrocarbon molecule that remains unchanged in the derivative — the carbon atoms and the hydrogen atoms attached to these atoms — is called an *alkyl* radical. The alkyl radicals corresponding to the first ten members of the methane series of hydrocarbons are:

Methyl	CH_3	Hexyl	C_6H_{13}
Ethyl	C_2H_5	Heptyl	C_7H_{15}
Propyl	C_3H_7	Octyl	C_8H_{17}
Butyl	C_4H_9	Nonyl	C_9H_{19}
Amyl	C_5H_{11}	Decyl	$C_{10}H_{21}$

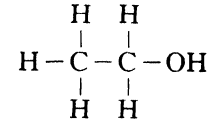
Speaking, for the present, of the derivatives of methane and its homologues, and of the compounds which contain only oxygen in addition to carbon and hydrogen, we find that six classes of derivatives make a convenient grouping of many organic compounds of great importance. These six classes are discussed below.

2. The Alcohols

The derivatives of hydrocarbons that contain one or more hydroxyl groups in place of one or more hydrogen atoms in a molecule are called *alcohols*. The most familiar alcohols are those which contain the *methyl* and *ethyl* alkyl groups, and which may be regarded as derivatives of methane and ethane respectively:

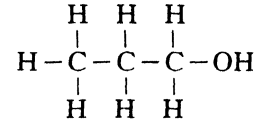


(methyl alcohol)

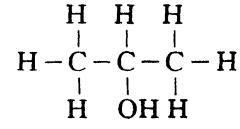


(ethyl alcohol).

For each of the first two alcohols only one structural formula is possible, and there is just one methyl and one ethyl alcohol. Isomerism makes its appearance in *propyl alcohol*, which has two isomeric forms. In one of these, the hydroxyl radical is attached to the carbon atom at the end of the chain, and in the other it is attached to the carbon atom in the middle.



Normal propyl alcohol



Isopropyl, or secondary propyl, alcohol

Butyl alcohol, the next in the series, has four isomeric forms:

normal, $CH_3 - CH_2 - CH_2 - CH_2 - OH$;
isobutyl, $(CH_3)_2 - CH - CH_2 - OH$;
secondary butyl, $CH_3 - CH_2 - CHOH - CH_3$;
and tertiary butyl, $(CH_3)_3 - C - OH$.

The names *methanol*, *ethanol*, *propanol*, etc., are sometimes used instead of methyl, ethyl, propyl, etc., to designate different alcohols. The terms *primary*, *secondary*, and *tertiary* alcohols, as used above, refer to compounds in which the following groups appear:

(1) Primary, $-CH_2OH$.

(2) Secondary, $-CHOH$.

(3) Tertiary, $-C-OH$.

All of the substances named above are *monohydric* alcohols (one – OH radical per molecule). *Glycol* and *glycerine*, or *glycerol*, are *dihydric* and *trihydric* alcohols, respectively.

Glycol, $OH-C(H)(H)-C(H)(H)-OH$

Glycerine, $OH-C(H)(H)-C(OH)(H)-C(H)(H)-OH$

There are several glycols. The substance mentioned above, $C_2H_4(OH)_2$, is *ethylene glycol*. It is used as an anti-freeze in automobile radiators.

3. Glycerine

Glycerine is produced as a by-product of soap making, and it is also made from propylene, a by-product of the petroleum cracking industry. It is a colorless, oily, sweet liquid. Besides its use in the manufacture of nitroglycerine, it is used to prevent the drying-out of many products, such as ink, cigarettes, and smoking-tobacco, and as an anti-freeze in automobile radiators. It is miscible with water in all proportions, and pure glycerine is very hygroscopic. This property makes glycerine suitable for use in lotions, soaps, and cosmetics. Because of its sweet taste it is also used in medicines and confections. Glycerine is used in the manufacture of glyptal resins, which when dissolved in certain solvents make high grade lacquers for use as automobile finishes, and for similar purposes.

4. Methyl Alcohol (Methanol), CH_3OH

This alcohol was produced until 1925 almost universally by the destructive distillation of wood (page 296), and, therefore, it came to be known as *wood alcohol*. At the present time, about 90 per cent of our methanol is produced by heating a mixture of hydrogen and carbon monoxide under pressure in the presence of zinc oxide or other catalysts.

Methanol is a colorless liquid, which boils at about 66°. It is extremely poisonous, when taken internally, or when the vapor is breathed. It produces blindness by its action on the optic nerve and often causes death. Industrially, methanol is widely used as a denaturant of ethyl alcohol, as an anti-freeze, and as a solvent in the manufacture of varnishes, shellacs, and other substances that water does not dissolve. It is also used extensively in the manufacture of formaldehyde, dyes, and drugs. The annual production of methanol in the United States is about 830,000,000 pounds.

5. Ethyl Alcohol (Ethanol) C_2H_5OH

This alcohol is produced by the fermentation of the sugar glucose, $C_6H_{12}O_6$:

$$C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2.$$

The starting material may be glucose itself, or other substances that can be converted readily into glucose. These substances include other sugars, such as sucrose (cane sugar) and maltose; fruit juices, which contain sugars; molasses; and starch, $C_6H_{10}O_5$.

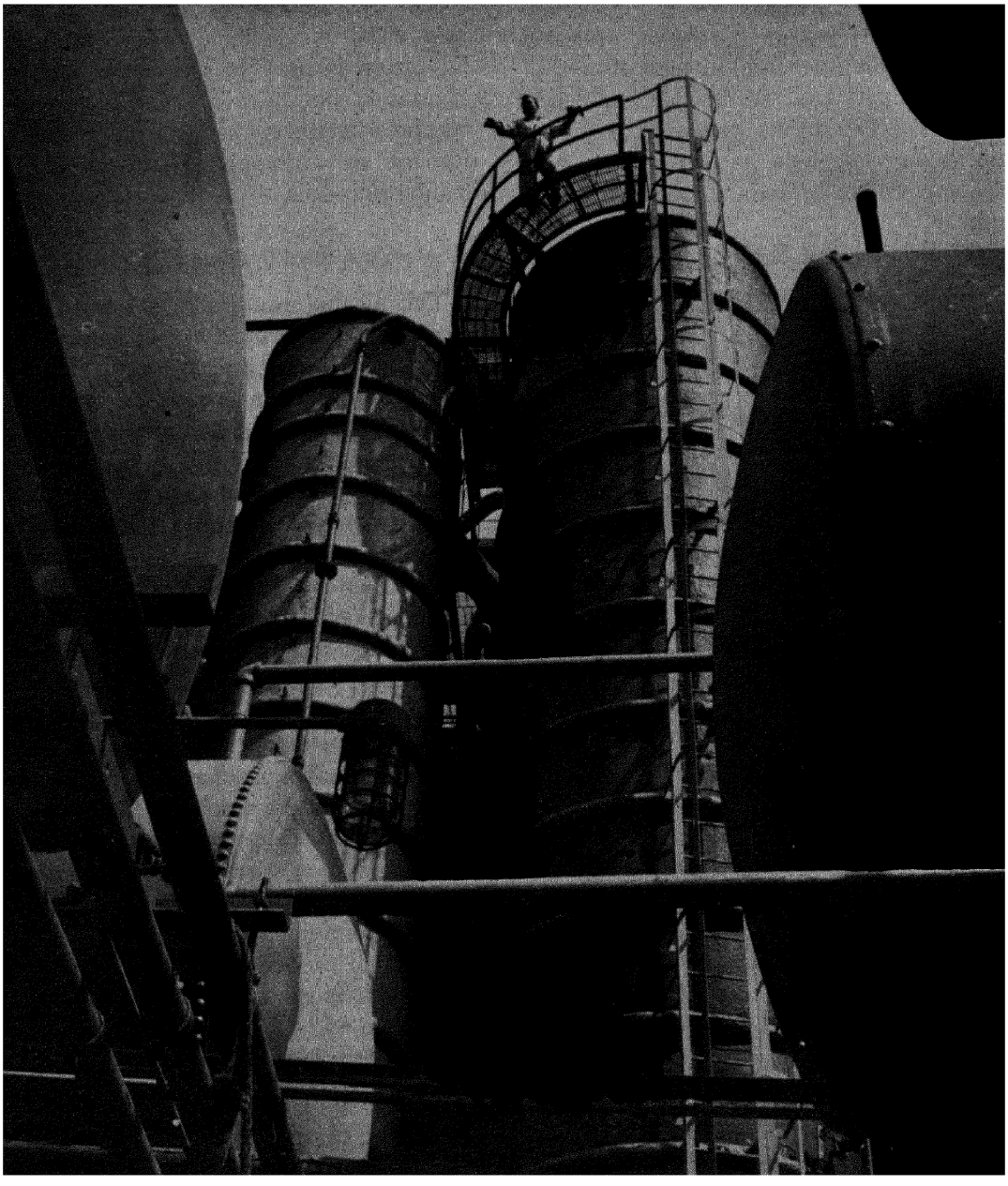


Figure 246. Stills Used in the Production of Methyl Alcohol

(Courtesy of Du Pont Company)

The fermentation process is catalyzed by certain substances called *enzymes*, which are produced by yeast cells. Cane sugar, starch, and cellulose are not changed directly into alcohol by yeast. Cane sugar, $C_{12}H_{22}O_{11}$, is first converted into sugars which have the formula $C_6H_{12}O_6$ by an enzyme called *invertase* produced by the yeast cells:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2\ C_6H_{12}O_6.$$

These simpler sugars are then converted into alcohol by a second yeast-enzyme called *zymase*. Starch first must be changed into sugars by boiling it with dilute hydrochloric acid or by the action of enzymes.

Solutions containing only 14 to 18 per cent of alcohol can be made directly by fermentation, because higher alcoholic concentrations kill the yeast cells. Higher proportions of alcohol are obtained by the fractional distillation of the naturally fermented product. By this means, a solution containing 95–96 per cent of alcohol can be produced. Absolute (or approximately 100 per cent alcohol) can be produced by treating 95 per cent alcohol with some dehydrating agent, such as quicklime, and distilling. Absolute alcohol is usually prepared on an industrial scale, however, by adding benzene to 95 per cent alcohol and distilling this mixture. The first portion of the distillate, which contains the benzene, water, and some alcohol, is discarded.

Ethyl alcohol is also produced synthetically from ethylene (page 408) and acetylene.

Pure ethyl alcohol is a colorless liquid, which boils at 78.3°, has a density of 0.789 (20°), and freezes at − 117°. Next to water, it is the most widely used solvent. It is used in the preparation of varnish, shellac, films, celluloid, artificial leathers, tinctures (iodine), perfumes, hair tonics, lotions, medicines, flavoring extracts, tooth pastes, and hundreds of other industrial and pharmaceutical products. It is used in the manufacture of ethylene, chloroform, ether, iodoform, and several thousand medicines. It is also used as a fuel and as an antifreeze in automobile radiators. Solid alcohol or "canned heat" can be made from soap and alcohol.

Wood alcohol is the most familiar denaturant of ethyl alcohol. Other denaturants are pyridine, low boiling petroleum hydrocarbons, and *aldehol*, a product obtained by oxidizing kerosene. Denatured alcohol is sold without the payment of the tax imposed upon untreated ethyl alcohol.

6. The Ethers

The alcohols, when dehydrated by the action of limited quantities of sulfuric acid at a temperature of about 140°, form substances called *ethers*. When ethyl alcohol is treated with a relatively small quantity of acid, *diethyl ether*, $(C_2H_5)_2O$ is formed. The reaction is shown by the following simplified equation, although intermediate steps which are not shown may occur:

$$C_2H_5\boxed{OH + H}OC_2H_5 \rightarrow H_2O + C_2H_5 - O - C_2H_5.$$

Diethyl ether is the substance commonly called *ether*. It boils at 35°, and its vapor is highly inflammable. Its best known use is as an anesthetic for general surgery. It is an excellent solvent for some water-insoluble substances such as fats, waxes, and gums. It is used as a solvent for the extraction of fats in analyzing products for their fat content. It is also used as a solvent in the manufacture of smokeless powder, collodion, and artificial silk.

Dimethyl ether is $CH_3 - O - CH_3$. *Ethyl methyl ether* is $C_2H_5 - O - CH_3$, and *propyl ethyl ether* is $C_3H_7 - O - C_2H_5$.

7. Aldehydes

When the alcohols undergo combustion, they are oxidized to carbon dioxide and water. But if the oxidation is carried out

at a relatively low temperature by means of some moderately active oxidizing agent, a substance called an *aldehyde* is produced, if the alcohol is a *primary* alcohol. The characteristic structure of an aldehyde is R – CHO where R represents an atom of hydrogen or, more often, an alkyl radical. *Formaldehyde*, HCHO, and *acetaldehyde*, CH_3CHO, are made from methyl and ethyl alcohol, respectively:

$$2\,CH_3OH + O_2 \longrightarrow 2\,H-\overset{\overset{O}{\|}}{C}-H + 2\,H_2O.$$

$$2\,C_2H_5OH + O_2 \longrightarrow 2\,CH_3-\overset{\overset{O}{\|}}{C}-H + 2\,H_2O.$$

Acetaldehyde is made from acetylene (page 408). It is used in the production of many organic compounds including acetic acid, ethyl alcohol, and acetone.

8. Formaldehyde

Formaldehyde is commonly known and used in the form of a 40 per cent solution, which is called *formalin*. This solution is used as a disinfectant and as a preservative of laboratory and museum specimens of organic materials. It is also used to disinfect grains and potatoes, and as a fly poison. About 540,000,000 pounds are produced annually. *Bakelite* and *Redmanol* are synthetic plastic products made from formaldehyde and phenol (carbolic acid).

9. Ketones

The ketones have the general formula R – CO – R, in which R represents an alkyl group. They may be produced by the oxidation of *secondary* alcohols. Thus, *dimethyl ketone* is produced by the catalyzed oxidation of secondary, or isopropyl, alcohol in air at about 450°:

$$2\,CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + O_2 \longrightarrow 2\,CH_3-\overset{\overset{O}{\|}}{C}-CH_3.$$

This substance, the most important of the

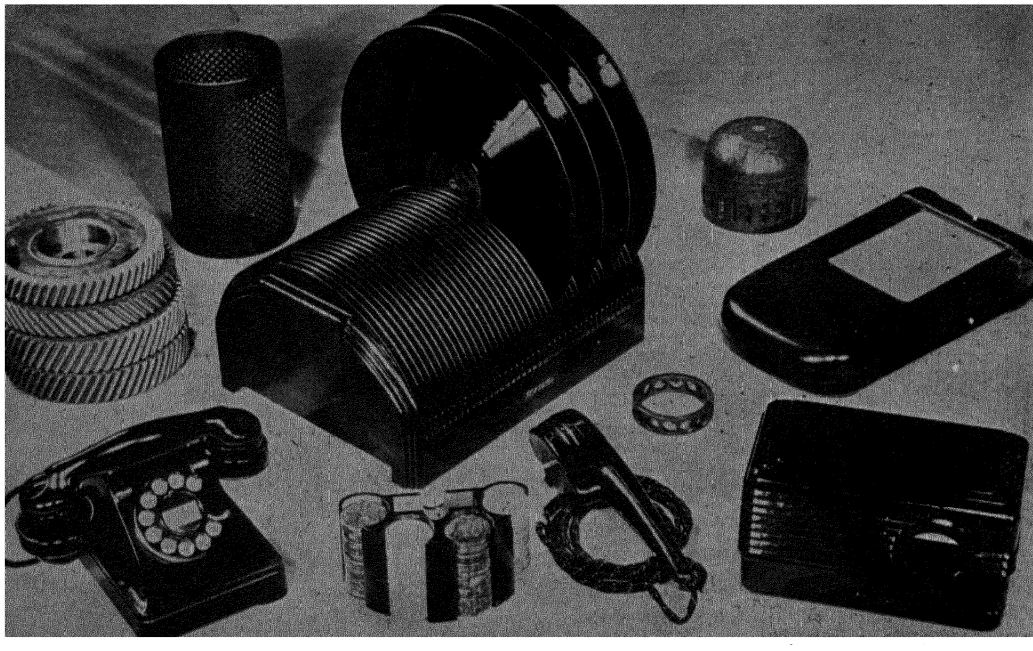


Figure 247. A Group of Articles Made of Bakelite
(Courtesy of Koppers Company)

ketones, is called *acetone*. It is produced also by bacterial fermentation of starch. In the laboratory, and in industry too, it may be prepared by heating dry calcium acetate:

$$Ca(C_2H_3O_2)_2 \longrightarrow CH_3 - CO - CH_3 + CaCO_3.$$

Acetone is an important organic solvent in the manufacture of varnishes, smokeless powders, paint and varnish removers, and many other materials. Its use as a solvent for acetylene has been mentioned previously (page 408).

10. Acids

Upon further treatment with moderately vigorous oxidizing agents, aldehydes are converted into substances that are relatively weak acids, and which contain the *carboxyl* radical, $-COOH$. It is the hydrogen atom of this radical that gives these compounds their properties as acids.

The oxidation of formaldehyde and acetaldehyde forms *formic acid* and *acetic acid*, the structural formulas of which are, respectively:

$$H - \overset{\overset{O}{\|}}{C} - OH \quad \text{and} \quad H - \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} - \overset{\overset{O}{\|}}{C} - OH.$$

These acids are the first members of a series commonly called the *fatty acids*, because compounds derived from some of the higher members of the series are found in fats (page 422).

Formic acid is present in some kinds of nettles and is responsible, in part, for the sharp irritation resulting from the bite of an ant and the sting of a bee. It is produced from CO and NaOH:

$$CO + NaOH \longrightarrow HCOONa.$$

The acid is liberated from sodium formate by adding sulfuric acid:

$$2\,(Na^+ + HCOO^-) + (2\,H^+ + SO_4^{=}) \longrightarrow (2\,Na^+ + SO_4^{=}) + 2\,HCOOH.$$

Formic acid is used to remove hair from hides in the leather industry and to coagulate rubber latex.

11. Acetic Acid

Much of the acetic acid now used is made directly from acetaldehyde produced from acetylene (page 408). The older methods produced it from wood or ethyl alcohol. The pyroligneous distillate resulting when wood is heated in the absence of air is usually treated with lime. This converts the acetic acid into calcium acetate, which is then treated with sulfuric acid and distilled. The acetic acid is volatile and, consequently, is easily recovered in this manner.

The production of acetic acid from ethyl alcohol involves the reactions occurring when cider is allowed to stand exposed to the air for some time. The sugars of the fruit juice are first fermented to produce ethyl alcohol. The "hard" cider is then placed in a container which has previously contained vinegar, or "mother of vinegar" is added to supply certain bacteria that aid in the oxidation of the alcohol to the acid. *Cider vinegar* contains about 4 per cent of acetic acid and has a brown color. *White* or *wine* vinegar is made by the action of bacteria upon colorless alcoholic solutions. The anhydrous, pure acid is sometimes called *glacial* acetic acid, because of the ice-like solid which it forms when cooled below 18°.

Acetic acid has many uses. It is used to prepare calcium acetate, from which acetone is derived; to make *white lead* for paints, and lead acetate, which is known as *sugar of lead;* in the manufacture of many dyes and other coal-tar products, such as aspirin; to produce *cellulose acetate*, which is somewhat similar to cellulose nitrate (page 354); to react with various alcohols to form compounds which are valuable as solvents and artificial flavors; in dyeing; and in the printing of silk and wool cloth. Cellulose acetate has an advantage over

pyroxylin (cellulose nitrate) in its non-inflammability. The product of the reaction of acetic acid with amyl alcohol is *amyl acetate*, or *banana* oil, which is a solvent extensively used in the production of pyroxylin lacquers, bronzing liquids, etc.

12. Other Organic Acids

The formulas and names of other more or less common *monobasic* organic acids are listed below.

Propionic, $CH_3 - CH_2 - COOH$
Butyric, $CH_3 - (CH_2)_2 - COOH$
Valeric, $CH_3 - (CH_2)_3 - COOH$
Caproic, $CH_3 - (CH_2)_4 - COOH$
Palmitic, $CH_3 - (CH_2)_{14} - COOH$
Stearic, $CH_3 - (CH_2)_{16} - COOH$
Oleic, $CH_3 - (CH_2)_7 - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} = \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - (CH_2)_7 - COOH.$

Oleic acid is unsaturated. The other acids in this list correspond to members of the paraffin series of hydrocarbons.

Some of the acids contain hydroxyl or other groups in addition to the carboxyl radical. Some also contain two or three COOH groups and are dibasic or tribasic, respectively.

Lactic Acid, $CH_3 - CHOH - COOH$, is present in sour milk.

Oxalic Acid, $(COOH)_2$, is dibasic. It is found in rhubarb and sorrel.

Citric Acid, $COOH - CH_2 - C(OH)(COOH) - CH_2 - COOH$, $(H_3C_6H_5O_7)$, a tribasic acid, is found in citrus fruits.

Tartaric Acid is $COOH - CHOH - CHOH - COOH$ $(H_2C_4H_4O_6)$. Crude tartar, from which the acid is prepared, collects in the containers in which wine or grape juice is stored. *Cream of Tartar* is the acid potassium salt of this acid, $KHC_4H_4O_6$.

13. Esters

Esters are the products of the reactions of acids with alcohols. They are produced from both organic and inorganic acids:

$$C_2H_5OH + (H^+ + NO_3^-) \longrightarrow H_2O + C_2H_5NO_3, \text{ ethyl nitrate.}$$

$$C_2H_5OH + HO - \overset{\overset{O}{\|}}{C} - CH_3 \longrightarrow H_2O + C_2H_5 - O - \overset{\overset{O}{\|}}{C} - CH_3, \text{ ethyl acetate.}$$

Because of the slowness of these reactions at ordinary temperatures, catalysts and a somewhat elevated temperature are required.

Since glycerine is an alcohol, it may also form esters. Nitroglycerine (page 354) is the glyceryl ester of nitric acid. Similarly, cellulose acetate and cellulose nitrate are esters of cellulose, which acts as an alcohol in their formation, and acetic and nitric acids.

Many of the esters have pleasant, flower-like or fruit-like odors. They are used in perfumes and as artificial fruit flavors. Amyl acetate is banana oil, and ethyl butyrate possesses the flavor of the pineapple.

14. Fats

The fats are esters of glycerine and different monobasic organic acids. The most familiar fats are glyceryl esters of palmitic, stearic, and oleic acids (Section 12). These esters are called *palmitin*, *stearin*, and *olein*, respectively.

Palmitin, $[CH_3 - (CH_2)_{14} - COO]_3C_3H_5$

Stearin, $[CH_3 - (CH_2)_{16} - COO]_3C_3H_5$

Olein, $[CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COO]_3C_3H_5$.

The hardness of a fat depends upon the relative amounts of the three esters that it contains. The liquid fats, such as olive oil, coconut oil, and cottonseed oil, contain 75 per cent or more of the ester of oleic acid, which is a liquid. Beef tallow, which contains about 25 per cent of olein and 75 per cent of palmitin and stearin, is one of the hardest of the natural fats. Lard, which is a softer

and more readily melted fat, contains 50–60 per cent of olein and about 40 per cent of palmitin. Butter, in addition to 12–14 per cent of water, contains olein and palmitin and about 4 per cent of *butyrin*, the glyceryl ester of *butyric acid* ($CH_3 - (CH_2)_2 - COOH$).

Fats are hydrolyzed in the body during digestion by certain enzymes:

$$(CH_3 - (CH_2)_{14} - COO)_3C_3H_5 + 3\ HOH \longrightarrow C_3H_5(OH)_3 + 3\ CH_3 - (CH_2)_{14} - COOH,$$

(Palmitin) (Glycerine) (Palmitic acid)

In the hydrogenation of liquid fats (page 74) hydrogen is made to combine with the carbon atoms that are linked together by the double bond in the molecule of olein.

$$\left[CH_3 - (CH_2)_7 - \overset{H}{\underset{H}{C}} = \overset{H}{\underset{H}{C}} - (CH_2)_7 - COO\right]C_3H_5$$

This reaction converts olein into stearin, which is a solid fat. By this method substitutes for lard and butter are produced from cottonseed oil, coconut oil, and other vegetable oils. Some butter substitutes are produced by mixing stearin, from beef fat, with oils to give a fat that has about the same degree of hardness as butter. The yellow color characteristic of butter is obtained by adding a yellow dye. Hydrogenation is also used to convert vegetable oils into solid fats that are used in making soaps.

15. Soaps and Saponification

The soaps are salts (usually sodium salts) of palmitic, stearic, and oleic acids. They are produced by the reaction of sodium or potassium hydroxide with fats, which are the glyceryl esters of the acids. Thus, sodium hydroxide reacts with glyceryl palmitate, for example, to form glycerine and *sodium palmitate*, a soap.

$$[CH_3 - (CH_2)_{14} - COO]_3C_3H_5 + 3\ (Na^+ + OH^-) \longrightarrow C_3H_5(OH)_3 + 3\ (NaOOC - (CH_2)_{14} - CH_3)$$

This and similar reactions are called *saponification*.

Fats are boiled in the *soap kettle* with sodium hydroxide, and the soap is produced in a colloidal state, from which it is precipitated, or *salted out*, by the addition of sodium chloride. The soap

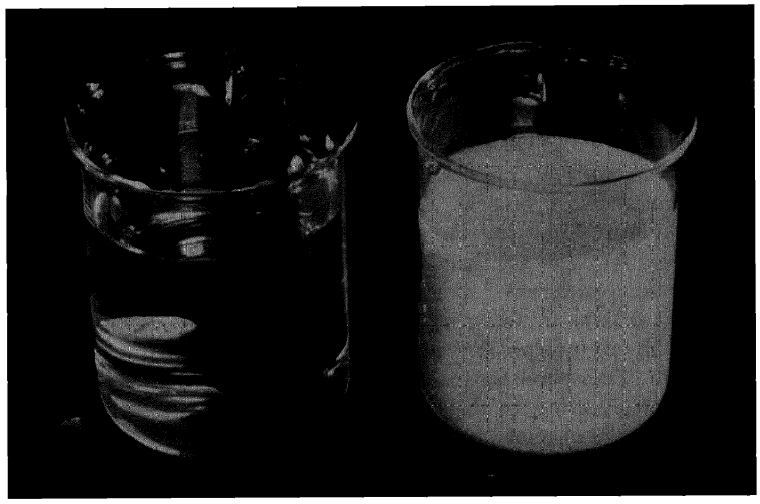


Figure 248. Effect of Hydrogenation

The beaker on the left contains clear oil before hydrogenation. The beaker on the right shows the same oil hardened by hydrogenation.

(Courtesy of Proctor and Gamble Company)

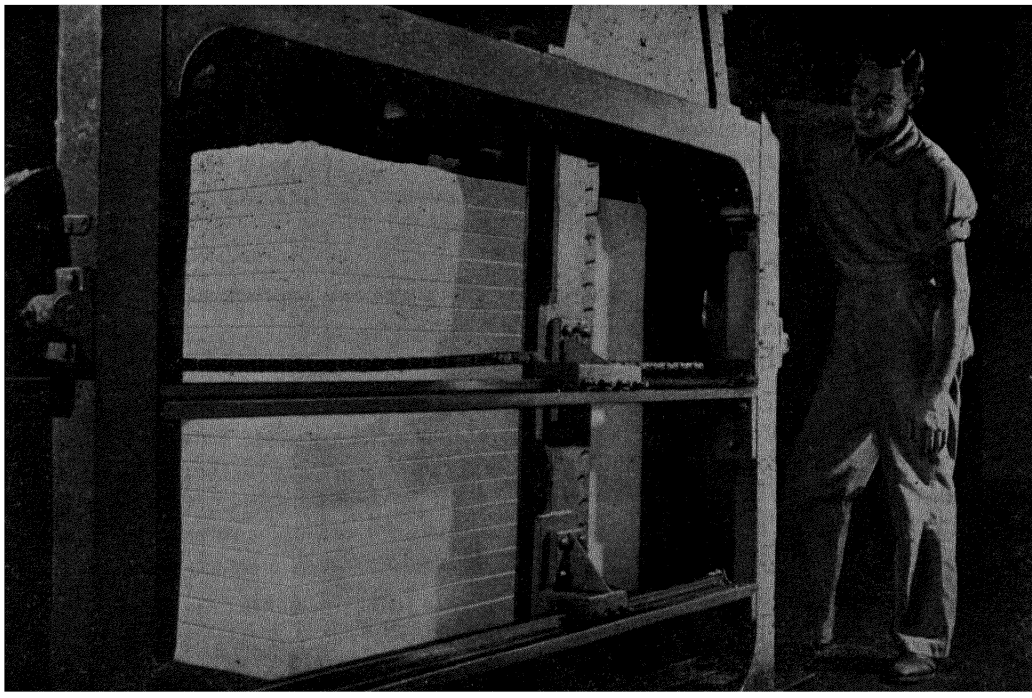


Figure 249. Cutting Soap into Bars

A mass of soap weighing 900 pounds is sliced into slabs by taut piano wires.
(Courtesy of Procter and Gamble Company)

settles out on the top of the mixture in the kettle. It is removed and mixed, while still soft, in the *crutcher* with many different substances such as coloring materials, perfumes, and fillers The fillers usually serve some purpose; borax, sodium silicate, and sodium carbonate form alkaline solutions in water, while rosin increases the lathering qualities of the soap. From the crutcher, or mixer, the soap is run into molds or *frames*. The hardened soap is then cut into cakes. Toilet soaps are usually prepared from fats that are liquid or semi-liquid at ordinary temperatures. Laundry soaps are made from hard fats. Floating soaps contain air bubbles which are incorporated with the soap in the crutcher. Transparent soaps are made by adding sugar or glycerine, or they are made by dissolving dry soap in alcohol and evaporating the excess of solvent. Scouring soaps contain large percentages of abrasive materials, such as diatomaceous earth, clay, finely powdered silica, or volcanic ash. Soap powders contain only about 10–25 per cent of soap. The remainder is sodium phosphate and sodium carbonate.

After the removal of the soap from the kettle in which the saponification is carried out, the solution is concentrated by evaporation, and the glycerine is recovered by distillation.

16. The Properties and Cleansing Action of Soaps

The cleansing action of soap depends upon several factors. One of these is the property of the soap which causes it to act as an emulsifying agent in the formation of an emulsion of oil and grease in water. In this way, the grease on skin or cloth is broken up into small droplets, which are washed away in an excess of water.

The cleansing action of soap also depends upon the effect of soap upon the surface tension of water. Soap solutions have a lower surface tension than pure water. This property causes water containing a soap suspension to spread very readily over

surfaces and to penetrate the pores of the skin or the spaces between the threads of cloth. The removal of particles of dirt depends, at least in part, upon the ability of the colloidal soap particles to adsorb and carry away the dirt.

A mixture of soap and water is at least in part, a colloidal dispersion of soap particles instead of a true solution. Calcium and magnesium ions form salts that are not soluble and that do not form colloidal dispersions. For this reason, the addition of soap to hard water produces a curdy precipitate of calcium and magnesium soaps; and hence, the soap does not form a lather, or "suds." This results in a waste of soap and is also undesirable in the laundry, because the insoluble soaps are left upon the cloth as gray, dirty deposits.

17. Other Detergents

During recent years new detergents have been discovered These are sodium salts of organic sulfates. A typical salt is produced in the following manner: (1) Lauric acid, $CH_3(CH_2)_{10}COOH$, is treated with hydrogen and converted into lauryl alcohol, $CH_3(CH_2)_{10}CH_2OH$; (2) Lauryl alcohol is then treated with sulfuric acid and converted into lauryl acid sulfate, $CH_3(CH_2)_{10}CH_2HSO_4$; (3) lauryl acid sulfate is then treated with sodium hydroxide to form sodium lauryl sulfate, $CH_3(CH_2)_{10}CH_2NaSO_4$. This substance and similar salts are sold under the name of *Dreft*. These substances are not soaps from a strictly chemical point of view, but they are excellent detergents. The calcium salt is as soluble as the sodium salt; hence, there is no formation of scum when they are mixed with hard water, and they lather equally well in cold or hot water and in soft and hard water.

18. Nitrogen Organic Compounds

The *amines* may be regarded as derivatives of ammonia in which one or more atoms of hydrogen are replaced by alkyl groups, such as CH_3. For example, there are three methyl amines — *methylamine*, CH_3NH_2; *dimethylamine*, $(CH_3)_2NH$; and

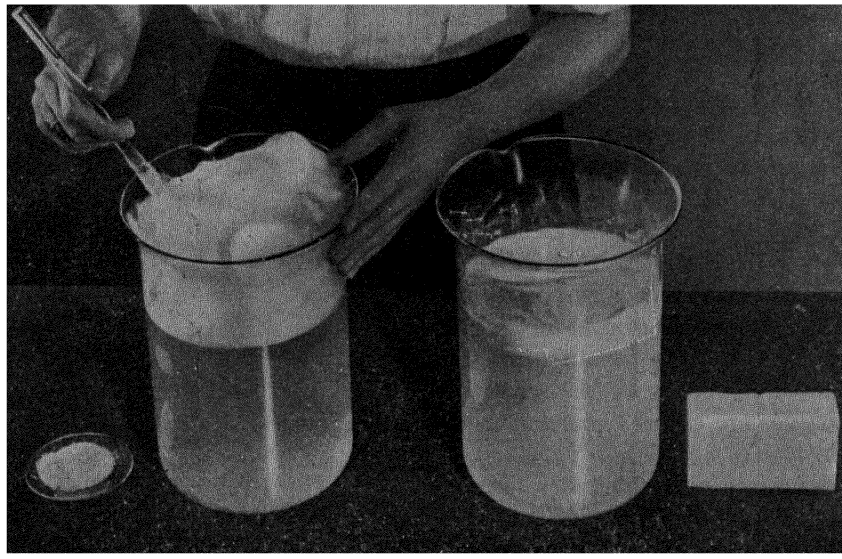


Figure 250. Comparison of the Lather-producing Qualities of Soap (right) and Synthetic Detergents (left) in Hard Water (*Courtesy of Du Pont Company*)

trimethylamine, $(CH_3)_3N$. The NH_2 group is called the *amino* group or radical. The *diamines* contain two of these groups in a molecule.

The amines are basic compounds, and their properties are somewhat like those of ammonia. Many of them are used extensively in the synthesis of dyes, drugs, and other organic compounds. Some of the diamines are used in the production of nylon.

The *amides* are compounds in which hydrogen atoms of ammonia are replaced by the R−C=O group of an organic acid in which R represents an alkyl group. The simplest and most important amides are those in which there is one NH_2 group in place of the OH group in the carboxyl radical of the acid. Thus, *acetamide*, a derivative of acetic acid and ammonia is CH_3-CONH_2.

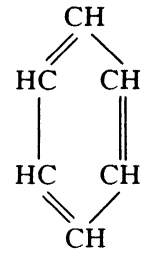
In the *amino acids* the amino (NH_2) group replaces hydrogen atoms in the alkyl group of the acid. Thus, *aminoacetic acid* is $NH_2–CH_2COOH$. These acids are produced by the hydrolysis of proteins.

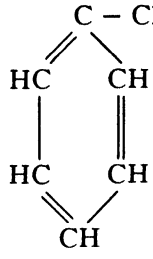
DERIVATIVES OF BENZENE AND OTHER AROMATIC HYDROCARBONS

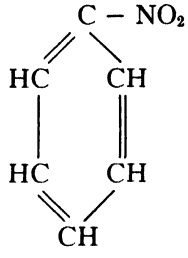
19. Coal Tar Compounds

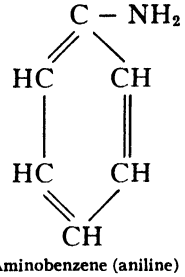
Benzene and toluene are recovered by washing coal gas in oil scrubbers (page 411). These hydrocarbons are also produced during the fractional distillation of coal tar, which also yields xylene, naphthalene, anthracene, phenol, cresols, and other substances of lesser importance. Each of these direct products of coal, or of coal tar, is the starting material for the manufacture of many valuable substances. In general, these derivatives are called "coal tar compounds."

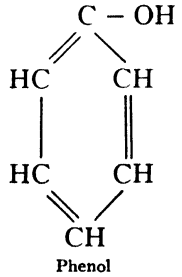
Corresponding to the aldehydes, acids, alcohols, and other derivatives of the methane hydrocarbons, there are many compounds of a similar nature that can be considered as derivatives of benzene and related hydrocarbons. Some of the derivatives of benzene are shown by the following structural formulas:

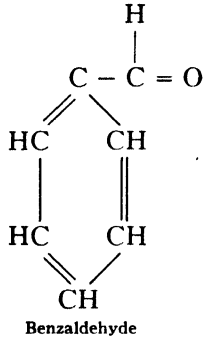

Benzene

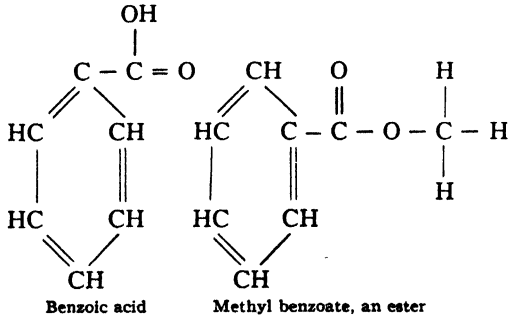

Chlorobenzene


Nitrobenzene


Aminobenzene (aniline)


Phenol


Benzaldehyde


Benzoic acid

Methyl benzoate, an ester

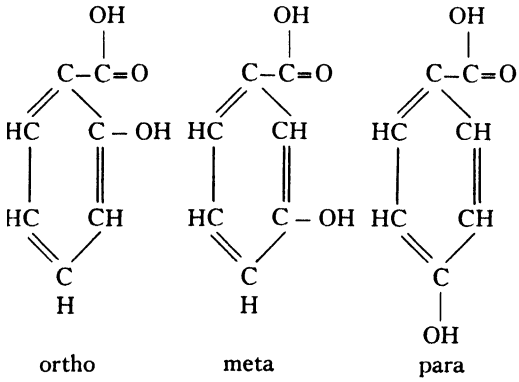
Aniline is an important substance from which many dyes and drugs are produced.

Phenol (C_6H_5OH), commonly called carbolic

acid, is used in making synthetic resins and picric acid. It is extremely corrosive in its action upon flesh. In dilute solutions it serves as an excellent antiseptic for destroying certain forms of bacterial life.

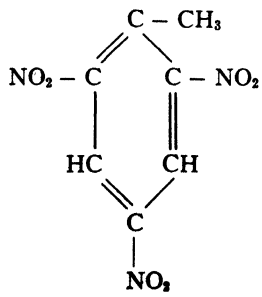
Phenol is also used to produce salicylic acid, $C_6H_4OHCOOH$, which is important because of its use in making *aspirin* and other drugs, also *methyl salicylate* (wintergreen), which is the ester of this acid and methyl alcohol, $C_6H_4OHCOOCH_3$. Aspirin is *acetyl salicylic acid.* In producing this drug salicylic acid acts as an alcohol, through its hydroxyl radical, and forms an ester with acetic acid.

In addition to salicylic acid there are two other acids that have the same empirical formula, $C_6H_4OHCOOH$, but different structural formulas, and, therefore, are isomers. These two acids are called *meta-* and *para*-hydroxybenzoic acids. Salicylic acid is also called *ortho*-hydroxybenzoic acid. These three acids are typical of many isomeric compounds in which two atoms or radicals are substituted in different positions relative to each other on the benzene ring. Thus, the three hydroxybenzoic acids are:



ortho meta para

Toluene is the starting material for *trinitrotoluene* (page 354), which is made by treating the hydrocarbon with nitric acid.



Benzoic acid is made by oxidizing toluene:

$$2\ C_6H_5CH_3 + 3\ O_2 \longrightarrow 2\ C_6H_5COOH + 2\ H_2O.$$

Sodium benzoate is widely used as a preservative of foods.

Chlorobenzene is used in making the insecticide DDT. It can also be converted into phenol.

REVIEW EXERCISES

1. Name the six classes of the oxygen derivatives of the hydrocarbons. What group, or radical, characterizes the compounds of each class?
2. Write the structural formulas of at least four isomers corresponding to the formula $C_5H_{11}OH$.
3. Give one example each of a primary and a secondary alcohol. What products are formed when these alcohols are mildly (not completely) oxidized?
4. Of what hydrocarbon is acetone a derivative?
5. Name two ways of producing methyl alcohol. Briefly describe each method.
6. For what purpose is yeast added in the production of ethyl alcohol from sugar?
7. Write an equation, using structural formulas, to show how diethyl ether is made from ethyl alcohol; how formaldehyde is made from methyl alcohol; and how acetone is made from secondary propyl alcohol.
8. Enumerate some of the important uses of methyl alcohol, ethyl alcohol, ether, formaldehyde, and acetone.
9. What changes occur in the production of vinegar from cider.
10. To what group of substances does the term *fatty acids* refer?
11. How does the reaction of an alcohol with an acid differ from the reaction of a base with the same acid?
12. Write an equation to show the hydrolysis of an ester.
13. Write an equation for each of the following reactions: Sodium butyrate and dilute sulfuric acid; palmitin and sodium hydroxide; glycerine and nitric acid.
14. What is the difference in composition of the liquid and the solid fats?

15. Describe the general nature of the chemical changes occurring in the following: Saponification; hydrogenation of fats; calcium acetate is heated; a soap is treated with HCl.
16. Explain the cleansing action of soaps.
17. Write formulas for nitrobenzene; phenol; orthonitrobenzoic acid; aniline; naphthalene.
18. By means of structural formulas show the relationships of ethyl alcohol, acetaldehyde, acetic acid, and ethyl acetate to one another and to ethane.
19. An alcohol was found to contain 60 per cent of carbon and 26.67 per cent of oxygen. Upon oxidation it produced a ketone. What is its structural formula?
20. What volume of absolute ethyl alcohol can be produced by the complete fermentation of 1 kilogram of glucose followed by distillation and operations necessary to remove all water?
21. What weight of diethyl ether can be produced from 100 liters of absolute ethyl alcohol?
22. What is the percentage of carbon in palmitic acid?
23. A cake of soap weighs 200 g. and contains 10 per cent of water and 90 per cent of sodium palmitate. What weight of sodium hydroxide was required to make it?
24. A sample of vinegar weighed 100 g., and 60 ml. of 1 N sodium hydroxide were required to neutralize the acetic acid in it. What percentage of acetic acid did the vinegar contain?
25. Of what hydrocarbon can glycerine be considered a derivative? What name for glycerine can you suggest that shows the relation to this hydrocarbon? (For example, CH_3Cl might be called chloromethane.)
26. Give the structural formulas of the following derivatives of propane: Alcohol, aldehyde, ketone, ether, acid, ester, amine.
27. How can acetaldehyde be converted into acetic acid?
28. What substances are produced when:
    (*a*) milk sours.
    (*b*) olein is hydrogenated.
    (*c*) cider is changed to vinegar.
    (*d*) propionic acid reacts with ethyl alcohol.
    (*e*) Methyl alcohol is mildly oxidized.
29. What reason is there for writing the formula of acetic acid as $HC_2H_3O_2$ rather than $C_2H_4O_2$?

REFERENCES FOR FURTHER READING

Texts of Organic Chemistry: There are many excellent textbooks in this field. The following are a few selections:

Abernethy, J. L., *Principles of Organic Chemistry*, Philadelphia: W. B. Saunders Company, 1949. Caldwell, W. T., *Organic Chemistry*, Boston: Houghton Mifflin Company, 1943. Cheronis, N. D., *Organic Chemistry*, New York: Thomas J. Crowell Company, 1941. Conant, J. B., and M. Tishler, *Chemistry of Organic Compounds*, Rev. Ed.; New York: The Macmillan Company, 1939. Hill, G. A. and Louise Kelley, *Organic Chemistry*, Philadelphia: The Blakiston Company, 1943. Porter, C. W., and T. W. Stewart, *Organic Chemistry*, Boston: Ginn and Company, 1943. Williams, R. J., *An Introduction to Organic Chemistry*, 4th ed.; New York: D. Van Nostrand Company, 1941.

Many chapters in the following books and in other similar books contain a vast store of information presented in an interesting manner on the different subjects of organic chemistry:

Foster, W., *Romance of Chemistry*. Arrhenius, S. A., *Chemistry in Modern Life*. Holmes, H. N., *Out of the Test Tube*, New York: Emerson Books, Incorporated, 1943. Stokley J., *Science Remakes Our World*, New York: Ives Washburn, 1942.

Read, John, *Explosives*, New York: Penguin Books, 1942.

Alcohols: *Ind. and Eng. Chem.*, **12,** 370 (1920); **32,** 1588 (1940).

Bakelite: J. Chem. Ed., **6,** 607 (1929); *Ind. and Eng. Chem.*, **1,** 149 (1909); **8,** 177 (1916).

Explosives: *J. Chem. Ed.*, **5,** 1213 (1928); *Ind. and Eng. Chem.*, **18,** 905 (1926).

Fats, hydrogenation: *Chem. and Eng. News*, **21,** 1238 (1943); *Ind. and Eng. Chem.*, **32,** 1193 (1940).

Glycerine: *J. Chem. Ed.*, **26,** 327 (1949).

Soap: *J. Chem. Ed.*, **2,** 1035, 1130 (1925); **19,** 172 (1942); **27,** 10 (1950), *Ind. and Eng. Chem.*, **21,** 60 (1929).

Synthetic Methyl Alcohol: *Ind. and Eng. Chem.*, **20,** 285 (1928); *J. Chem. Ed.*, **2,** 429 (1925); **3,** 385 (1926); **21,** 15 (1944).

34

CARBOHYDRATES AND PROTEINS

1. Carbohydrates

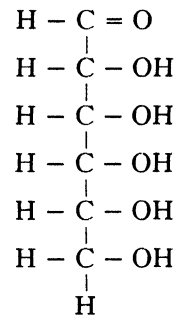
The carbohydrates are compounds of carbon, hydrogen, and oxygen in which the hydrogen and oxygen are usually present in the same proportion as they occur in water, i.e., two atoms of hydrogen for every atom of oxygen. This does not mean that these two elements exist as water molecules in the molecule of the carbohydrate. The oxygen is often present as a part of a hydroxyl, an aldehyde, or a ketone group, and the hydrogen is combined directly with carbon (as in a hydrocarbon) or is a part of a hydroxyl radical. The most important carbohydrates are sugars, starch, cellulose and substances closely related to them.

2. Sugars

Sugar is the name applied to a certain group of carbohydrates which are best known because of their sweet taste. They may be classified as *monosaccharides*, which have the empirical formula $C_6H_{12}O_6$, and *disaccharides* which have the formula $C_{12}H_{22}O_{11}$. Each group consists of several isomers. The most important monosaccharides are *glucose* and *fructose*. *Sucrose*, *maltose*, and *lactose* are the most important disaccharides.

3. Glucose

This sugar is also called *dextrose* or *grape sugar*. It has the following structural formula:



Glucose, therefore, possesses the structural characteristics of a pentahydric alcohol (five OH groups) and also those of an aldehyde.

Glucose occurs in the juices of many fruits. It can be produced, also, from the disaccharides and from starch. Thus, the hydrolysis of ordinary cane sugar (sucrose) yields glucose and fructose:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{fructose}}{C_6H_{12}O_6} + \underset{\text{glucose}}{C_6H_{12}O_6}.$$

This reaction is catalyzed by acids and, in the process of digestion, by certain enzymes. Maltose gives upon hydrolysis two molecules of glucose; lactose hydrolyzes to form glucose and galactose, which is an isomer of glucose.

When corn starch is boiled with water containing hydrochloric acid, a product called "corn

sugar" is obtained. The acid acts as a catalyst in the hydrolysis of the starch:

$$(C_6H_{10}O_5)_x + x\ H_2O \longrightarrow x\ \underset{\text{glucose}}{C_6H_{12}O_6}.$$

The "corn sugar" is obtained by neutralizing the acid with sodium carbonate and evaporating the solution. Corn syrup is used for sweetening in baking pastries, in making candies, as a table syrup, and as a syrup for the sweetening of various soda-fountain products. It is also fermented to produce ethyl alcohol.

4. Sugar in the Body

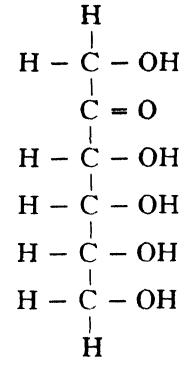
Starch and the disaccharide sugars, such as cane sugar, are converted into glucose, or some of its isomers, during digestion. Glucose passes without further change through the walls of the intestines and into the blood, by which it is carried to the various parts of the body. The blood, normally, contains about 0.1 per cent of this sugar. Since it is available immediately as nourishment without undergoing any of the digestive changes that other foods must pass through in the stomach or intestinal tract, a solution of glucose sometimes is injected directly into the blood of patients seriously in need of immediate nourishment.

In cases of the disease known as *diabetes mellitus*, or simply diabetes, the body becomes unable to assimilate glucose, and this sugar must then be eliminated from the blood through the kidneys.

The detection of glucose is based upon the reduction of copper in *Fehling's solution*, which is made by dissolving cupric sulfate in one solution and sodium hydroxide and potassium sodium tartrate (Rochelle salts) in another. The two solutions are mixed just before the test is made. When a few drops of a solution containing glucose is added to this mixture, and the mixture is heated, red or yellowish red cuprous oxide is precipitated. Glucose is called, therefore, a reducing sugar.

5. Fructose

This sugar is also called *levulose* and *fruit sugar*. It is a white solid and is several times sweeter than cane sugar. It occurs with glucose in honey and in many fruits. The structural formula of fructose is given below:



This sugar contains the ketone group.

Fructose can be produced by the hydrolysis of *inulin* $(C_6H_{10}O_5)_x$, which is a substance closely related to ordinary starch. Inulin is present in certain tubers, such as dahlia bulbs, and in the Jerusalem artichoke.

6. Sucrose ($C_{12}H_{22}O_{11}$)

Sucrose is the most familiar sugar. Cane, sorghum, sugar beets, the sugar maple, pineapples, and strawberries contain sucrose. Cane and sugar beets furnish most of the world's supply. The former contains about 15 per cent and the latter about 18 per cent of sucrose. Contrary to a somewhat general opinion, cane and beet sugars are identical, if they are carefully purified. Sucrose is likewise the sugar which is present in maple syrup and maple sugar; the characteristic flavor of these products is caused by other substances.

Sucrose melts at about 185°. If the liquid is heated to about 215°–220°, partial decomposition occurs, and the sugar turns brown. The product is *caramel*, which is used in making candies and as a coloring material for many foods and beverages.

Sucrose hydrolyzes in the presence of a dilute aqueous solution of an acid:

Sucrose + Water ⟶ Glucose + Fructose.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

The mixture of glucose and fructose produced by hydrolysis is called *invert sugar*. The properties of invert sugar are considerably different from those of sucrose. It does not crystallize and, therefore, is preferable to sucrose in baking pastries and in making candies, concentrated syrups, and other food products in which crystallization is undesirable. It is also used as a moistening agent for tobacco and other products to prevent them from drying out upon standing. Honey is largely invert sugar. The bee gathers sucrose from flowers but this sugar is inverted, before it is deposited in the comb, by the action of formic acid in the bee's body or by the action of enzymes. Invert sugar is also present in the molasses produced in the refining of cane sugar. Invert sugar is not as sweet as sucrose.

When sucrose is dissolved in water and yeast is added, an enzyme produced by the yeast cells, called *invertase*, first causes the sucrose to be converted into glucose and fructose. A second enzyme called *zymase* then acts upon the simpler sugars to form ethyl alcohol and carbon dioxide (page 302). Enzymes in the body convert sucrose into glucose and fructose during digestion.

7. Maltose ($C_{12}H_{22}O_{11}$)

Maltose is produced by the action of an enzyme called *diastase* upon starch. When barley and other grains germinate and start to grow, the starch that they contain is converted into maltose by the action of this enzyme. If the germinated grain is heated and dried, a product containing diastase and known as *malt* is produced. Malt causes starch to be hydrolyzed, thus producing a mixture of maltose and *dextrin*, which is a close relative of starch.

$$\underset{\text{(Starch)}}{(C_6H_{10}O_5)_x} + H_2O \xrightarrow{\text{(diastase)}} \underset{\text{(Maltose)}}{C_{12}H_{22}O_{11}} + \text{dextrin}.$$

The product, called *dextrimaltose*, is used as a food for infants, in candies, and in making malted milk drinks. If yeast is added to the solution containing maltose, enzymes convert the maltose into glucose and the glucose into ethyl alcohol. This is the method of producing *malt liquors*, such as beer.

Maltose is converted into glucose by the action of the enzyme *amylopsin* during digestion. The *ptyalin* in saliva starts the conversion of starch into maltose, and the production of glucose is later completed in the intestines. Maltose is a very nutritious food, since one molecule produces two molecules of glucose upon hydrolysis.

8. Lactose ($C_{12}H_{22}O_{11}$)

The only source of natural lactose is milk. Cow's milk contains about 5 per cent, and human milk about 7.5 per cent, of this sugar. It is commonly called milk sugar. It is not as sweet as sucrose and it is not as soluble in water. Its slight solubility is responsible for the granular texture of some ice creams, because the sugar may crystallize at the low temperature at which the ice cream is prepared. The addition of gelatin furnishes a protective colloid (page 229) and prevents this condition.

Milk sours when the lactose in it is converted into lactic acid by the action of certain bacteria which are found everywhere in the air.

$$\underset{\text{(Lactose)}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow 4\ \underset{\text{(Lactic acid)}}{CH_3CHOHCOOH}.$$

When milk is pasteurized it is heated to a temperature of about 65° for forty to sixty minutes to kill the bacteria in it. To preserve pasteurized milk, it must, of course, be kept out of contact with air. The object of pasteurization, however, is not to keep milk from souring but to kill typhoid bacilli and other bacteria of a harmful character that may have been present originally in the milk.

The hydrolysis of lactose yields equal

numbers of molecules of glucose and galactose, an isomer of glucose. This change occurs under the influence of enzymes during digestion.

9. Starch and Dextrin

We usually represent the composition of starch by the formula $(C_6H_{10}O_5)_x$, which shows only the proportions of the three elements. The exact molecular weight is unknown, but it must be very large. It is known that the starch molecule contains hydroxyl groups and, therefore, possesses some of the properties of the alcohols; it reacts, for example, with nitric acid, as glycerol does, to form a nitrate much like the nitrate of glycerine.

The chief source of starch in the United States is corn; in Europe it is the potato. Some starch, however, is present in all grains, in tubers, and in fruits. Unripened fruits contain a large percentage of starch, which is partially converted into sugar as the fruit ripens.

The size, shape, and other characteristics of the granules in which starch occurs differ for different sources. Thus, potato starch can be distinguished from the starch of rice or corn by a microscopic examination of the granules. Cooking causes the starch granules to burst, and the starch of cooked foods is more directly attacked, therefore, by the digestive fluids than uncooked starch.

When dry starch is heated, it undergoes a partial decomposition, and *dextrin* is formed. This change occurs to some extent on the surface of bread which is toasted. Dextrin has the same simple empirical formula as starch $(C_6H_{10}O_5)_x$; the difference is in the value of x, which is smaller for dextrin than it is for starch. Dextrin has a sweet taste. It is used chiefly as an adhesive on stamps, envelope flaps, etc. Along with maltose and glucose it is also produced when starch is boiled with water containing a little hydrochloric acid (page 429).

A suspension is made by boiling starch in water, and the so-called *soluble* starch is made by the action of a dilute solution of cold hydrochloric acid upon starch. When starch is treated with iodine, a blue color is produced (page 56). This change is used as a simple test for both iodine and starch. The test should be made upon cold materials, as the blue color of the treated starch disappears upon heating.

The use of starch in the laundry is familiar to everyone, and its use in producing corn sugar and corn syrup has already been mentioned (page 429). Starch is also used in large quantities to produce ethyl alcohol by first converting it into glucose and maltose with the subsequent action of yeast, or by the action of malt and yeast (page 431).

10. Glycogen $(C_6H_{10}O_5)x$

Corresponding to the starch of plants, animals produce *glycogen* as a storage food. This substance is very much like ordinary starch. It is found in the liver and in the muscles. Like starch, glycogen is hydrolyzed to form glucose, and it is converted by the enzymes of the body into maltose and glucose.

11. Cellulose $(C_6H_{10}O_5)x$

Cellulose has the same empirical formula as starch. Its structural formula and molecular weight are unknown, but the latter has been estimated as 570,000. The chief sources of industrial cellulose are cotton and wood.

Cellulose can be converted into glucose by the action of hot dilute sulfuric acid:

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6.$$

The reaction must be carried out at high temperatures and under pressure.

It is the opinion at present that the cellulose molecule consists of long chains of units resembling those of glucose and containing OH groups; a unit might be represented, perhaps, as $C_6H_7O_2(OH)_3$. Cel-

lulose, therefore, is in part an alcohol, and its hydroxyl radicals react with nitric acids, and other acids, to form esters (page 422). The moderate action of a mixture of nitric and sulfuric acid produces *cellulose nitrate*, which contains from 10–12 per cent of nitrogen. This is the product known as *pyroxylin* (page 354). More complete nitration yields *gun cotton* (page 354).

Gun cotton is used chiefly in producing explosives, such as smokeless powders, cordite, and gelatin dynamites. Pyroxylin is used in the manufacture of photographic film, lacquers, artificial leather, *celluloid*, *pyralin*, and *collodion*. When used as a base for modern lacquers, cellulose nitrate is dissolved in a volatile solvent such as amyl acetate. Artificial leathers are made by impregnating canvas cloth with solutions of cellulose nitrate. This fabric is used as coverings for automobile seats, for the upholstering of furniture, and in making book bindings, luggage, window shades, screens, etc. Collodion is prepared by dissolving cellulose nitrate in a mixture of alcohol and ether. Celluloid is prepared by making a plastic mass of cellulose nitrate, camphor, and alcohol. The mass is pressed into blocks by means of hydraulic presses which are operated at moderately high temperatures. Upon cooling the material becomes hard and is then cut up into sheets of the desired thickness.

12. Mercerization

Cotton cloth is made stronger and more durable by a process called mercerization. The process consists simply of treating the cloth with a solution of sodium hydroxide. Natural cotton fibers are twisted, flat, and shriveled. During the treatment with sodium hydroxide, the cellulose is partially hydrated and the threads are filled out, becoming straight and round. Mercerized cotton has a smoother, softer texture than cloth made of untreated cotton.

13. Paper

The paper for newsprinting and the cheaper grades for other purposes are made from wood, but cotton rags, straw, and similar materials are also used.

Before it is used in making paper, wood must be chipped and then treated chemically to dissolve *lignin*, which binds together the fibers of cellulose in the natural wood. Young plants and the growing tips of older plants are more tender than older twigs and branches, because the woody part of the plant is at first almost pure cellulose, but later it develops into *lignocellulose*, which in paper making must be reconverted into pure cellulose by chemical treatment. Calcium bisulfite is usually employed for this purpose. The chips are cooked in a solution of this substance, until the lignin is dissolved, and the fibers are thoroughly separated. The pulp is then washed with water and bleached. This material is poured upon one end of a moving screen, made of wire cloth, which acts as a filter and allows the water to drain through it, leaving the cellulose fibers enmeshed in the form of a wet, thick sheet of raw paper. At the other end of the screen, this sheet passes between two large cylinders which remove the water by pressure. The paper is finally dried by passing it between cylinders which are heated by steam on the inside. Many substances, such as clay, rosin, dextrin, glue, aluminum silicate, barium sulfate, alum, and pigments or dyes are added to the pulp in producing paper of special properties. The materials added depend upon the desired color, texture, weight, and degree of opacity. Rosin, for example, makes the paper resistant to ink, and prevents spreading. Starch, glue, dextrin, and similar materials are used as sizing to fill up the spaces between the cellulose fibers and to give a smooth finish.

14. Proteins

In addition to fats and carbohydrates,

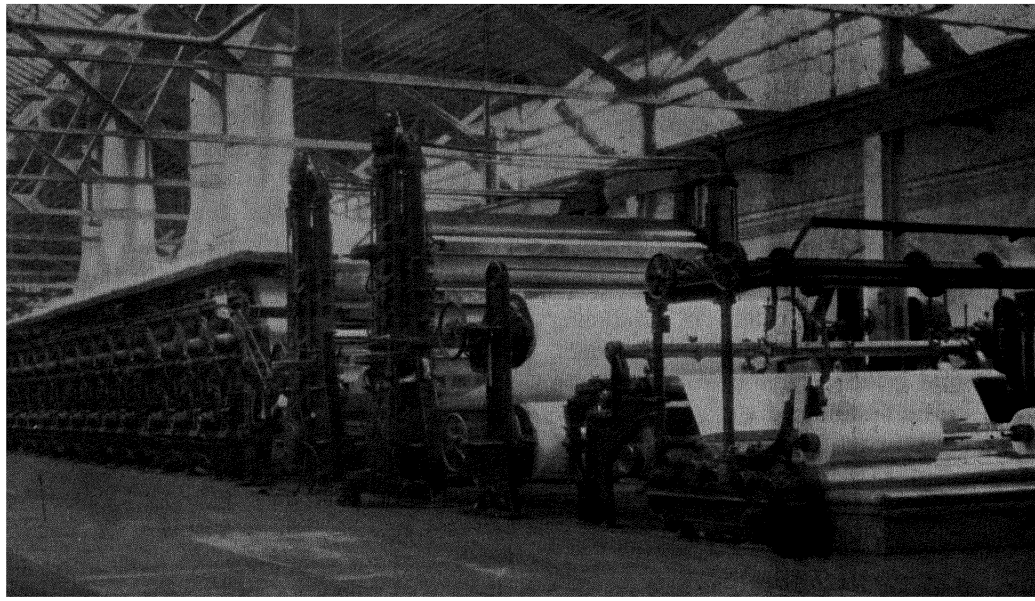


Figure 251. Paper Manufacturing Machine
(Courtesy of S. D. Warren Company, Boston)

the food of man must contain certain complex compounds of nitrogen called proteins. The *casein* of milk, the *hemoglobin* of blood, the *albumen* of eggs, and the *gluten* of flour are familiar examples of protein materials. Silk, wool, feathers, skin, muscles, nerves, hooves, and nails are all proteins in large part. Among our foods that are rich in proteins are milk, cheese, meats of all kinds, eggs, and cereals.

The exact chemical character of proteins has not been determined. It is known, however, that their molecular constitution must be very complex and that their molecular weights are very large, in some instances as great as 15,000,000.

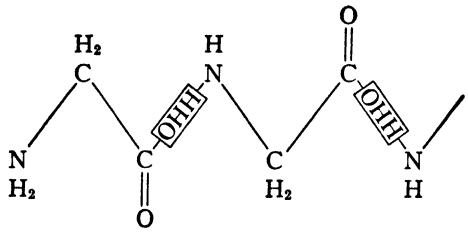
When they are hydrolyzed the proteins yield *amino acids*. During digestion proteins are acted upon by the enzyme *pepsin* and the digestive fluids of the stomach and are changed into *peptones* and *proteoses*. In the small intestine other enzymes help to hydrolyze the peptones and proteoses, converting them into amino acids. One of the enzymes of the intestines is *trypsin*. The amino acids pass into the blood and are carried to all parts of the body to be used in building up the complex proteins found in the animal body or to be oxidized as a source of energy. The oxidation of proteins in worn-out tissues produces *urea*, $CO(NH_2)_2$, uric acid, and other nitrogenous compounds that are eliminated from the body in urine.

The fact that amino acids are produced by the hydrolysis of proteins is responsible for the opinion that proteins are produced in plants and animals by combinations of the acids with one another. The amino acids contain the $-NH_2$ (amino) radical. Thus, one of the simplest amino acids is *glycine*, or *aminoacetic acid*, in which the $-NH_2$ group replaces a hydrogen atom of the methyl radical.

$$CH_2NH_2COOH$$

The amino radical is derived from the molecule of ammonia by replacement of a hydrogen atom: $H-NH_2$. The acid, therefore, possesses the basic properties of ammonia and, also, the acid properties which accompany the presence of the carboxyl group with its ionizable hydrogen atom.

The amino acid is consequently an amphoteric substance. For this reason two amino acids might combine.



This combination might be continued, of course, until it included a very large number of the same or different amino acid molecules. It is thought that this mechanism should result in the formation of substances which are proteins or like proteins in composition and character.

THE FOOD OF MAN

Man depends directly or indirectly upon plants for his food. Some of the materials that we consider essential parts of our food supply — butter, milk, meat, certain fats — are obtained from animals, but they are produced by animals that use plants or materials made by plants as food. For starch, sugar, and certain oils, we depend directly and completely upon plants, and plants furnish us, also, with a considerable portion of our protein requirements.

15. Photosynthesis by Plants

The synthesis of starch, sugar, and cellulose by plants is profoundly influenced by light and, therefore, involves *photochemical reactions*. The energy of sunlight plays an important part in these reactions, because the production of carbohydrates, which the plant manufactures from water and carbon dioxide, requires that energy be absorbed and stored in the carbohydrates that are made. We can readily understand that energy must be absorbed as these substances are produced, when we consider the amount of heat that is liberated when the same substances are burned to form water and carbon dioxide once more. The chlorophyl, or green-coloring matter, of the plant also has an important function in this process, probably by acting as a sensitizer, which makes possible the absorption of the energy in the rays of light. The exact character of the reactions which occur is not known. It appears, however, that relatively simple compounds of carbon, hydrogen, and oxygen are first formed and that these then combine, probably by polymerization, to form glucose and fructose.

These monosaccharides may then be converted into sucrose or starch. The sugars are changed into insoluble starch when the food is stored in fruits, seeds, or tubers for the use of the next generation of plants. The growing plant is also able to convert sugar or starch into cellulose from which it builds the extensions of its woody structure as it grows.

16. Food

A diet consisting of pure fats, carbohydrates, and proteins will not maintain health or even life for very long. Certain other substances must be present. Strictly speaking water and oxygen are foods, if by food we mean the substances which the body requires, from external sources, for the maintenance of life. Minerals are also necessary. These include the calcium and phosphorus from which calcium phosphate of the bones must be made, and salt to supply the hydrochloric acid of the gastric juice, and for other purposes. But the addition of all these does not make a satisfactory diet. Small amounts of other substances must also be present, if health is maintained, and if the body's growth and the functioning of its different organs and structures are normal. Among these requirements of the body are several substances known generally as *vitamins*.

17. Vitamins

Because of the small amounts of the vita

mins in foods, they are difficult to extract and to obtain in the pure state. Many of them have, however, been isolated, their composition and molecular structure have been determined, and some of them are now produced by synthetic methods to the extent of many tons each year.

Vitamin A promotes normal growth; increases resistance to infections; aids vision especially at night; and appears to be necessary for the proper functioning of the glands of the body, for a healthy condition of the eyes, skin, teeth, and gums and for a general feeling of strength and vigor. Certain fish-liver oils, e.g., cod-liver oil, or concentrates of such oils, are supplied for use as a supplement to the diet of children or others who show that they are suffering from a deficiency of this vitamin. *Carotene*, sometimes referred to as plant vitamin A, is found in many green vegetables and during digestion is converted into vitamin A. The vitamin itself is present in milk and butter and in the yolk of eggs, carrots, tomatoes, and liver. Recently it has been synthesized, and the manufactured product is now widely used.

The *vitamin B* complex consists of several different substances among which are vitamin B_1, or *thiamin;* B_2 or *riboflavin;* B_6 or *pyridoxin; biotin; pantothenic acid; inositol; nicotinic acid* or *niacin;* and *folic acid.* All of these have been shown to be present in vitamin B extracts. Most of them can be produced synthetically. Each compound of the complex serves certain purposes in the body, and the complex as a whole prevents beriberi and other disorders of the nervous system; prevents pellagra; promotes normal growth; and performs important functions in metabolism and other life processes. It is present in many animal tissues and products, such as liver, brain, kidney, milk, and eggs; it also occurs in whole grain cereals, yeast, and many vegetables.

Vitamin C, or *ascorbic acid*, occurs in citrus fruits, tomatoes, apples, carrots, and leafy vegetables. It is produced synthetically in large quantities; it was estimated that the production in 1944 was 8,000,000 lbs. It prevents and cures scurvy and is related to tooth and bone formation and to the prevention of dental caries, gum infections, anemia, pyorrhea, and impairment of the connective tissues of the body.

Vitamin D, ergosterol or *calciferol*, has been extracted and purified. It is the vitamin which is so essential in the normal development of the bones of children, and it prevents the disease known as rickets. It is abundant in oranges, milk, and cod-liver oil. Exposure to ultra violet light converts the substance *ergosterol* into vitamin D. Since ergosterol is present in the skin, the ultra-violet rays of the sun are beneficial in increasing the quantity of this vitamin which is available for the body's use. Certain food products containing ergosterol are sometimes irradiated before use to increase their content of vitamin D. There is a number of forms of this vitamin; these are designated as D_1, D_2, D_3, D_4, etc.

Vitamin E consists of three substances, all called *tocopherols*, which are prepared synthetically and extracted from an oil produced from wheat-germs. A deficiency of this vitamin results in sterility and weakness of the muscles. It is found in vegetable oils, lettuce, beans, wheat, rice, barley, meat, liver, milk, and eggs.

Vitamin K is found in green vegetables, tomatoes, certain vegetable oils, egg yolk, and oat sprouts. The synthetic form of this vitamin is known as *menadione*. It aids in preventing hemorrhage and is used in post-operative treatment and in certain diseases such as jaundice.

18. The Functions of Food

The mineral constituents of food are required for the formation of the solid portions of the body's structure, i.e., bones and teeth. Fats and carbohydrates are oxidized and serve as a source of heat for the maintenance of the body's temperature and also to provide muscular energy. Proteins supply the material required for growth and for the replacement of worn-out tissues. About 20 per cent of the total diet (by weight) should consist of foods rich in proteins.

The *calorific value* of food is of considerable importance, since it is a measure of the energy released when the food is oxidized in the body. The average energy requirement of an individual is between 2,000,000 and 3,000,000 calories per day. A very active person engaged in manual labor requires at least 4,000,000 calories daily.

The composition and calorific value of some of the common food-stuffs are given in Table 21.

TABLE 21. COMPOSITION AND CALORIFIC VALUE OF FOOD MATERIALS *

(Values are given in approximate percent and as approximate number of calories per pound)

Food	Water	Fat	Carbohydrates	Protein	Calories per pound **
Eggs	74	10		13.5	675
Cheese	30	35	0.4	29	2000
Potatoes	75	0.5	20	2.5	450
Beef	60	20		18	1200
Ham	50	20		23	1250
Bread (white)	35	1.5	52	9	1200
Milk	88	4	5	3.5	300
Butter	14	85		1	3500
Peas	75	3	15	7	500
Lettuce	95	0.2	3	1	90
Bananas	75	0.5	20	1.5	450
Fish	70	8		20	800

* Since the composition and the calorific value of any food material varies with the individual sample, the values given above represent only the relative amounts of three classes of food materials to be found in some of the common kinds of foods. They are not the results of any one analysis.
** The unit of heat used in this table is the large calorie (1 Cal = 1000 calories).

REVIEW EXERCISES

1. How do glucose and fructose differ as regards the structure of their molecules?
2. Describe two methods that can be used to produce glucose (in an impure state) from starch.
3. What happens to starch and sugars during the digestive process?
4. What are the sources, or methods of producing, sucrose, maltose, and lactose?
5. What is the chemical nature of each of the following? corn sugar; invert sugar; dextrose; dextrin; and dextrimaltose.
6. What is malt? How does it affect starch?
7. Identify: Pyroxylin; glycogen; mercerized cotton; lignin; pepsin; casein; peptone; amino acid; and invertase.
8. Criticize the following diet: Eggs, fish, cheese, lettuce, and bananas.
9. In what respects is milk a better diet, in itself, than potatoes or beef?
10. What weight of each of the following substances will provide 2500 Calories (1 Cal. = 1000 calories): milk, white bread, butter, lettuce, potatoes?
11. What evidence indicates that starch and cellulose contain hydroxyl groups?
12. Carbohydrates and fats are both composed of carbon, hydrogen, and oxygen. What are some of the differences in their structures or atomic groups?
13. What changes occur during the digestion of the following foods? Cane sugar, glucose, milk.
14. What portion of the glucose molecule is responsible for its reducing action?
15. How could you distinguish between starch and sucrose? starch and cellulose?
16. What is an amino acid? How are amino acids thought to be combined in the building up of protein molecules?
17. How does paper differ in composition from the wood pulp of which much of it is made?

REFERENCES FOR FURTHER READING

Harris, R. S., and K. V. Thimann, *Vitamins and Hormones.* New York: Academic Press, Inc., 1943.

Hensen, Emil, *The Chemistry of Cellulose.* New York: John Wiley and Sons, Inc., 1944.

Ott, Emil, *Cellulose and Cellulose Derivatives.* New York: Interscience Publishers, Inc., 1943.

Williams, Roger J., *What to do with Vitamins.* Norman: University of Oklahoma Press, 1945.

Witham, G. S., Sr., *Modern Pulp and Paper Making.* New York: Reinhold Publishing Corporation, 1942.

Food and Nutrition: McCollum, E. V., E. Keiles, and H. G. Day, *Newer Knowledge of Nutrition.*

5th ed.; New York: The Macmillan Company, 1939. Rose, M. D., *Foundations of Nutrition.* 3d ed.; New York: The Macmillan Company, 1938. Rose, M. D., *Feeding the Family.* 4th ed.; New York: The Macmillan Company, 1940. Sherman, H. C., *The Chemistry of Food and Nutrition.* 5th ed.; New York: The Macmillan Company, 1937.

Paper: *J. Chem. Ed.*, **7,** 1739 (1930); **26,** 154 (1949).

Photosynthesis: *J. Chem. Ed.*, **26,** 628, 631, 639 (1949).

Proteins: *J. Chem. Ed.*, **18,** 274 (1941).

Sugar: *Chem. and Met. Eng.*, **23,** 421 (1920); **24,** 605 (1921); **30,** 857, 902 (1924); **32,** 352 (1925); **47,** 119 (1940); *J. Chem. Ed.*, **3,** 390 (1926); **7,** 2326 (1930); **10,** 323, 421, 453 (1933).

Vitamins: *J. Chem. Ed.*, **3,** 1240, 1416 (1926); **4,** 66, 214, 323, 474 (1927); **8,** 652, 875 (1931); **10,** 13, 97 (1933); **11,** 13, 69, 203 (1934); **12,** 357, 429 (1935); **20,** 40, 401 (1943); **21,** 48 (1944); *Ind. and Eng. Chem.*, **29,** 980 (1937); *News Edition*, **18,** 670 (1940); *Chemical Reviews*, **28,** 477 (1941).

35

OTHER NATURAL AND SYNTHETIC ORGANIC PROBLEMS

1. Introduction

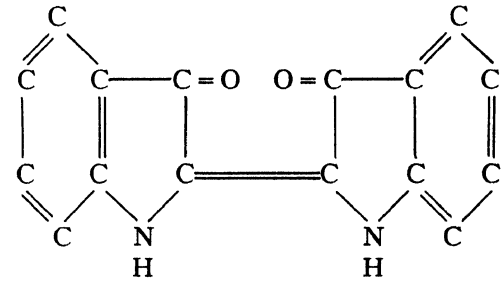
In the preceding chapters that dealt with organic compounds we have discussed from time to time several synthetic products. In this chapter we wish to describe briefly additional products of this kind. Many of these are the results of fairly recent research and industrial developments. A few naturally occurring substances of importance, especially in medicine, are included in our discussion.

2. Dyes

Until about the middle of the nineteenth century, dyes were obtained from natural sources. Indigo was produced from the indigo plant; alizarin, a red dye, was obtained from the roots of madder; and other coloring materials were obtained from plants and a few, including cochineal and Tyrian purple, came from animal sources. The first synthetic dye was made, quite by accident, in 1856 by William Henry Perkin. Perkin had set out to synthesize the drug *quinine*. In the course of his experiments he treated aniline with an oxidizing agent, chromic acid. The result was not the substance he had hoped to produce but a violet-colored compound, which Perkin recognized as a possible dyestuff and to which he gave the name *mauve*.

Most dyes are now produced from substances obtained from coal tar, such as benzene or phenol, or from other substances, such as nitrobenzene and aniline, which are derived from coal tar products. More than two thousand coal tar dyes have been synthesized.

One of the greatest triumphs was the synthesis of *indigo*. The structural formula (with hydrogen atoms on the benzene rings omitted) was found to be:



When the structure of the indigo molecule was known, the next step was to determine the substances that might be used to make it and the methods that could be used to cause them to react in such a way that the structure of indigo would be produced. The successful synthesis of indigo on a large scale required almost twenty years of investigation and cost several million dollars. At last, the process was successfully completed, and it soon replaced the production of indigo from plant sources. By the time of the outbreak of the first World War, German dye manufacturers had acquired almost complete monopoly of the

indigo market. At the outbreak of the second World War, the dye industry of the United States was supplying almost every need for all dyes in this country.

In addition to their use in coloring fabrics, certain dyes are used to color food products, as indicators, as stains for biological materials that are to be examined microscopically, and as antiseptics.

3. Classification of Dyes

Dyes can be classified according to the methods used in applying them to fabrics. The classification that we give below is a very general one. The methods of application differ considerably, depending upon the chemical nature of both the dye and the material to be dyed.

Direct Dyes. A direct dye is one that is attracted and held either in chemical combination or mechanically by the material to be dyed. Most of these dyes are acids or bases. The cloth to be dyed is immersed in a solution containing a *salt* of the dye. If the dye is an acid, this solution also contains acetic or dilute sulfuric acid to release the dye from its salt. If the dye is basic in nature, the solution contains a salt of the dye and a base. This method of dyeing is widely used in the coloring of silk and wool. Animal fibers appear to undergo hydrolysis in water, forming acid and basic substances which then may react with the dye.

Vat Dyes. These dyes are not soluble in water. To apply them to cloth, they must first be converted into substances that are soluble. This change is, ordinarily, a reaction in which the dye is reduced to a "leuco" compound. The cloth is impregnated with a solution of this compound, usually in the presence of an alkali. The "leuco" compound is then oxidized to form the dye which, since it is not soluble, is precipitated on and in the fibers of the cloth. Indigo is a vat dye.

Developed Dyes. Some dyes are made, or developed, directly on the cloth. The cloth is first impregnated with one reactant and then treated with another substance which will react with the first to make the dye. The dye produced must, of course, be insoluble if a "fast" color is to be obtained.

Mordant Dyes. To produce "fast" colors, many dyes must be used with a *mordant.* This is especially true when these dyes are used to color cotton or linen. The use of a mordant is illustrated by the following example in which aluminum hydroxide serves to hold the dyestuff in permanent combination upon cotton. The cloth is soaked in a solution of aluminum acetate, which readily hydrolyzes to form insoluble aluminum hydroxide. This reaction is favored by exposing the cloth, which has been soaked in a solution of the salt, to steam. The aluminum hydroxide is formed throughout the cloth and is held by the cotton threads and fibers. The cloth is now dipped into a bath containing the dye, which is adsorbed or chemically precipitated by the aluminum hydroxide. The attachment of the dye and the hydroxide is permanent and consequently the color of the cloth is made "fast." The common mordants include the salts of aluminum and iron, tartar emetic, tannic acid, and potassium dichromate.

4. Plastics

The term *plastic* is applied to any material which, under pressure, can be given a definite form or shape that is retained after the pressure is removed. Clay, beeswax, and pitch are natural plastics. So, too, are the resins found in the gums that exude from breaks in the bark of certain trees. Because they resemble plant resins, synthetic plastic materials are sometimes called *synthetic resins.*

Among the first synthetic plastics produced were certain materials containing cellulose nitrate and acetate. *Celluloid*

(page 433) is a plastic of this kind. These plastics are softened by heat, and when they are in this state, they can be molded into any desired shape. For this reason they are classified as *thermoplastics*. Others when heated and then molded while still soft, set to a hard mass that does not melt or soften when heated again; these are called *thermosetting* plastics.

5. Classes of Plastics

There are many types of synthetic plastics of which a few of the more important will be described.

(1) The *Vinyl plastics* are produced by the polymerization of ethylene, of vinyl acetate, $CH_3COOCH = CH_2$, or other derivatives of ethylene and which contain the $CH_2 = CH -$ group.

(2) The polymerization of methyl methacrylate, the methyl ester of methyl acrylic acid, $CH_2 = C(CH_3)COOCH_3$, produces a colorless plastic that can be molded, sawed, and tooled. It is used to make lenses and prisms for optical instruments. There are several resins, or plastics, in this group, including the one known by the trade name of *Lucite*. Light introduced at one end of a tube made of Lucite is transmitted through the rod and comes out at the other end, although the rod may be bent one or more times at right angles.

(3) The *Phthalic acid resins* are made from phthalic acid, $(HOOC)_2C_6H_4$, which is a derivative of benzene, and glycerine. These are also called the *Glyptal* resins.

Rubber, and all the so-called synthetic rubbers, such as Neoprene, Buna, and Thiokol, may be classified as plastics. So, too, are certain substances derived from rubber.

More and more uses for plastics are being found It is said that the modern airplane of the

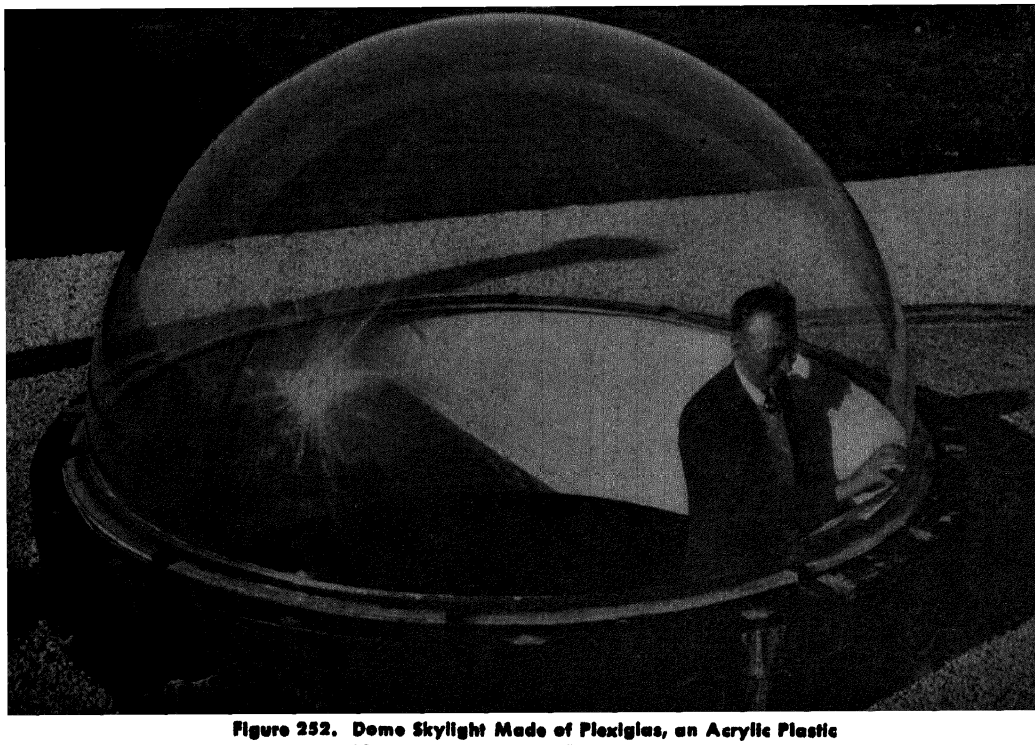


Figure 252. Dome Skylight Made of Plexiglas, an Acrylic Plastic
(Courtesy of Rohm and Haas Company)

bomber type contains 120 or more plastic parts, including the nose of the plane. Whole airplane bodies, car fenders, furniture, door knobs, drinking glasses, spectacle lenses, cigarette cases, radio cabinets, telephone receivers, buttons, cooking utensils and moving picture films are but a few of the countless articles that have been or are made from different plastics.

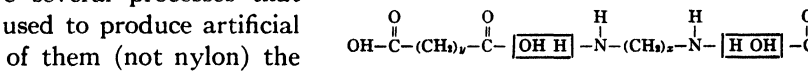
6. Artificial Silk

Probably the most widely known kind of artificial silk is *Rayon*. It is similar to silk in texture and certain other physical properties, but unlike silk in composition. Silk is an animal fiber consisting of nitrogenous substances; rayon is a form of cellulose. There are several processes that have been or are used to produce artificial silk, but in most of them (not nylon) the essential principle involves the formation of a colloidal dispersion of cellulose, or some compound made from cellulose, in a liquid. The liquid mixture is then forced through small openings in a platinum disc or nozzle into a bath containing a reagent which causes the cellulose to form again in its solid state. Since the solution enters the precipitating bath in a small stream, the cellulose forms a very small thread.

Rayon is made by the *viscose* process. Cellulose from wood pulp and from cotton is first cleaned and bleached; and then it is treated with a concentrated solution of sodium hydroxide. It is next treated with carbon disulfide, which converts it into a gelatin-like material, which forms a colloidal dispersion when mixed with a solution of dilute sodium hydroxide. This mixture is used to make the threads, which are precipitated as the liquid is forced through the small openings of a nozzle into a bath of dilute sulfuric acid and sodium bisulfate. The threads produced from one nozzle are gathered together and twisted into a larger thread, which is used in producing rayon fabrics. *Cellophane* is made in the same manner, but the cellulose is precipitated in the form of thin sheets instead of threads.

7. Nylon

Of the new fabrics none has created more interest than Nylon, a product of the Du Pont laboratories. Chemically, it is classified as a *polyamide* (page 426). Diamines, consisting of two amine, NH_2, groups connected by a chain of CH_2 groups — $(NH_2) - (CH_2)_x - NH_2$ — react with dibasic organic acids also of the straight chain type — $HOOC - (CH_2)_y - COOH$ — to form compounds consisting of long molecules made up of alternate diamine and acid units. Molecules of water are removed by the reaction of NH_2 and COOH groups of different molecules, thus providing the bonds that link the nitrogen atom of one molecule to the carbon of a carboxyl group of the other molecule:



The product is similar to a protein in composition (see page 433). It is made into thread by forcing the Nylon, after it has been melted, through small openings. When the threads have solidified, they are made into yarn, which is woven into cloth that resembles silk both in composition and in properties. It is said to be more durable and more elastic than silk, wool, or cotton. Its first use was in making hosiery, but it is now used to make brush bristles, strings for tennis rackets, insulation for electrical wiring, and many other articles formerly made of natural silk, and other fabrics.

SUBSTANCES RELATED TO MEDICINE

8. Alkaloids

Alkaloids are basic nitrogenous substances obtained from plants. Most of them are powerful drugs and many are very deadly poisons. The salts of alkaloids with sulfuric or hydrochloric acid are used in medicine instead of the pure alkaloids. Some of the most important alkaloids are listed in Table 22. Other alkaloids include caffeine from coffee and muscarine from toadstools.

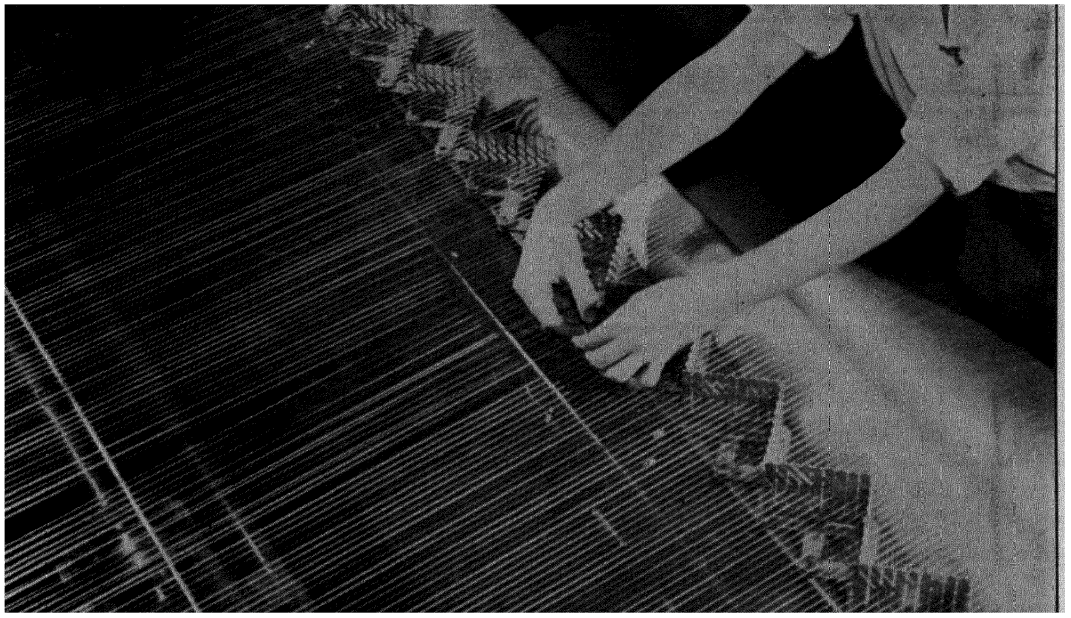


Figure 253. Cordura Rayon Yarn

Cordura, a high tenacity rayon yarn, is tied into the warp beamer during weaving operations.



Figure 254. Hanks of Nylon

This form of Nylon is used to make the bristles of tooth and hair brushes.
(Courtesy of Du Pont Company)

TABLE 22. SOME IMPORTANT ALKALOIDS

Alkaloid	Source	Formula	Use
Quinine	Bark of Chincona tree	$C_{20}H_{24}N_2O_2$	Treatment of malaria Hair tonics
Strychnine	Nux vomica	$C_{21}H_{22}N_2O_2$	Tonic, stimulant
Morphine	Poppy	$C_{17}H_{19}NO_3$	Produces sleep
Atropine	Belladonna	$C_{17}H_{23}NO_3$	Dilates pupil of eye
Nicotine	Tobacco	$C_{10}H_{14}N_2$	Very poisonous, insecticide
Cocaine	Cocoa leaves	$C_{17}H_{21}NO_4$	Local anesthetic
Novocaine	Synthetic	$C_{13}H_{20}N_2O_2$	Local anesthetic

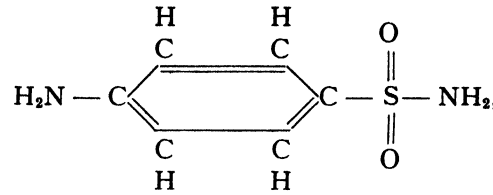
During the recent war this country could not obtain quinine, which was badly needed for the treatment of malarial cases, from the Dutch Indies, the usual source of supply. Research developed an effective substitute called *atabrine*.

9. Hormones

Hormones are produced by the ductless glands of the body, and pass directly into the blood. Minute traces of them affect biological processes profoundly. The exact number of these substances produced in the body is unknown but some twelve or more have been identified. The hormone *adrenalin*, or *epinephrine*, is produced synthetically. It is also produced in the body by the adrenal glands. It acts as a stimulant of the heart and lungs. *Insulin*, a hormone produced in the pancreas, aids in the metabolism of sugar. The male sex hormone, *androsterone* and the female hormones, *estrone* and *estriol*, are also known and some have been synthesized. *Thyroxin* is produced in the body by the thyroid gland. A lack of this substance causes goiter and the disease known as cretinism.

10. Sulfa Drugs

The medical profession has long been deeply interested in the discovery of drugs that can be used effectively and safely to combat the bacteria that produce diseases such as tuberculosis, typhoid, pneumonia, cholera, and others. About 1935, the organic compound, *sulfanilamide*,



was found to be an effective bactericidal agent especially when used against the streptococci responsible for the condition generally described as "blood poisoning." Since that time, many other closely related substances have been produced, and their effectiveness as bactericidal agents has been tested. Some of them have proved more effective than sulfanilamide itself. They are called, in general, the *sulfonamides* or more commonly, the *sulfa drugs*. Some of the most widely used members of this group are *sulfapyridine*, which has been effective in the treatment of pneumonia, *sulfathiazole*, and *sulfadiazine*. The production of these drugs in 1950 is estimated at about 5,000,000 pounds.

11. Antibiotics

Recently a group of drugs even more effective in overcoming the infections produced by certain bacteria have been produced from products of the metabolism of certain molds, fungi, and bacteria of the soil. The first of these to be discovered was *penicillin*, which is a product of a mold. This drug is effective in the treatment of

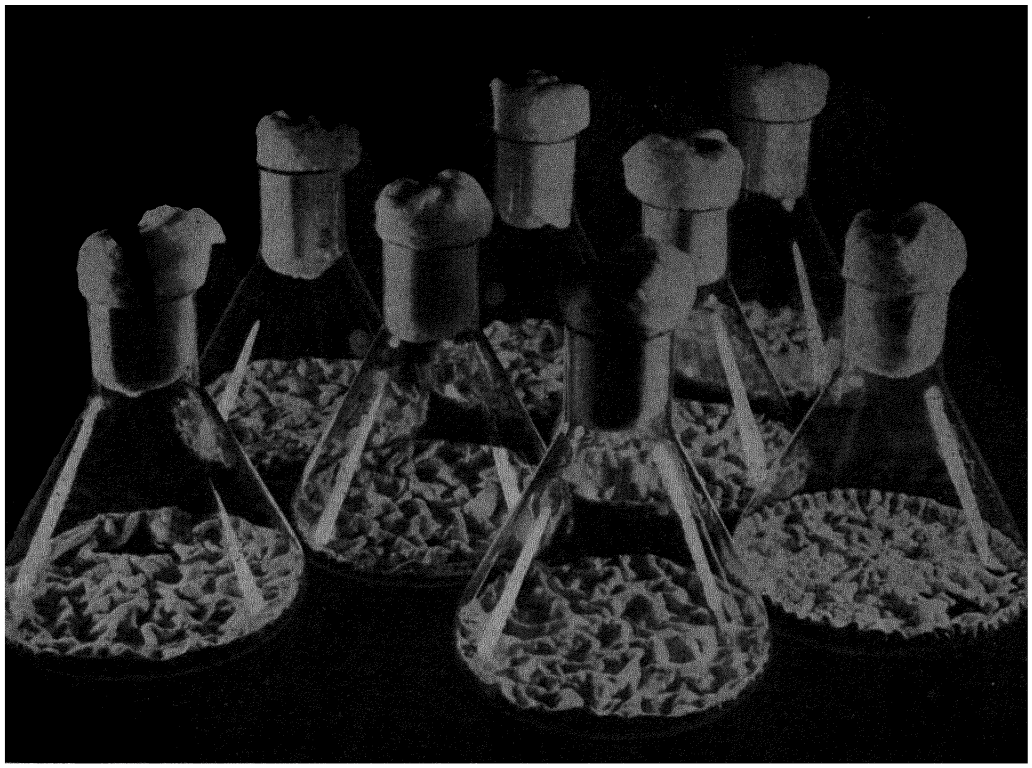
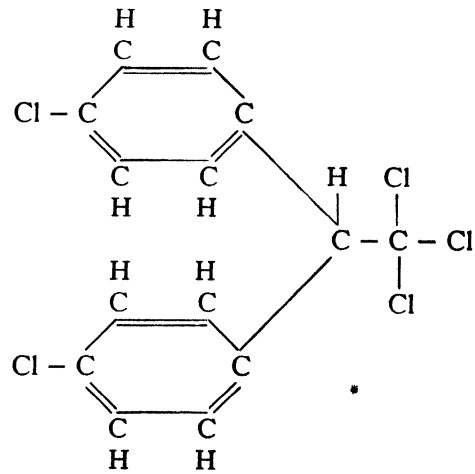


Figure 255. Flasks Containing the Molds from Which Penicillin is Produced
(Courtesy of Corning Glass Works)

pneumonia, gonorrhea, meningitis, and many types of bacterial infections. Other antibiotics include *aureomycin*, which is effective in treating scarlet fever, whooping cough, pneumonia of the so-called virus type, undulant fever, and various infections caused by both streptococci and staphlococci; *streptomycin*, obtained from a fungus-like organism, is used in the treatment of tularemia, typhoid, meningitis, and tuberculosis; and *tyrothricin* which is used in treating ulcers and infections of the ear, nose, and throat.

12. A New Insecticide

A new insecticide, commonly known as DDT, has recently received much publicity. Its chemical name is *dichlorodiphenyltrichloroethane*, and its formula is



DDT has been found very effective in killing many insects that are instrumental in causing or carrying certain diseases. It kills, for example, the malarial mosquito, the louse that spreads typhus, and the

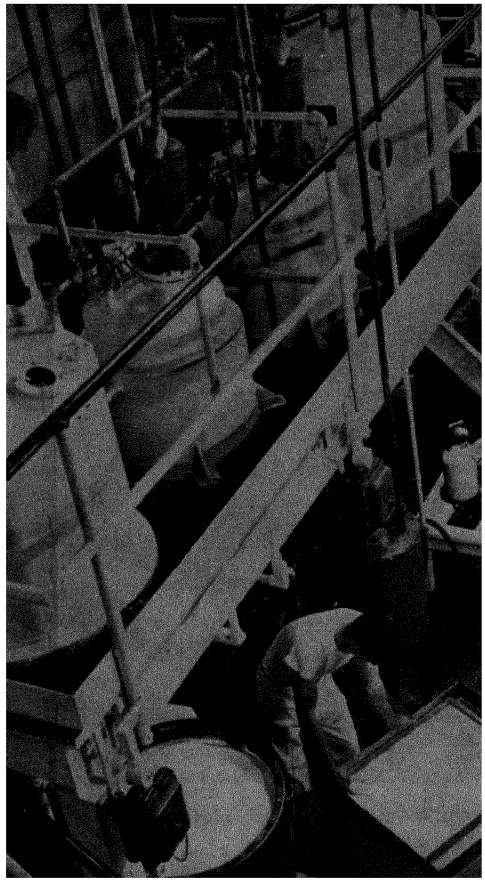


Figure 256. Production of Penicillin

Drying trays at the bottom of the picture contain the penicillin salt.

(Courtesy of Merck and Company)

common house fly. It is also used to kill moths, and many other insects. The annual production of this insecticide is about 38,213,000 pounds.

REVIEW EXERCISES

1. Classify dyes according to the methods used in applying them to cloth.
2. What is a mordant? How is it used in dyeing?
3. Many synthetic dyestuffs are sometimes called coal tar dyes. Why is this name appropriate for them?
4. What property do all those substances called plastics possess?
5. Describe the process by which Rayon is made. What is its chemical nature?
6. What kinds of substances are used to produce Nylon? Why can it be said that Nylon more closely resembles natural silk in composition than Rayon?
7. Distinguish between thermoplastics and thermosetting plastics.
8. Enumerate some of the important groups of synthetic plastics and name the substances or kinds of substances used to make them.
9. What are some of the plastics that have been discussed in previous chapters?
10. What is the source of the antibiotics? Name two.
11. Identify: cellulose triacetate, cellophane, atabrine, nicotine, quinine, sulfanilamide, penicillin, insulin, and indigo.

REFERENCES FOR FURTHER READING

Alkaloids: *Chem. Ed.*, **2,** 886 (1925).

Dyes: *J. Chem. Ed.*, **3,** 973, 1128, 1259 (1926); **6,** 544 (1929); **24,** 2, 380 (1947); **26,** 583 (1949).

Hormones. *J. Chem. Ed.*, **3,** 41, 135 (1926); **8,** 661, 2175 (1931); **10,** 174, 338 (1933); **13,** 3 (1936).

Medicines: *J. Chem. Ed.*, **2,** 191, 431, 677 (1925); *Ind. and Eng. Chem.*, **31,** 126 (1939); *News Ed.*, **18,** 385 (1940); Stieglitz, *Chemistry in Medicine*, The Chemical Foundation.

Nylon: *Ind. and Eng. Chem.*, **34,** 53 (1942); *Chem. and Met. Eng.*, **47,** 628, 650 (1940); **48,** 98 (1941); *J. Chem. Ed.*, **21,** 88 (1944).

Perfumes: *Ind. and Eng. Chem.*, **14,** 359 (1922).

Plastics: *J. Chem. Ed.*, **19,** 9 (1942); **21,** 15, 144 (1944); **23,** 306 (1946); *Ind. and Eng. Chem.*, **28,** 275 (1936); **31,** 145 (1939); **32,** 965 (1941); **34,** 53, 68, 1387 (1942); *Chem. and Eng. News*, **22,** 890 (1944); *Chem. and Met. Eng.*, **44,** 427 (1939); **47,** 240 (1940).

Rayon: *J. Chem. Ed.*, **2,** 864 (1925); **3,** 408 (1926); **4,** 1260 (1927); **7,** 2354, 2543 (1930); **9,** 1143 (1932); *Chem. and Met. Eng.*, **46,** 25, (1939).

Sulfa Drugs: *Chem. and Eng. News*, **21,** 1159 (1943); *J. Chem. Ed.*, **19,** 167 (1942).

Textiles from Test Tubes: *J. Chem. Ed.*, **6,** 141, 357, 541, 753 (1929).

36

ELECTROCHEMISTRY

1. Introduction

In discussing the metals in the closing chapters of this book we shall be concerned with electrical energy, because it is used to produce them from their natural sources and to refine and to purify them; it is used to plate one metal upon another; and it is produced in electrochemical cells and batteries in which metals and their compounds react in such a way that a portion of the chemical energy that they contain is converted into electrical energy.

2. Electrical Units

The unit of resistance is the *ohm*, which is defined as the resistance (at 0°) of a column of mercury 106.300 cm. long and weighing 14.4521 g. In order that the electrons may flow through the conductor the *difference of potential* between the terminals of the conductor must be great enough to overcome the resistance. This difference arises from a difference in the relative numbers of electrons at the two terminals. Depending upon the number of electrons, there is a certain electron pressure or "escaping tendency" at each terminal, or electrode, and the difference in these pressures is called a difference of electrode potentials; when the terminals are connected this difference gives rise to a force called the *electromotive force* (e.m.f.), which causes electrons to flow from the terminal of greater electron pressure through the conductor to the other terminal. The volt is the unit of e.m.f. It is defined as the e.m.f. required to cause a current of one ampere to pass through a conductor whose resistance is one ohm. The *ampere* is the unit of the current's strength. The strength of a current which will deposit 0.0011180 g., or 0.00001 of a gram atomic weight, of silver per second in the electrolysis of a solution containing silver ions is one ampere. The *quantity of electricity* that flows through a conductor is equal to the product of the current strength by the time in seconds. The unit of quantity is the *coulomb*.

$$\text{Coulombs} = \text{Amperes} \times \text{Seconds}.$$

The current strength, e.m.f., and resistance are related as follows:

$$\text{C (in amperes)} = \frac{\text{E (in volts)}}{\text{R (in ohms)}}$$

The *quantity of energy* associated with the passage of electricity through a conductor depends upon the quantity of electricity and the voltage (intensity). The unit of *electrical energy* is the *joule*, which is defined as the product of one coulomb by one volt.

$$\text{Joules} = \text{Coulombs} \times \text{Volts}.$$

Electrical power refers to the rate at which electrical energy is made available and used. The unit of power is the *watt*, which is defined as one joule per second or one volt-ampere.

$$\text{Watts} = \text{Amperes} \times \text{Volts}.$$

One *horse-power* is equivalent to 746 watts. The *kilowatt* is 1000 watts, and the *kilowatt-hour* is one kilowatt for one hour, or 3,600,000 joules.

3. The Production of Electrical Energy by Means of Oxidation-Reduction Reactions

Let us consider the simplest possible kind of an oxidation-reduction reaction,

the direct combination of two elements. For the two elements, let us select chlorine and zinc. When metallic zinc is placed in a vessel filled with chlorine, or is immersed in water which is saturated with chlorine, zinc is oxidized and chlorine is reduced. This reaction involves a transfer of two electrons from a zinc atom to two chlorine atoms, each chlorine atom accepting one electron:

$$Zn \longrightarrow Zn^{++} + 2 \text{ electrons}$$
$$Cl_2 + 2 \text{ electrons} \longrightarrow 2\ Cl^-.$$

The reaction occurs spontaneously. If the zinc and chlorine are in contact with each other, all the energy liberated is converted into heat.

Strange as it may seem, the reaction between zinc and chlorine can be carried out under conditions that do not require the two elements to be in contact with each other. Only under these conditions is it possible to convert any of the energy, into electrical energy.

Let us place a solution of some inactive electrolyte in each of two beakers. Sodium chloride serves this purpose very well, since it reacts with neither zinc nor chlorine and at the same time forms a solution of excellent conducting properties. A small glass tube bent into the form of the letter U is also filled with the salt solution and is used as a conducting bridge (Figure 257) between the solutions in the two beakers. One of the solutions is saturated with chlorine and a graphite electrode is partially immersed in it. A zinc rod is placed in the other solution, and the two electrodes are connected by a copper wire. We now have a simple *electrochemical cell*, which may be used as a source of an electrical current. A cell of this kind is called a *voltaic cell* to distinguish it from electrochemical cells in which electrolysis occurs and in which an outside source of energy is supplied to produce chemical changes in the cell. The voltaic cell is, itself, a source of energy.

At the surface of the zinc, atoms pass

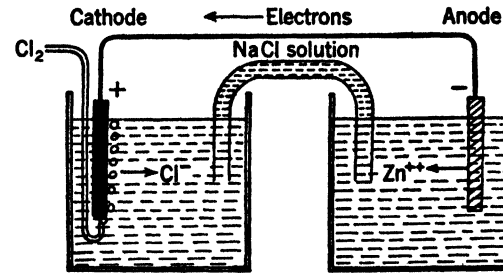


Figure 257. An Electrochemical Cell Based Upon the Reaction: $Zn + Cl_2 \longrightarrow Zn^{++} + 2Cl^-$

into the solution as zinc ions Zn^{++}, leaving two electrons, per atom, upon this electrode. Now electrons will flow out of the zinc through the wire and into the graphite electrode where they are, in turn, removed by the formation of the chloride ions from free chlorine. Each chlorine molecule makes two chloride ions and in doing so removes two electrons from the graphite electrode. The flow of electrons through the wire connecting the zinc and the graphite constitutes an electrical current, which can be used to light a lamp, run a motor, or in other useful ways within the limits of the energy supplied by the cell.

The tube filled with a solution of sodium chloride serves as a conducting bridge by allowing the ions to migrate through the solution and, at the same time, it prevents the chlorine and the zinc from coming into contact and reacting directly.

The chlorine electrode of the cell pictured in Figure 257 is called the *cathode*. It is to this electrode that electrons flow through the conductor, and it is at this electrode that *reduction* occurs; i.e., free chlorine is reduced to Cl^- ions. The zinc electrode is called the *anode*. At this electrode electrons enter the external circuit, and it is here that oxidation occurs; i.e., zinc is oxidized to Zn^{++} ions. In any voltaic cell the anode is the electrode from which electrons enter the external circuit, and the cathode is the electrode which electrons enter from the external circuit.

Other spontaneous oxidation-reduction reac-

tions, can be used to produce electrical energy. We might use chlorine in one half of the cell and a solution of ferrous sulfate ($FeSO_4$) in the other, with small pieces of platinum foil serving as the electrodes. This reaction would involve the conversion of ferrous ion (Fe^{++}) into ferric (Fe^{+++}), each ferrous ion giving up one electron to the electrode with which its solution is in contact. At the other electrode, chlorine molecules are changed into chloride ions as before. Some reactions cannot be used to produce an electric current although they involve oxidation. The oxidation of carbon by oxygen, for example, cannot be used, because these two substances react only when they are in contact with each other. The same condition is true for other reactions forming covalent rather than ionic compounds.

4. Electromotive Force of the Cell

In the zinc-chlorine cell described above, electrons are left on the zinc electrode as zinc ions are formed, and they are removed from the chlorine electrode as chlorine is converted into chloride ions. These changes result in a relatively high electron pressure on the zinc electrode and a relatively low pressure on the chlorine electrode. The flow of electrons is the result of a force (e.m.f.) which drives or forces the electrons through the conductor and which depends upon the difference in the electron pressures at the two electrodes, just as the flow of water from a region of high pressure to one of lower pressure depends upon the difference in water pressure.

The electromotive force of a cell depends upon the chemical properties of the reacting substances, e.g., zinc and chlorine, and especially upon their tendencies to change into ions by acquiring or losing electrons. It also depends upon the concentrations of the ions in the solutions in contact with the electrodes. Let us recall that the reactions involving zinc and chlorine are reversible. If, therefore, the concentration of the zinc ions in the solution around the zinc electrode is increased, the reverse reaction, $Zn^{++} + 2$ electrons $\rightleftarrows Zn$, is favored by the change, and, as a result, the electron pressure at the zinc electrode is decreased. Similarly, an increase in the concentration of the chloride ions in the solution around the chlorine electrode causes an increase in the number of electrons on that electrode, $2\ Cl^- \rightleftarrows Cl_2 + 2$ electrons. Both of these effects, therefore, cause a decrease in the electromotive force of the cell, because they reduce the difference in the pressures of electrons on the two electrodes.

5. The Zinc-Copper Cell

Let us now consider an electrochemical cell based upon the replacement of copper by zinc:

$$Zn + Cu^{++} \rightleftarrows Zn^{++} + Cu.$$

In order that a current of electricity may be produced, we must use two electrodes, one consisting of a zinc rod partially immersed in a solution containing zinc ions, and the other consisting of a copper rod dipping into a solution containing cupric ions (Figure 258). These two electrodes act as the two parts of an electrochemical cell when they are properly connected by a metallic conductor, and when the two solutions are connected by an inverted U tube filled with a solution of some inactive electrolyte, such as sodium chloride.

The reactions at the two electrodes are:

$$Zn \rightleftarrows Zn^{++} + 2 \text{ electrons}$$
$$2 \text{ electrons} + Cu^{++} \rightleftarrows Cu.$$

Zinc has a much stronger tendency to change into ions than copper. Therefore, the pressure of electrons at the zinc elec-

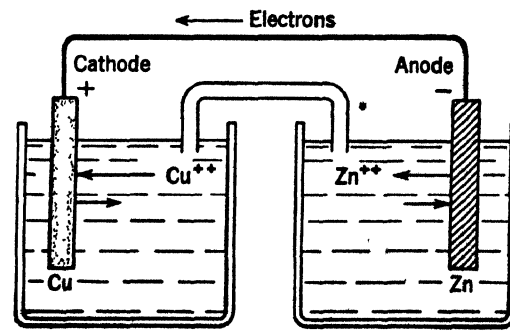


Figure 258. The Zinc-Copper Cell

trode is greater than that on the copper electrode, and a difference of potential is produced between the two metals. The electrons liberated on the surface of zinc flow out of that electrode through the conductor to the copper, where they are used to convert cupric ions into atoms of copper.

In this cell, as in the zinc-chlorine cell, the concentrations of the ions in the solution around the electrodes have an important effect upon the electromotive force. The electromotive force depends at the zinc side of the cell, upon the conversion of zinc into zinc ions and, therefore, is favored by a small concentration of zinc ions in the solution; the greater this concentration becomes, the stronger is the tendency for the reverse reaction to occur, and this reaction, it will be noted, removes electrons from the zinc electrode and reduces the electromotive force. At the copper electrode, however, the production of the electromotive force depends upon cupric ions removing electrons from copper, and, therefore, the greater the concentration of cupric ions, the greater the electromotive force of the cell.

6. Electrode Potentials

When we studied the subject of *p*H we described the construction and use of the hydrogen electrode (page 327). When the concentration of the hydrogen ion is 1N and the hydrogen is under a pressure of 1 atm., this electrode is referred to as the *normal hydrogen electrode* and as such is sometimes used as a reference electrode to measure the potential of other electrodes, e.g., a metal immersed in a solution containing the ions of the metal.

The potential produced when an element acts as an electrode and dips into a solution containing its ions is called the *single electrode potential of that element.* The electrical potential changes with the concentration of the ions, and, therefore, it is necessary to use some standard concentration when the single electrode potentials of different elements are to be compared. The concentration usually employed for this purpose is unit activity, i.e., an effective concentration of one gram-ion per 1000 g. of the solvent.

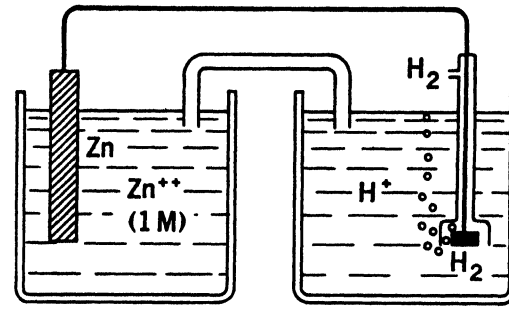


Figure 259. The Measurement of Electrode Potentials

This cell explains the theoretical basis of the method; in practice, electrodes other than the hydrogen electrode are sometimes employed, but their potentials are expressed in terms of the hydrogen potential.

To measure the electrode potential of a metal an electrochemical cell is set up, consisting of the metal and a solution of its ions as one half of the cell and a hydrogen electrode (or some other reference electrode) as the other half (Figure 259). The two halves of the cell are connected by a curved glass tube filled with a solution of potassium chloride, or some other electrolyte, and also by a wire that connects the metal with the platinum foil of the hydrogen electrode. The potential difference of the cell as a whole can now be measured.

The potential of the hydrogen electrode is usually defined arbitrarily as zero for the sake of convenience. When this is done, *the entire electromotive force of the cell may be regarded as the difference of potential between the metal and its solution.* The measured potential of this electrode is consequently not the real potential, which would be equal to the observed potential corrected for the potential of the hydrogen electrode. The latter, however, is constant for the potential measurements of a series of metals. The e.m.f. values obtained by such measurements are called the electrode potentials of the metals.

TABLE 23. ELECTRODE POTENTIALS *

Element	Ion	Reaction at the Electrode	Potential (volts)
Potassium	K^+	$K \rightleftarrows K^+$	2.924
Calcium	Ca^{++}	$Ca \rightleftarrows Ca^{++}$	2.87
Sodium	Na^+	$Na \rightleftarrows Na^+$	2.71
Magnesium	Mg^{++}	$Mg \rightleftarrows Mg^{++}$	2.34
Aluminum	Al^{+++}	$Al \rightleftarrows Al^{+++}$	1.70
Manganese	Mn^{++}	$Mn \rightleftarrows Mn^{++}$	1.10
Zinc	Zn^{++}	$Zn \rightleftarrows Zn^{++}$	0.762
Sulfur (at Pt electrode)	$S^=$	$S^= \rightleftarrows S$	0.55
Iron	Fe^{++}	$Fe \rightleftarrows Fe^{++}$	0.44
Cadmium	Cd^{++}	$Cd \rightleftarrows Cd^{++}$	0.401
Cobalt	Co^{++}	$Co \rightleftarrows Co^{++}$	0.28
Nickel	Ni^{++}	$Ni \rightleftarrows Ni^{++}$	0.23
Tin	Sn^{++}	$Sn \rightleftarrows Sn^{++}$	0.14
Lead	Pb^{++}	$Pb \rightleftarrows Pb^{++}$	0.12
Hydrogen	H^+ (or H_3O^+)	$H_2 \rightleftarrows 2\,H^+$	0.00
Copper	Cu^{++}	$Cu \rightleftarrows Cu^{++}$	−0.34
Mercury	Hg^{++}	$Hg \rightleftarrows Hg^{++}$	−0.80
Iodine (at Pt electrode)	I^-	$I^- \rightleftarrows \frac{1}{2} I_2$	−0.54
Bromine (at Pt electrode)	Br^-	$Br^- \rightleftarrows \frac{1}{2} Br_2$	−1.07
Chlorine (at Pt electrode)	Cl^-	$Cl^- \rightleftarrows \frac{1}{2} Cl_2$	−1.36
Gold	Au^+	$Au \rightleftarrows Au^+$	−1.50
Fluorine	F^-	$2\,F^- \rightleftarrows F_2$	−2.85

* The electrode potentials which are given in this table are based upon comparisons with the normal hydrogen electrode, which is arbitrarily taken as having a potential of 0 00 volts. The temperature is 25° C., and the pressure of the hydrogen is one atmosphere. The concentrations of the ions in the different solutions are 1 molal or, as more accurately expressed, the values as given are for an *activity* (page 325) of *unity*.

7. The Electrochemical Series

Measurements of the electrode potentials of different metals made in the manner described in the preceding section may be used to determine the relative positions of these metals in the electrochemical series. When used as electrodes in one half of the cell we find that some metals will dissolve, forming positive ions. The formation of the ions leaves electrons upon the metal, which consequently acquires a negative charge. If the metal is connected by a conductor (external to the solution) with the hydrogen electrode, these electrons will flow from the metal to the hydrogen electrode, where they are used to convert hydrogen ions into neutral atoms of hydrogen. This condition results whenever the metal has a greater tendency to form positive ions (by losing electrons) than hydrogen has. The electromotive force of such a cell, in which zinc (and Zn^{++} ions at unit activity) is used as the metal, is 0.76 volts. This is called the *electrode potential* of zinc. It is sometimes given a negative sign, but we shall make the sign of zinc's electrode potential positive to indicate that, as compared to hydrogen, the metal produces a relatively high concentration of positive ions in the solution.

When other metals than zinc are used, the electromotive force of the cell will have different values, depending upon the relative tendency of the metal (as compared with hydrogen) to give up positive ions to the solution. Lead, for example, gives an electromotive force of only 0.12 volt, because its atoms have a smaller tendency than zinc atoms to become positive ions. Or, to put the matter in another way, there is only a slight difference between lead and hydrogen in their tendency to change into positive ions. It is clear, therefore, that if we measure the electromotive forces of cells in which we use different metals, the results

will give us the order of these metals in the electrochemical series, in which the position of a metal depends upon the ease with which its atoms lose electrons and become positive ions.

When we replace zinc or lead with copper, we find that hydrogen has a stronger tendency to form positive ions than the metal. Hence hydrogen is changed into hydrogen ions at the hydrogen electrode, thus increasing the number of electrons upon the electrode. These electrons flow from the hydrogen electrode to copper, where they are used to convert cupric ions into atoms of the metal. The electromotive force of this cell is 0.34 volts, which is the single electrode potential of copper. We give it a negative sign because copper produces relatively few positive ions in the solution as compared with hydrogen.

If the non-metallic elements are included in the electrochemical series, we find that they have negative electrode potentials, because electrons flow from the normal hydrogen electrode toward the non-metallic electrodes where they are used to produce negative ions.

The electrochemical series in Table 23 contains the electrode potentials of some of the non-metals as well as both active and inactive metals. The positions of the elements in this table represent the relative ease with which the elements can be oxidized by losing electrons. Those at the top are most easily oxidized. Conversely, the free non-metals and the ions of the metals at the bottom are most easily reduced and serve, therefore, as the best oxidizing agents. It should also be noted that the higher a non-metallic element stands in the series, the more readily its negative ions are oxidized to the free state of the element.

TYPES OF ELECTROCHEMICAL CELLS

8. The Daniell Cell

In the Daniell cell electrical energy is made available by means of the reaction:

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu.$$

The construction of the cell is shown in Figure 258. The electrodes are made of metallic zinc and copper. Each electrode is placed in a solution of the ion corresponding to the metal, and the solutions are connected by means of a siphon U tube, filled with a solution of some electrolyte such as potassium chloride. Now if solutions containing the ions of the metals (unit activity) are used, the potential difference between copper and the solution of cupric ions will be $-$ 0.34 volt and that between zinc and the solution of zinc ions will be $+$ 0.76 volt. From the signs of the potentials it is evident that zinc has a much greater tendency to form ions than copper has; and hence, at the zinc electrode, the metal passes into solution as Zn^{++} ions, thus leaving electrons on this electrode. These electrons flow through the conductor that connects the electrodes to copper, where they are used to convert cupric ions into copper atoms. The differences of potential produced at the two electrodes act in the same direction, namely, to cause electrons in the external circuit to flow toward copper. For this reason the electromotive force of the cell is equal to the sum of the two electrode potentials:

$$0.34 + 0.76 = 1.10 \text{ volts.}$$

This is the theoretical voltage of the Daniell cell in which solutions containing Zn^{++} and Cu^{++} ions of unit activity are used. If solutions containing different ionic concentrations are used, the voltage will vary. The voltage of the cell may be increased by using more dilute solutions of zinc ion and more concentrated solutions of cupric ions. Can you show why these changes in concentration should favor the production of a higher e.m.f.?

9. The Gravity Cell

The gravity cell makes use of the same

reaction as the Daniell cell. The copper electrode consists of three sheets of copper which are fastened together and placed on the bottom of the cell. The metallic copper is placed in a saturated solution of cupric sulfate. To keep the solution saturated, crystals of cupric sulfate are placed in the bottom of the vessel. To provide more surface, a branched, or *crowfoot* zinc electrode is used. This is suspended near the top of the cell in a dilute solution of zinc sulfate, which floats on the heavier solution of cupric sulfate.

At first the voltage is comparatively high, but it falls off as the zinc dissolves, since the concentration of the zinc ions in the solution surrounding the zinc electrode gradually increases.

10. The Dry Cell

The outside of this cell is a zinc cup, lined with porous paper. Zinc acts as one electrode, and a carbon rod in the center embedded in MnO_2 is the other electrode. The rest of the cell is filled with ammonium chloride, and some porous, inactive solid. The cell reaction consists of the conversion of zinc into zinc ions (oxidation) at the outer electrode, and the conversion of the ammonium ion into ammonia and of manganese dioxide into Mn_2O_3 (reduction) at the carbon electrode:

$$Zn \longrightarrow Zn^{++} + 2\,e$$

$$2\,MnO_2 + 2\,NH_4^+ + 2\,e \longrightarrow Mn_2O_3 + 2\,NH_3 + H_2O.$$

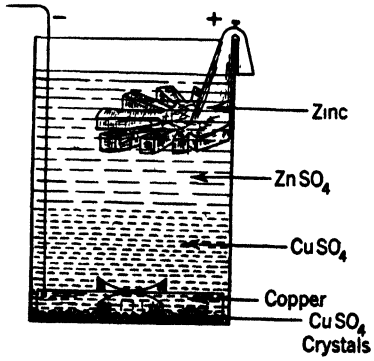


Figure 260. The Gravity Cell

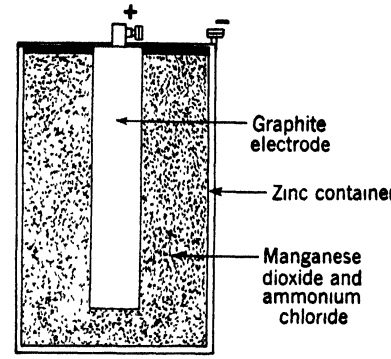


Figure 261. The Dry Cell

The first of these reactions leaves electrons on the zinc electrode, and the second reaction removes them from the carbon rod. Therefore, electrons will flow through a conductor connecting the electrodes from zinc to carbon. The ammonia that is liberated reacts with zinc ions to form complex ions, $(Zn(NH_3)_4)^{++}$, thus reducing the concentration of zinc ion and making it possible for the zinc electrode to become more negative.

11. The Storage Battery

As its name implies, the storage battery acts as a cell in which energy may be stored. When the battery is undergoing charge, electrical energy is supplied and is used to produce certain substances which later may take part in an oxidation-reduction reaction that produces a difference of potential and, hence, makes possible the generation of an electric current.

In the lead storage battery which has been discharged, both of the poles are covered with a deposit of lead sulfate ($PbSO_4$), and the solution in the battery consists of a dilute solution of sulfuric acid. To charge the battery we connect the poles to a generator producing a direct current of about 110 volts. At one pole, lead ions of the lead sulfate are reduced to metallic lead, and the sulfate ion is released in the solution. At the other pole lead ions of the lead sulfate are oxidized and deposited as lead dioxide (PbO_2), each atom of lead giving up two

more electrons to the pole as this reaction takes place. The complete reaction which occurs during *charging* may be represented by the following equation:

$$2\ PbSO_4 + 2\ H_2O \longrightarrow Pb + PbO_2 + 2\ H_2SO_4,$$

Since sulfuric acid is produced as the battery is charged, the extent to which the charging has been completed can be determined by measuring the specific gravity of the solution from time to time.

The fully charged battery may now be used as a cell to liberate electrical energy. During its discharge, the lead of the anode is converted into lead ion which, in turn, is precipitated as lead sulfate, since this substance is only slightly soluble:

$$Pb^{++} + SO_4^{=} \longrightarrow PbSO_4 \downarrow + 2\ e.$$

This reaction leaves electrons on the electrode at which it occurs. At the cathode lead dioxide is converted into lead sulfate (reduction):

$$PbO_2 + SO_4^{=} + 4\ H^+ + 2\ e \longrightarrow PbSO_4 \downarrow + 2\ H_2O.$$

The complete reaction which occurs as the battery is discharged is represented by the following single equation:

$$Pb + PbO_2 + 2\ H_2SO_4 \rightleftarrows 2\ PbSO_4 + 2\ H_2O.$$

The fully charged cell has a voltage of about 2.2 volts, and its solution has a specific gravity of about 1.2. The voltage of the battery, when it is ready to be charged again, is about 1.9, and the specific gravity of the solution is about 1.05.

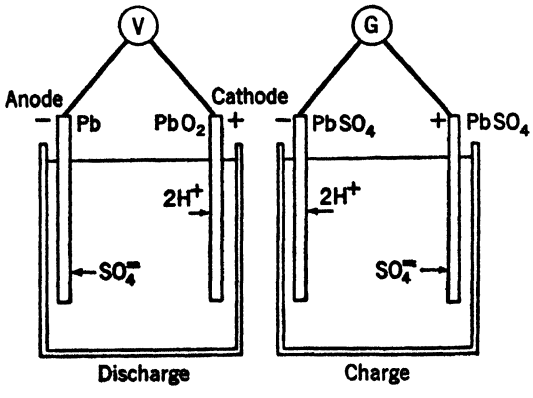


Figure 262. The Lead Storage Battery

12. Metallic Couples

When a strip or rod of zinc is placed in a solution of hydrochloric acid, hydrogen is liberated on the surface of the metal, and the metal passes into the solution. Atoms of zinc pass into solution as Zn^{++} ions and, as each ion is formed, two electrons are left on the metal. Hydrogen ions in contact with the metal remove these electrons and become neutral atoms of hydrogen. The atoms then form molecules, which collect in bubbles of gas and finally escape from the solution or cling to the surface of the zinc.

Let us now consider a solution of the acid in which strips of both zinc and copper are placed and are either allowed to touch or are connected by a wire. We may now observe that the zinc continues to dissolve, but hydrogen is liberated on the surface of the copper. As zinc ions are formed, electrons are left on the zinc, as before, but they are transferred to the copper where they are used to convert hydrogen ions into neutral atoms and molecules of hydrogen; it is on the surface of copper, therefore, that hydrogen is liberated.

Two metals in contact, as the copper and zinc combination that we have just described, form a *metallic couple.*

Impure, or ordinary, grades of zinc contain small crystals of copper and other metals, and these crystals form numerous metallic couples with the zinc. Hydrogen is liberated on the surfaces of these small crystals of other metals and the zinc, with a surface left free and clean, readily dissolves.

13. Electroplating

In the manufacture of many metallic articles — tableware, hardware, plumbing fixtures — one metal is often covered with another, sometimes to protect the first

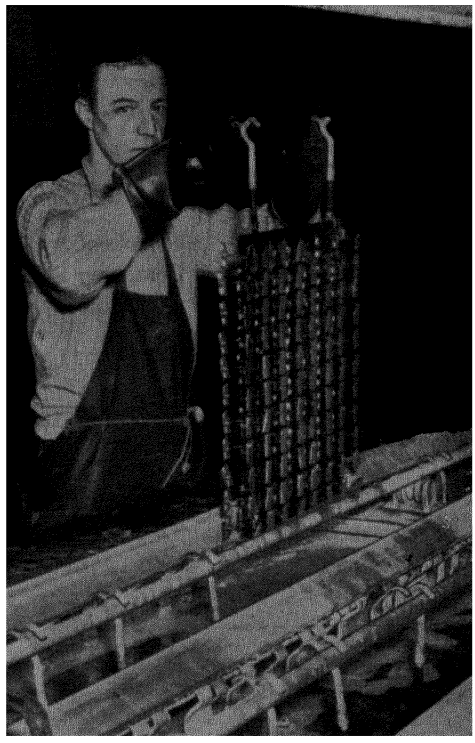


Figure 263. Electroplating

Metal parts are lowered into an electroplating bath to receive a protective metallic coating.
(Courtesy of Du Pont Company)

metal from oxidation and sometimes to give a metal like iron a more pleasing appearance. The article to be plated is placed in a bath containing a salt of the metal that is to be deposited. The article to be plated is made the cathode and the metal to be deposited is made the anode of the cell. The character of the deposit varies with many conditions, such as the temperature, the concentration of the ions, the surfaces of the anode and cathode, and the presence of other substances in the electrolyte.

REVIEW EXERCISES

1. A current of five amperes is passed through a solution of silver nitrate for ten minutes; the same current is also passed through a solution of cupric sulfate for five minutes. What weights of silver and copper are liberated at the cathodes in the two experiments?
2. What are some of the essential conditions that must be fulfilled before a chemical reaction can be used to produce a current of electricity?
3. How are the positions of the metals in the electrochemical series determined?
4. What factors determine the difference of potential that exists between a metal and a solution of its ions?
5. Why do some metals have a positive electrode potential, while others have a negative potential when compared with the normal hydrogen electrode?
6. Describe the hydrogen electrode and explain how it is used in determining the electrode potentials of the metals.
7. Calculate the electromotive force of cells made of the following substances, assuming ionic concentrations in the solutions with which each element is in contact are the same as that for which the values in Table 23 are given. Zinc and mercury; copper and mercury; nickel and copper; zinc and tin.
8. Draw a diagram of an electrochemical cell that might be used for the generation of an electric current from one of the reactions mentioned in (7).
9. Draw a diagram of a cell that might be based upon the use of the reaction between iron and chlorine to generate an electrical current. What materials would you use as the electrodes?
10. Describe the construction and operation of the following cells: Daniell; gravity; dry cell.
11. Describe the construction of a lead storage battery and explain the nature of the chemical changes that occur during charging and discharging.
12. Which of the metals in Table 23 should give the greatest electromotive force when used in a voltaic cell? What should be the theoretical voltage of such a cell? Why is it not a practical cell?
13. If a current of 15 amperes is used, how much chlorine can be produced in ten hours by the electrolysis of a solution of sodium chloride?
14. Chlorine is produced by the electrolysis of a

solution of NaCl in a cell operated at a voltage of 2.4. Calculate the cost of the energy used in the production of 10 kilograms of chlorine at 12 cents per kilowatt hour.

15. What weight of copper will be deposited by electrolysis when a current of 3 amperes is passed through a solution of cupric chloride, $CuCl_2$, for one hour?
16. Why does the specific gravity of the electrolyte in a storage battery indicate the extent to which such a battery is charged or discharged?
17. What is the difference between a voltaic cell and an electrolytic cell? Consider the purposes for which they are used and the nature of the reactions that occur in them.
18. Give an example of a reaction involving oxidation and reduction that could not be used as the basis of a voltaic cell. Why can it not be so used?

REFERENCES FOR FURTHER READING

Mantel, C. L., *Industrial Electrochemistry*, New York: McGraw-Hill Book Company, 1940.

Vinal, G. W., *Storage Batteries*, 3d ed.; New York: John Wiley and Sons, 1940.

Primary Cells: *J. Chem. Ed.*, **4,** 770 (1927); **6,** 117 (1929).

Storage Batteries: *Ind. and Eng. Chem.*, **19,** 1124 (1925); *J. Chem. Ed.*, **27,** 63 (1950).

37

METALS

1. Introduction

The remaining chapters of this book will deal with the metals. The atoms of the metals contain relatively small numbers of electrons — usually one, two, or three — in their outermost shell, while the atoms of the non-metals have a larger number. The metals tend, therefore, to form ionic compounds in which their atoms lose electrons, which are transferred to non-metals. We should also recall that some elements form hydroxides that act either as an acid or a base, and they appear in solutions of their salts both as simple positive ions and in negatively charged radicals. Other elements form compounds like those of the metals, when they are in their lower oxidation states, and compounds like those of the non-metals when they have higher oxidation numbers.

The structure of the metals and their properties such as malleability and electrical conductivity have been dicussed on page 175.

2. Occurrence and Uses

After oxygen and silicon, the six next most abundant elements in the earth's crust are metals: aluminum, iron, calcium, sodium, potassium, and magnesium. Manganese, barium, chromium, vanadium, nickel, and strontium are the only other metals that are present in the earth's crust to an extent greater than 0.01 per cent. The importance of these elements as free metals, however, does not depend upon their relative abundance. Instead, their importance is determined by the occurrence of the free metal, or its compounds, in deposits — in some instances, just a few known deposits in all the world — that are at least moderately rich in metal-content; upon the ease with which their ores can be reduced to the metals; and upon the useful properties of the metal. It happens, therefore, that some of our most widely used metals are not very abundant in nature, while others that are relatively abundant are used very little. Four of the most abundant metals — sodium, potassium, calcium, and magnesium — have limited uses as metals, because they do not lend themselves to the purposes for which metals usually serve. They are not durable and are entirely unsuited for the manufacture of metallic articles or for the construction of metallic structures of any kind. Alloys containing some of these metals are more useful than the metals themselves.

Silver and gold, which occur as native metals, were used at least 8000 years ago, chiefly in making ornaments. Of the metals that occur as compounds, copper and tin were very early produced by the reduction of their oxides with carbon or carbonaceous material. An alloy of these

two metals was also produced at least 5000 years ago. This alloy is called *bronze*. Although iron is produced very easily from its ores, it was not until long after the time when brass and bronze had been produced, that man learned of its great usefulness and how it can be produced. The very extensive development of the automobile industry, the railroads, and the wide use of machinery and tools of every kind has made iron and its alloys, and also non-ferrous metals and their alloys, extremely valuable and important commodities. The many uses that require metals have stimulated the search for economical methods of reducing the metals from their ores. When the pure metals have not met the requirements, alloys of many kinds have been made to provide metals with the definite properties required for specific needs. Thus, there has been produced brass harder than copper; steels which are tough and strong; steels which are resistant to chemical action; steels that do not lose their "temper" when heated; stainless steels; gold alloys harder than pure gold and colored green, white, or pink; and alloys of many kinds that withstand the wear and tear of moving gears and bearings more satisfactorily than any pure metal.

3. Ores of Metals

Ores are the natural materials in which metals or their compounds occur in the earth. They usually contain large amounts of worthless earthy material, called *gangue*. Some of the least active metals are often found in the free state. These are said to be *native* ores.

The most important classes of ores, in addition to native ores, are listed below:

(1) *Oxides.* Oxides are important natural sources of iron, aluminum, manganese, and tin.

(2) *Sulfides.* Ores containing the sulfides of the metals are important sources of zinc, cadmium, mercury, copper, lead, nickel, cobalt, silver, arsenic, and antimony.

(3) *Carbonates.* Iron, lead, zinc, and copper occur as carbonates, and ores containing these compounds are important sources of these elements. They are not as important, however, as the oxide or sulfide ores of the same metals. Calcium, magnesium, barium, and strontium also occur in nature as carbonates.

(4) *Sulfates.* Calcium, barium, and strontium occur abundantly as sulfates. A minor ore of lead contains lead sulfate.

(5) *Halides.* The chlorides of sodium, magnesium and potassium are important sources of these metals and their compounds.

(6) *Silicates.* Silicates of aluminum, calcium, potassium, sodium, and magnesium are very abundant, and silicates containing many other metals (page 391) are well known. Usually, however, the naturally occurring silicates are of little value as the sources of the metals which they contain. They are so difficult to decompose, that the recovery of the metals from them is not economical.

METALLURGY

4. Treatment of Ores

Metallurgy deals with the different processes that are used in the production of metals from their ores. Most of these processes involve chemical reactions, but before such reactions can be used, there must be *preliminary treatments* to remove a considerable portion of the worthless material and to concentrate that part of the ore which contains the metal. These treatments are followed by *smelting*, and the metal is finally purified by *refining*.

In the preliminary treatment, the ore is first crushed, and the material is then separated into two or more fractions by various methods. We have already (page 231) described the oil flotation method of concentrating ores. The separation may also depend upon differences in the rates of settling of different kinds of particles in water. If the particles containing the metal are attracted by a magnet, they can be separated

from other material by passing the crushed ore on a continuously revolving belt or screen beneath a large electromagnet. Shaking tables may also be used, if the particles containing the metals are heavier than those composed of worthless materials. Cottrell electrical precipitators (page 228), or devices based upon the same principle, are sometimes used to separate parts of the finely crushed ores which readily become charged when brought into a strong electrical field from materials that are not readily charged.

The preliminary treatment of the ore may also include certain chemical changes by which the metallic compounds are converted into substances that are more easily reduced. Most sulfide ores, for example, are *roasted* in the air to convert the sulfides into oxides of the metals and to remove the sulfur as sulfur dioxide. Ores that contain water chemically combined in hydrates, or ores which contain carbonates of the metals, are usually heated to expel the water, and to decompose the carbonates by liberating carbon dioxide.

After the preliminary treatment, the ore is ready for reduction in the *smelter*. This is a furnace in which the metal is produced in large quantities and from which it is drawn off in the liquid condition. Since most ores contain considerable quantities of gangue, even after concentration by the preliminary treatment, a *flux* is added to convert the *gangue* into *slag*. If the gangue is silica or silicates, a basic flux is added. This is usually lime or limestone, which reacts with silica to produce the slag, calcium silicate. If the gangue is a basic substance, such as lime or limestone, which produces lime upon heating, an acid flux, such as silica, is added. The slag must be a substance that is easily melted and can easily be separated from the fused metal, preferably by forming a top layer, which protects the metal from oxidation. As it collects, it can be drawn off from the furnace from time to time.

5. Metallurgical Methods

For the present we shall consider only the most important general types of reactions employed in the reduction of metals from their ores.

(1) The oxide ores are usually reduced by carbon. This is the method which is used, for example, in the production of iron:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO.$$

Either carbon monoxide or carbon dioxide may be produced, depending upon the temperature to which the charge of the furnace is heated and the quantity of air supplied. If carbon monoxide is produced at first, it may cause further reduction:

$$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2.$$

(2) Metals which occur in the free state are separated from the gangue of their ores by heating until the metals are melted, or by adding substances in which the metals dissolve. By one or the other of these methods the metal can be separated from the infusible or insoluble portions of the ores.

(3) Aluminum is used to reduce some oxides. Carbon is not a satisfactory reducing agent for some metals because of its tendency to combine with them, forming carbides, and also because its use requires excessively high temperatures. Reduction by aluminum is used to produce chromium and manganese and also to reduce iron in small quantities, e.g. in welding steel rails.

The heat required to fuse the ends of the steel rails that are to be welded is furnished by the reaction of a mixture containing the oxide of iron and aluminum powder, called *thermite*. The mixture is placed in a dry fireclay crucible embedded in sand. A small amount of an ignition mixture containing barium peroxide and powdered magnesium is placed in a small depression in the top of the mass and is ignited by means of a burning strip of magnesium ribbon. The reaction produces sufficient heat to melt the iron, which flows between the rails and welds them.

(4) Other reducing agents are used in special cases. Sodium, potassium, and magnesium may be used to reduce the oxides or chlorides of less active metals. Hydrogen may also be used in some cases (page 75).

(5) Electricity is used in metallurgy for two purposes. (1) It may be used to provide the heat necessary for the reaction and for the melting of the products. Some ores are smelted in an electric furnace, and carbon is added to act as the reducing agent. (2) Electricity is also used more directly in the recovery of sodium, potassium, calcium, magnesium, aluminum, and certain other metals by electrolysis.

6. Refining

Since refining consists of separating the metal from the impurities that it contains, advantage is taken of differences in melting point, volatility, ease of oxidation, etc. Electrolysis is also widely used in the refining of many metals, such as gold, copper, lead, zinc, aluminum, and chromium. The impure metal is used as the anode in an electrolytic cell containing a solution of a salt of the metal. The refined metal is deposited on the cathode, which is made of pure metal of the same kind.

ALLOYS

When two or more metals are melted together and the mass is cooled, the solid that forms is called an *alloy*. Coins, jewelry, silver plate, the metallic parts of automobiles, tools, ornaments, dishes, etc., are made of alloys. Various kinds of steel are alloys of iron with nickel, manganese, tungsten, chromium, and other metals. They



Figure 264. Refining Nickel by Electrolysis
(Courtesy of the International Nickel Company)

also usually contain certain percentages of carbon, silicon, and traces of other non-metals.

7. The Composition and Nature of Alloys

Alloys are usually prepared by mixing two or more metals in their liquid states. These liquids behave in the same way as other liquids under similar conditions. They may mix in all proportions; they may mix in certain proportions; or they may separate into different layers without mixing at all. They may also react chemically with each other to produce compounds. When the mixture cools, the composition of the solid that forms depends largely upon the relations that existed between the metals in the liquid mixture. The composition of alloys may, therefore, show the following differences: (1) The crystals may be those of the pure metals, which are segregated as solidification occurs. (2) If the fused metals dissolve in each other, they may form a solid solution upon cooling. (3) If the metals react, the alloy will contain crystals of their compounds. Many alloys contain two, or even all three, of these states of their components.

8. Eutectic Mixtures

Let us consider a mixture of two metals, such as antimony and lead. These metals form a solution of one in the other, when the metals are heated together. The melting point of pure lead is 327° C. and that of pure antimony is 630.5° C. In Figure 265, temperature is plotted vertically and the composition of the alloy is plotted horizontally along the line at the bottom. The shorter (left) curve represents the different temperatures at which lead freezes from solutions containing different percentages of antimony. If we drop a perpendicular line from any point on this curve to the line at the bottom, the point of intersection will represent the composition of the lead-antimony solution from which pure lead

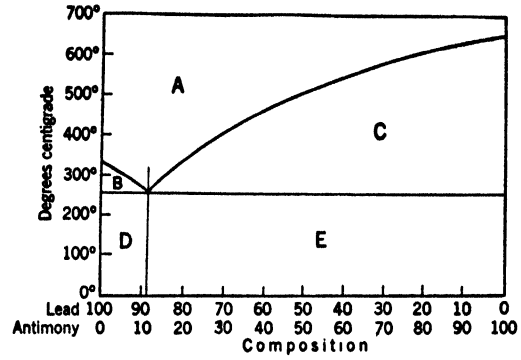


Figure 265. Lead-Antimony Alloy Diagram

will crystallize at the temperature corresponding to the point on the curve. Similarly, the longer (right) curve shows the effect of increasing amounts of lead upon the freezing point of antimony. If a perpendicular line is drawn from the point where the two curves meet, to the bottom line, the point of intersection indicates the composition of a mixture from which both lead and antimony will crystallize at the temperature (247°) corresponding to this point. This temperature is called the *eutectic temperature* and the mixture of metals is called the *eutectic*. It contains about 90 per cent of lead and 10 per cent of antimony, and is composed of a mixture of very small crystals of the two metals.

9. Properties of Alloys

The properties of an alloy cannot be predicted from its composition. As shown above, the freezing or melting point of a binary alloy may be lower than that of either component, but this is not always true. The hardness of an alloy is usually greater than that of the pure metals composing the alloy. The color, sometimes, is what we might expect from a mixture of two metals of different colors. Brass is made less red than copper by the presence of zinc, but often the color of the alloy fails to reveal the effect of the color of one metal, and it may be entirely different from that

of either. A five-cent piece does not show by its color that it contains any copper, and silver and gold may be alloyed to form "green gold." The alloy is usually a poorer conductor of electricity than its components. In general, it is more resistant to chemical changes, such as corrosion.

10. The Structure of Alloys

The structure of an alloy depends upon several conditions. When a solution of fused metals cools, crystals of one metal form at first, and the solution becomes less rich in that component. As cooling continues, the crystals of the first metal that separates become larger. Finally, the eutectic temperature and the eutectic composition of the solution are reached. At this point, the solution remaining crystallizes, usually, as small crystals of both metals. Hence, alloys made in this manner usually contain large crystals of one metal embedded in a matrix of very small crystals of the eutectic mixture. Alloys made by rapid cooling and from mixtures having a composition near that of the eutectic mixture are usually composed of small crystals and have a fairly homogeneous structure. These are characteristics that are desirable in many alloys.

COMPOUNDS OF METALS

11. Oxides and Hydroxides

The most important compounds of the metals are their oxides, hydroxides, and salts. The oxides of the metals above mercury in the electrochemical series can be produced directly by the reactions of the metals with oxygen. The oxides of all but the most active metals — alkalis — can be produced by heating the hydroxides and, except for the alkali metals and a few other active metals, by heating the carbonates and nitrates. The hydroxides of the alkali metals and barium are readily soluble; those of calcium, strontium, and magnesium dissolve sufficiently to make their solutions alkaline; and the hydroxides of other common metals are only very slightly soluble. Most hydroxides, therefore, can be produced by adding sodium hydroxide to solutions of soluble salts of the metals. A few of the hydroxides can be prepared by treating the oxides with water; this is true, for example, of the oxides of calcium, strontium, barium, and magnesium.

12. Intermetallic Compounds

The compounds that metals form with one another are called *intermetallic compounds*. Their formulas indicate that forces other than those responsible for ordinary ionic and covalent compounds determine the composition and molecular structure of these compounds. A few examples of intermetallic compounds are: Cu_2Mg, $AgCd_8$, $CuAl_2$, $FeSn_2$, and Cu_3Sn.

13. Salts

The most widely used salts are nitrates, chlorides, sulfates, acetates, carbonates, phosphates, sulfides, and silicates. The solubilities of these salts in water vary greatly, although it is possible to classify them as relatively soluble or slightly soluble, and this we have attempted to do in Table 24. With the help of such information it is possible to predict whether double decomposition reactions involving these salts will occur or how complete such reactions will be. This information is also helpful in selecting methods to be used in the production of these salts and, also, in producing other substances from them.

14. Reactions of Salts in Fused Mixtures

Double decomposition reactions may occur when certain solid substances are heated together until they melt. The melted mass acts as a solution of one salt in the other. Let us consider the reaction between barium sulfate and sodium carbonate. Barium sulfate dissolves more readily in

TABLE 24. THE SOLUBILITY OF SALTS

	Na	K	NH_4	Mg	Ca	Sr	Ba	Al	Cr	Zn	Fe	Ni	Co	Mn	Cu	Bi	Hg(-ic)	Cd	Sn	Ag	Pb	Hg(-ous)
	all soluble																					
	all soluble (silver acetate is only moderately soluble)																					
	soluble																				insoluble *	
	soluble				insoluble					soluble											(ins)	
	soluble									insoluble												
	soluble									insoluble												
	soluble									insoluble												
	soluble									insoluble †												

* Lead chloride is moderately soluble.

† The sulfides of Mg, Ba, Ca, Sr, Al, and Cr are strongly hydrolyzed by water; the sulfides of the first four of these metals form soluble acid sulfides, while the sulfides of Al and Cr are converted into insoluble hydroxides. In other cases hydrolysis may result in the formation of insoluble compounds; thus, the hydrolysis of bismuth chloride, which is soluble, produces insoluble bismuth oxychloride, BiOCl. ——soluble; ——insoluble.

the melted sodium carbonate than it does in water. A reaction consequently occurs, and sodium sulfate and barium carbonate are formed. The latter is not soluble in the melt, and its precipitation helps the reaction to go to completion.

$$(Ba^{++} + SO_4^{=}) + (2\ Na^+ + CO_3^{=}) \longrightarrow BaCO_3 \downarrow + (2\ Na^+ + SO_4^{=}).$$

If the fused mass is allowed to cool and is then placed in hot water, the two products can be separated. The sodium sulfate dissolves and the barium carbonate does not. The latter may be removed by filtration, and can be treated with acids to form other desired salts, such as the chloride, nitrate, or acetate of barium. This procedure is often used in converting insoluble salts of the metals, such as barium sulfate, into soluble compounds, which can then be detected by analytical tests, or which may be used, on a larger scale, for commercial or laboratory purposes.

THE CORROSION OF METALS

15. Some of the Factors Influencing Corrosion

The extent to which a metal in contact with air is corroded depends, of course, upon the chemical properties, and especially upon the activity, of the metal. However, some of the relatively active metals are corroded less rapidly than some of the less active. Iron, for example, corrodes more rapidly than aluminum. The corrosion of aluminum produces a very firmly adhering coating of hydrated aluminum oxide, which excludes the air from contact with the metal and, therefore, prevents further oxidation. Copper, nickel, cobalt, and tin (and magnesium to a much less extent) are also protected from rapid corrosion by similar coatings of their oxides. Lead and zinc are protected in a similar manner by thin layers of firmly adhering basic carbonates. The oxide of iron, however, is a light, powdery substance which does not adhere to the surface of iron but falls away, leaving a fresh surface exposed to the air.

Air and water both appear necessary for corrosion, because metals like iron will not corrode in dry air or in water in which there is no dissolved air. The corrosion of metals is also strongly affected by strains such as those that may be produced by bending or cutting the metals. Corrosion is hastened by the presence of impurities of certain kinds, by couples which a metal makes with other metals (page 454), and, in the case of iron, by the rust itself. The rusting of iron appears to proceed more rapidly beneath patches of rust than it does on a clean surface.

16. Explanations of Corrosion

Several theories designed to explain corrosion have been offered, and of these we shall briefly discuss two that are generally used in studies of this subject.

The first of these theories is based upon the principle that corrosion depends upon the presence of an acid, usually carbonic acid. It is assumed that iron, for example, first reacts with carbonic acid to form ferrous carbonate, $FeCO_3$, and hydrogen; that ferrous carbonate then hydrolyzes to form ferrous hydroxide, $Fe(OH)_2$, which is oxidized to ferric hydroxide or to hydrated forms of ferric oxide, which we can represent as $Fe_2O_3.xH_2O$.

The most generally accepted theory of corrosion is based upon certain electrochemical principles. According to this theory, iron, for example, reacts with water or with an acid to form ferrous ion, Fe^{++}, and free hydrogen. Because of this reaction the iron at the point where corrosion occurs becomes an anode, while the point where hydrogen ions are changed into atoms of hydrogen acts as a cathode of an electrochemical cell. Action will soon cease because of the collection of hydrogen on the cathode. However, the oxygen of the air is thought to remove this hydrogen, thus permitting the action of the cell to continue and promoting the corrosion of the metal at the points which act as anodes.

17. The Prevention of Corrosion

Metals are protected from the effects of corrosion in many ways. Nickel, chromium, silver, gold, copper, zinc, and tin are deposited electrolytically upon other metals that corrode rapidly. Iron and steel are coated with zinc by dipping them into molten zinc or by baking them in zinc dust. Tin plate is produced by dipping sheets of iron in molten tin or by electrodeposition of tin on the surface of the iron. Metals are protected also by coatings of paints, enamels, varnishes, and lacquers. Iron is sometimes protected by forming a layer of the magnetic oxide, Fe_3O_4, upon its surface by heating the iron at a high temperature with steam. Stove-pipe is protected in this manner. Many metals that corrode readily are protected by the addition of alloying metals, as in stainless steel. Corrosion in boilers may be reduced by removing the oxygen of the air dissolved in the water by passing the water over iron scraps or turnings, or by preheating the water, before it enters the boilers.

REVIEW EXERCISES

1. Summarize the principal differences between the elements that are classified as metals and those that are classified as non-metals. Consider chemical properties and atomic structures.
2. Define: Ore, gangue, flux, slag.
3. Describe some of the methods that are most generally used in the production of metals from their ores.
4. What factors determine the amount of a metal that is used? Illustrate by referring to the production of the following metals: Iron, aluminum, sodium, and copper.
5. Why is aluminum more expensive than copper?
6. What is an alloy? How do alloys differ from one another in composition?
7. Define eutectic mixture. Starting with a mixture containing equal weights of lead and antimony at a temperature of 550°, describe the nature of the crystals that form as th mixture is cooled.
8. Starting with barium sulfate describe th methods that you would use in preparin barium acetate.
9. Describe the methods that you would use i converting the following substances into th products indicated: Sodium chloride int sodium sulfate; silver nitrate into silver chlo ride; barium chloride into barium sulfate calcium carbonate into calcium nitrate; an sodium carbonate into sodium sulfate.
10. How would you separate sodium chlorid from silver chloride? Starting with a solu tion containing lead (Pb^{++}) and cupri (Cu^{++}) ions what reagent could you add tha would precipitate the lead ions from the solu tion without precipitating the cupric ions?
11. What does the extent of hydrolysis of th chloride of a metal indicate concerning th strength of the metal's hydroxide as a bas and the general basic character of the metal
12. The solubility of barium sulfate at 18° i 0.00001 g. mol. wt. per liter. What weigh in grams of barium sulfate is contained i 100 ml. of a saturated solution?
13. A solution at 18° contains 0.01 g. atomi weight of barium, as Ba^{++} ions, per liter an an equal concentration of sulfate ion. Wha is the weight of the precipitate of bariun sulfate that forms in one liter of this solu tion?
14. A solution containing barium chloride i treated with a solution of sodium sulfate and the precipitate of barium sulfate is re moved by filtration. If the concentration o the sulfate ion in the filtrate (at 18°) is 0.001 g. ion weight of $SO_4^{=}$ per liter, what is the concentration of the barium ion in the same solution?
15. Starting with a solution that contains the nitrates of barium, silver, and nickel, what ions would you add to precipitate first silver, then nickel, and finally barium? What ion (anion) could you add to the mixture that would precipitate barium only?
16. Barium sulfate does not dissolve in a solution containing hydrochloric acid but barium carbonate does. Explain.
17. From earlier discussions in this book define

and give examples of normal, acid, basic, double, and complex salts.

18. From what has been said in earlier chapters describe the structure of metals and explain their electrical conductivity and malleability.
19. What three general operations are used in recovering metals from their ores?
20. Suggest some substance that could be used in place of (1) limestone and (2) silica as a flux.

REFERENCES FOR FURTHER READING

Arrhenius, S. A., *Chemistry in Modern Life.*

Austin, L. S., *Metallurgy of the Common Metals,* New York: John Wiley and Sons, 1926.

Carpenter, H., and J. M. Robertson, *Metals,* New York: Oxford University Press, 1939.

Findlay, A., *Chemistry in the Service of Man,* New York: Longmans, Green and Company, 1940.

Alloys: *Chem. and Met. Eng.*, **41,** 549 (1935); **42,** 383 (1936); **43,** 518 (1937); **45,** 631 (1938); *J. Chem. Ed.*, **10,** 669 (1933); **13,** 53, 106 (1936); *Ind. and Eng. Chem.*, **26,** 281 (1934).

Corrosion: *J. Chem. Ed.*, **4,** 1477 (1927); **10,** 141, 215, 297 (1933).

Metallic State: *J. Chem. Ed.*, **12,** 53 (1935).

38

THE ALKALINE EARTH FAMILY

1. Introduction

In the early days of chemistry, certain substances now recognized as slightly soluble oxides of metals, such as Fe_2O_3, were called *earths*. A few of these earths were known to form alkaline mixtures with water and, in general, to resemble the alkalies. For this reason they were called the *alkaline earths*. Until the early part of the nineteenth century, these substances were thought to be elements, but, in 1808, by electrolyzing the fused hydroxides of the alkaline earths, Davy produced four metals, which he called *calcium*, *strontium*, *magnesium*, and *barium*. These elements, together with beryllium and radium, are the metals to be studied in this chapter.

2. General Physical Properties

The elements of this family are decidedly metallic in appearance and in their general physical properties. They have a bright white luster on newly prepared surfaces, but they readily tarnish and corrode. Beryllium and magnesium, however, tarnish less readily than the others. All of the metals of this group are relatively light, the density of the heaviest (radium) being less than that of iron, nickel, copper, or zinc. They are good conductors of the electric current, and although somewhat brittle, they are ductile and malleable to a certain extent. In general, they are not as soft as the alkali metals. Beryllium is very hard, but the hardness of the metals of the family decreases with increasing atomic weight.

3. General Chemical Properties

Each of the metals has one valence number, positive 2. They form oxides corresponding to the formula XO, hydroxides $X(OH)_2$, and salts XCl_2. The hydroxides are basic and never acidic, except beryllium hydroxide, which is amphoteric. The oxides of the five heaviest metals of the family react readily with water to form hydroxides, which, to the extent that they dissolve, act as strong bases. The solubility increases with increasing atomic weights of the metals. Magnesium oxide reacts very slowly with water, and the hydroxide is less soluble than calcium hydroxide. Barium hydroxide is much more soluble than either. Beryllium oxide does not react with water.

The activity of the metals increases with increasing atomic weight. Magnesium decomposes cold water very slowly, and barium reacts much more rapidly. The electrode potential for magnesium is 2.34 volts, while for barium it is almost as great as for potassium, 2.9 volts. The ionizing potentials (page 156) decrease and the atomic radii increase as the atomic weights increase from beryllium to barium and

radium. Their compounds usually are ionic, but there are some that are covalent, particularly compounds of beryllium.

All of the metals of the group, when heated, burn in oxygen or in the air. They also react with nitrogen to form nitrides. They combine readily with many of the non-metals, such as sulfur and the halogens. They also liberate hydrogen from non-oxidizing acids, and beryllium, because of its amphoteric character, liberates hydrogen from sodium hydroxide.

As compared to the alkali metals in the same period — i.e., sodium with magnesium, and so on — the alkaline earth metals have smaller atomic radii, greater ionization potentials, and greater nuclear charges. Hence, we may conclude that, as a family, the alkaline earths should lose electrons less readily than the alkali metals. It might be expected that they would also stand lower in the electrochemical series (page 451) than the alkalis. Actually, however, the electrode potentials for calcium, strontium, and barium are higher than that of sodium. This is explained by the fact that the ions of these three alkaline earths have much higher heats of hydration than the sodium ion. This rather strong tendency to combine with water is at least one reason why calcium, strontium, and barium form ions by losing electrons more readily than the sodium ion.

CALCIUM

4. Occurrence

Calcium is the most abundant of the alkaline earth metals. It occurs in *limestone* and *marble*, $CaCO_3$; *dolomite*, $CaCO_3.MgCO_3$; *gypsum*, $CaSO_4.2\,H_2O$; *fluorspar*, CaF_2; and *phosphorite*, $Ca_3(PO_4)_2$. Compounds of calcium are present in sea water, in deposits of salts formed by the evaporation of sea water, and in certain plant and animal structures and products. Bones contain calcium phosphate as their essential inorganic constituent.

5. Production of Metallic Calcium

The production of calcium by electrolysis is shown in Figure 266. The electrolyte is fused calcium chloride, which is contained in a graphite vessel that also serves as the anode. The cathode is made of iron and dips just below the surface of the liquid. Calcium is deposited on the cathode and is made to form a stick of the metal by slowly raising the cathode as electrolysis proceeds. This stick of calcium acts, therefore, as the real cathode of the cell. In producing metallic calcium in large quantities, graphite anodes are suspended in a bath of fused calcium chloride. The metallic calcium is deposited on the top of an iron cathode, which is continuously raised as electrolysis proceeds. The metal as produced contains considerable calcium chloride, from which it is separated by melting and casting in an atmosphere of argon or by distillation.

6. Properties and Uses

Calcium is a white, silvery metal when freshly prepared but it combines readily with both oxygen and nitrogen and tar-

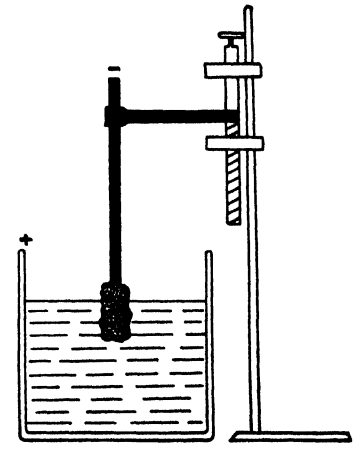


Figure 266. The Preparation of Metallic Calcium

nishes to produce a gray and slightly yellow surface. It tends to have a crystalline structure, and is much harder than barium. It is, however, malleable and ductile. Because of its tendency to react with water, the metal is used, sometimes, in drying organic liquids, such as alcohol. It is an excellent reducing agent and is used to produce certain metals by reduction of their compounds. In recent years, several new uses for calcium have been introduced. Small amounts have been found to be of value in the lead used in storage batteries; it is used in the production of steel, nickel, magnesium, aluminum, and other metals to remove impurities; in the purification of lead; as an alloying metal to improve the quality of magnesium and aluminum; to remove the last traces of oxygen and nitrogen in the production of high vacua; and in bearing metals, such as *Frary metal.*

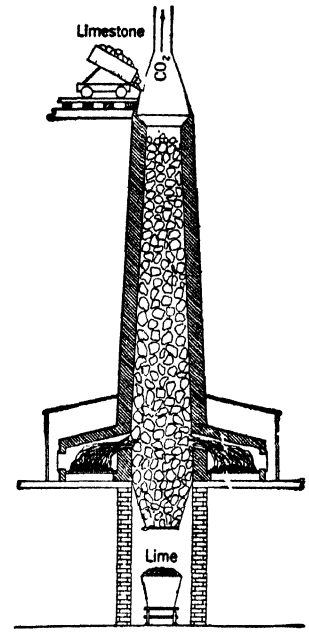


Figure 267. Lime Kiln

COMPOUNDS OF CALCIUM

7. Calcium Oxide (CaO)

This is the substance commonly called *quicklime.* It is produced commercially by the calcination of limestone:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

Since this reaction is reversible, the carbon dioxide must be removed rapidly in order that the decomposition of the limestone may be complete. Therefore, the reaction is carried out in a continuous current of air, which sweeps the carbon dioxide away from the solid materials as rapidly as it is formed.

Lime is made commercially in *kilns,* which are large chimney-like furnaces about 60 feet in height and 10 to 15 feet in diameter. They may be either "straight up and down," or they may have a bowl two thirds of the way down with tapering walls both above and below. Limestone is dumped in at the top, and the lime is drawn off into cars at the bottom. Heat for the calcination is supplied by fire boxes near the bottom. These open directly into the kiln and provide a draft which draws in air at the bottom of the kiln to aid in removing the carbon dioxide. Coal is the usual fuel employed in the lime kiln, but wood or gas is sometimes used. The temperature at which the carbonate is decomposed is around 1000° C. Very high temperatures produce "dead-burned" lime, which is relatively inert, probably because of the fusion of the silicates contained in the stone or made by the reaction of the lime with silica. Lime is also produced in rotary kilns, similar to those used in the cement industry (page 475). Powdered coal or gas is used as fuel in these kilns.

8. The Properties and Uses of Lime

Commercial lime may be slightly brown or yellow in color due to the presence of iron compounds and other substances. The pure oxide is a white, amorphous substance. It melts at about 2570° and boils at 2850°. When heated to a high temperature it emits brilliant light, called *lime-light.* Freshly prepared lime reacts

vigorously with water to form the hydroxide and to liberate heat in large quantities. This reaction is called *slaking*, and in commercial practice the hydroxide is called *slaked lime* or *hydrated lime*.

$$CaO + H_2O \longrightarrow Ca(OH)_2.$$

Since it combines readily with water, calcium oxide is often used as a drying agent for ammonia, and certain other gases and liquids. A mixture with sodium hydroxide (solid) is called *soda-lime*, which is used to dry air or other gases and, at the same time, to remove carbon dioxide from them. When quicklime is left exposed to the air for some time, it absorbs water from the air to form the hydroxide and carbon dioxide to form calcium carbonate. *Air-slaked* lime is practically worthless.

Other uses of lime include the following: as a flux in the smelting of many ores of the metals; in the manufacture of glass; as a polishing powder (Vienna lime); and in the production of calcium carbide, calcium cyanamide, and other compounds of calcium.

9. Calcium Hydroxide ($Ca(OH)_2$)

If heated to 450–500°, the hydroxide decomposes into water and calcium oxide. Calcium hydroxide is a white, powdery substance. Contrary to the general rule, its solubility in water increases as the temperature decreases. At 10° 1.76 g. and at 100° 0.8 g. dissolve in a liter of water.

Calcium hydroxide has many uses. It is a moderately strong base, and because of its low cost it is often used when a base is required. For this purpose a solution in water (limewater), or a suspension of the solid in water, can be employed. The following are some of the most important commercial applications of this substance: The production of ammonia, sodium hydroxide, bleaching powder, and insecticides, such as lime-sulfur sprays; the treatment of acid soils; the removal of hair from hides in making leather; the softening of water; the production of mortar, plaster, stucco, and similar structural materials; and the manufacture of cement, whitewash, and other materials.

10. Mortar

This material is made by mixing about one part of calcium hydroxide (slaked lime) with three parts of sand and adding enough water to make a thick, pasty mass. The hardening of mortar is due to several changes: (1) The water evaporates; (2) carbon dioxide is absorbed from the air and forms calcium carbonate; (3) there is also a slow reaction which forms calcium silicate. The sand makes the mortar more porous and prevents undue shrinkage upon drying. Mortar may also contain cement. It is used to hold in place various structural materials, such as stone, brick, tile, concrete blocks, etc.

11. Plaster

At one time the interior walls of buildings were covered with plaster made from calcium hydroxide, sand, and hair, with a "finish coat" of pure slaked lime. Most of the plaster which is used today is composed principally of plaster of Paris, $(CaSO_4)_2.H_2O$. *Stucco* is plaster which is used to cover the outside walls of buildings. It is composed of sand and a mixture of lime and cement to bind the grains of sand together.

12. Calcium Carbonate ($CaCO_3$)

This is the most abundant calcium compound found naturally. It has two crystalline forms, both of which are found in the earth: *Calcite*, the more stable form, and *aragonite*. The most familiar form of calcium carbonate is limestone. This occurs as stratified layers of rock, which have been formed by the deposition of calcium carbonate on the floors of seas. Subsequent

geological changes have elevated the deposits above the surface of the water and have converted them into hard masses. Other deposits of sandstone and shale may later have been deposited upon the limestone, which is often found below strata of these rocks. Limestone is never pure calcium carbonate. Its color may be white, yellow, brown, blue, gray, or black because of impurities. Almost all limestones contain some magnesium carbonate, clay, sand, and compounds of iron and aluminum. Some contain considerable quantities of organic material. The fossil remains of various shell creatures of the seas from which the deposit was formed are very often found in the rock.

Other natural forms of calcium carbonate are: *Chalk; marl*, a mixture of calcium carbonate and clay; *Iceland spar*, which is practically pure calcite; *marble*, which has been made from limestone under the influence of heat and high pressures, and which is composed of small crystals of calcite; *pearls; coral; shells; stalactites* and *stalagmites*, which are deposits formed upon the roofs or floors of caves by the water which seeps into the cave from above and which contains calcium bicarbonate in solution; and *aragonite*.

A large part of the limestone quarried in the United States each year is used in building macadamized roads and concrete structures. Large quantities are also used as building stone. It is also used to neutralize the acids in soils; as a flux; and in the manufacture of glass, cement, lime, and many calcium compounds. *Whiting*, finely ground and carefully cleaned chalk, is used in polishes, pigments, and putty. Some dental preparations contain *precipitated chalk*.

13. Calcium Bicarbonate ($Ca(HCO_3)_2$)

Calcium carbonate is only slightly soluble in water. It dissolves much more readily in water that contains carbon dioxide in solution, because of the conversion of the insoluble normal carbonate into the more soluble acid carbonate.

$$CaCO_3 + H_2O + CO_2 \rightleftarrows Ca(HCO_3)_2.$$

The addition of H^+ ions from the carbonic acid reduces the concentration of $CO_3^=$ ion, because the two ions combine to form the slightly ionized bicarbonate ion, HCO_3^-. The reduction in the concentration of the carbonate ion causes more calcium carbonate to dissolve.

The water which falls as rain contains carbon dioxide, which is dissolved from the air. Surface waters also dissolve carbon dioxide from soils where it is produced by slow oxidation and decay of organic materials. When these waters come into contact with limestone rocks in the earth, the stone disappears due to the reaction described above. This is an important factor in the formation of caves in limestone regions. If this water finds its way through the rocks into a cave, the water slowly evaporates, carbon dioxide is liberated, and calcium carbonate is deposited. If this deposit accumulates at a point on the cave's ceiling, where drops of solution seep through, the formation is called a *stalactite*. If it is built up by drops falling at some point on the floor, it is called a *stalagmite*.

Calcium bicarbonate is converted very readily into the normal carbonate, when a solution in which it is dissolved is heated to boiling.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2 \uparrow.$$

14. Calcium Chloride

Calcium chloride is a by-product of the Solvay process (page 244). It is best known in the laboratory as the hexahydrate, $CaCl_2.6\,H_2O$. When heated, the hexahydrate loses water and forms a porous, very deliquescent material containing the monohydrate, $CaCl_2.H_2O$, possibly other hydrates, and some calcium oxide. It is used as a drying agent for gases and organic

liquids because of its tendency to react with water. When heated to a higher temperature the monohydrate is changed to the anhydrous salt. During dehydration some calcium oxide is produced by hydrolysis:

$$CaCl_2 + H_2O \longrightarrow CaO + 2\,HCl\uparrow .$$

This causes the anhydrous salt, as it is usually prepared, to have an alkaline reaction.

Calcium chloride is used to prevent dust upon highways. Because of its deliquescence the salt removes water from the air and forms a solution, which is very highly concentrated and which, therefore, has a very low aqueous vapor pressure and does not readily evaporate. It is also used in the manufacture of cement and in curing concrete, since it prevents such materials from drying out too quickly. A solution of calcium chloride in water serves as an excellent brine for use in cold storage and refrigerating plants. A mixture freezing as low as $-55°$ can be prepared by dissolving the hexahydrate in water.

15. Calcium Sulfate ($CaSO_4$)

This substance occurs in nature as *gypsum*, $CaSO_4.2\,H_2O$. The anhydrous form of calcium sulfate occurs as the mineral *anhydrite*. *Alabaster*, *satin spar*, and *selenite* are crystalline forms of the dihydrate. Gypsum occurs in extensive deposits in New York, Ohio, Iowa, Michigan, Texas, Colorado, Utah, California, Oklahoma, and Nevada. Our common crayon (chalk) is made from it. It is also used in cement to retard the rate of setting, in certain fertilizers, in some paints, and in paper. In fertilizers it converts ammonium carbonate into ammonium sulfate, which is more stable than the carbonate and, therefore, allows more ammonia to be retained in the soil. Anhydrous calcium sulfate is used as a drying agent for gases and organic liquids.

Plaster of Paris is made by partially dehydrating gypsum at a temperature of about 130°. The product is $(CaSO_4)_2.H_2O$. When this substance is mixed with water it is converted quickly once again into the dihydrate, $CaSO_4.2\,H_2O$. Because of its rapid rate of setting and its tendency to expand as it solidifies, plaster of Paris is used in making surgical casts, models, molds, statuary, etc. Its most important use is in the manufacture of plaster for covering the interior walls of buildings. These plasters may also contain lime. *Stucco* may be made from plaster of Paris and glue, which acts as a binding agent. *Wall board* is made from a mixture of plaster of Paris and wood pulp, or by binding sheets of paper together with layers of plaster of Paris.

16. Calcium Sulfite and Bisulfite

Calcium sulfite, $CaSO_3$, is only slightly soluble and is produced as a white precipitate when a solution of any soluble sulfite is mixed with a solution containing calcium ion. The acid sulfite, or bisulfite, $Ca(HSO_3)_2$, is soluble and, therefore, the normal sulfite of calcium dissolves when treated with sulfurous acid — a solution containing sulfur dioxide and water. Calcium sulfite is produced by treating a suspension of calcium hydroxide in water with sulfur dioxide, or by passing sulfur dioxide over wet limestone:

$$(Ca^{++} + 2\,OH^-) + H_2SO_3 \longrightarrow CaSO_3\downarrow + 2\,H_2O.$$

or, in the presence of an excess of SO_2,

$$(Ca^{++} + 2\,OH^-) + 2\,H_2SO_3 \longrightarrow (Ca^{++} + 2\,HSO_3^-) + 2\,H_2O.$$

$$CaCO_3 + 2\,H_2SO_3 \longrightarrow (Ca^{++} + 2\,HSO_3^-) + 2\,H_2O + CO_2\uparrow .$$

Calcium bisulfite is used extensively in the manufacture of paper (page 433).

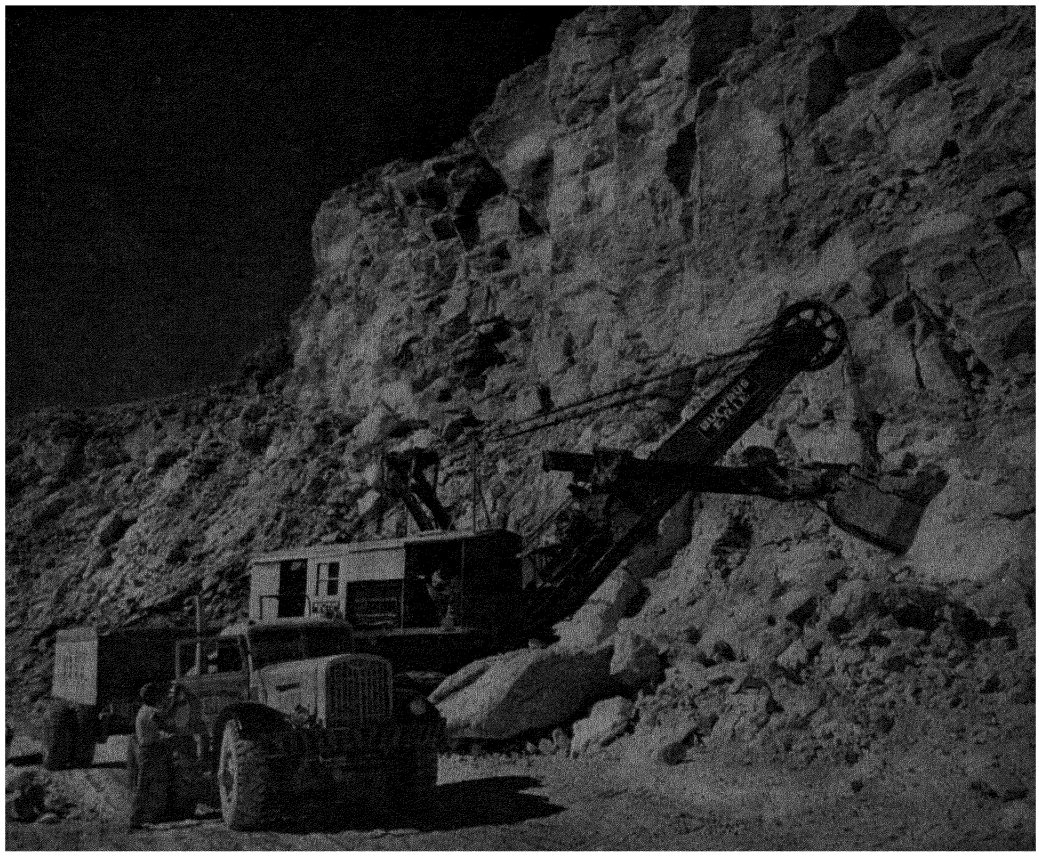


Figure 268. Gypsum Quarry
(Courtesy of United States Gypsum Company)

17. Other Compounds of Calcium

The carbide, cyanamide, and phosphates of calcium have been discussed in other portions of this book. Other important compounds of this element include the nitrate, $Ca(NO_3)_2$, which is used as a fertilizer; calcium hypochlorite and bleaching powder; calcium acetate, from which acetone is prepared; calcium chlorate $Ca(ClO_3)_2$, which is used to kill weeds; calcium oxalate, CaC_2O_4 (page 422); calcium sulfide, CaS, and persulfides, such as CaS_4; calcium silicate, $CaSiO_3$, which is the mineral known as wollastonite; calcium tungstate, $CaWO_4$, which is used in making luminous paint; calcium borates, which are found in California and from which borax may be made (page 394); and calcium fluoride (page 265).

18. Hard Water

Although the bicarbonate of calcium, $Ca(HCO_3)_2$, is the most common substance found in "hard" water, it is not the only substance that is present in such waters. Magnesium bicarbonate may be produced in the same manner as calcium bicarbonate and causes similar losses of soap in the laundry (page 425) and produces scale when the water in which it is dissolved is used to generate steam in boilers. Both of these substances produce *temporary hardness*, or *carbonate hardness*, of water, which is given this name because the hardness may be

overcome by boiling the water. In boiling water the bicarbonates are converted into normal carbonates which are insoluble, and hence, as these precipitate the magnesium and calcium ions are removed from the solution.

Calcium sulfate, magnesium sulfate, and smaller amounts of other salts, such as the chlorides of calcium and magnesium are responsible for the *permanent hardness*, or *noncarbonate hardness*, of water. The metallic ions of permanently hard water cannot be removed by boiling. Instead, substances must be added to convert calcium and magnesium ions into insoluble compounds.

The following materials are examples of substances that are widely used to soften water:

(1) *Sodium Carbonate.* This substance, by supplying carbonate ion, causes the precipitation of calcium as the very slightly soluble carbonate, thus relieving permanent hardness.

(2) *Calcium Hydroxide.* A suspension of milk of lime converts the bicarbonate into the normal carbonate but has little or no effect upon calcium sulfate or chloride. It also converts soluble magnesium salts, such as the chloride or sulfate, into the slightly soluble hydroxide.

$$HCO_3^- + OH^- \longrightarrow H_2O + CO_3^{=}.$$
$$Mg^{++} + 2\,OH^- \longrightarrow Mg(OH)_2 \downarrow .$$

A solution of ammonia ($NH_4^+ + OH^-$) is used sometimes in a similar manner.

(3) *Trisodium Phosphate*, Na_3PO_4. This salt hydrolyzes to form an alkaline solution in which the hydroxyl ions convert bicarbonate into carbonate ions. The phosphate ion precipitates calcium and magnesium as phosphates, both of which are slightly soluble.

(4) *Zeolites and Permutite.* The zeolites (page 393) are naturally occurring sodium aluminum silicates, which, for convenience, may be represented by the formula $NaAlSiO_4$, although the zeolites contain several

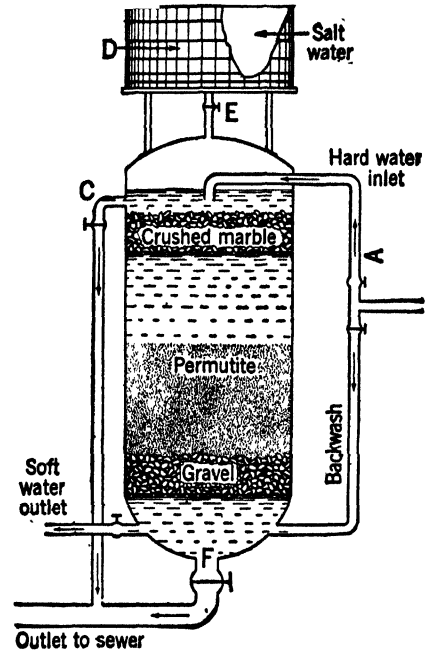


Figure 269. The Permutite Water Softener

The water to be treated enters through A. Brine for the regeneration of the permutite is stored in D, flows into the permutite chamber through E, and out as waste through F.

rather complex compounds. Permutite is a manufactured product of about the same nature. When water containing calcium or magnesium ions in solution passes slowly through layers of this material, the sodium in the zeolite is replaced by calcium or magnesium, and the water is freed of the latter:

$$2\,NaAlSiO_4 + Ca^{++} \longrightarrow 2\,Na^+ + Ca(AlSiO_4)_2 \downarrow$$

This process of water softening can be operated continuously, since the calcium aluminum silicate can be reconverted into the sodium compound by treating the zeolite, after it has been used for some time, with a concentrated solution of sodium chloride:

$$Ca(AlSiO_4)_2 + 2\,Na^+ \longrightarrow Ca^{++} + 2\,NaAlSiO_4.$$

The reversal of the reaction depends upon the use of a solution containing a high con-

centration of sodium ion. The material which has been thoroughly washed with the brine is washed with pure water and is then ready to be used over again in softening more water. This process is used in laundries, in homes, and elsewhere to soften water that is too hard to be used without great waste of soap and the undesirable effects accompanying the formation of calcium and magnesium soaps as deposits upon clothing. It relieves both permanent and temporary hardness.

(5) Other substances that are used in water softening are sodium silicate, sodium fluoride, borax, and sodium hexametaphosphate. The last named of these compounds is said to form calcium and magnesium compounds which, although soluble, do not react with soap.

19. Cement

When we think of cement, we have in mind, usually, the material known as *hydraulic cement* or *Portland cement*, which is one of the most important of structural materials. *Concrete* is the name applied to the hardened mass that forms when a mixture of sand, crushed stone, cement, and water is poured into "forms" and allowed to stand. If steel wire, cables, or rods are placed in the mixture to become embedded in the solid structure, reinforced concrete is produced.

Portland cement is produced from a mixture of limestone, or marl, and clay or shale. These substances are finely ground and mixed. The mixture is then heated or "burned" in a rotary kiln (Figure 270). At the lower end of the kiln, heat is supplied by burning gas or powdered coal, and the ground raw materials are fed in from a hopper at the upper end. The material moves slowly down through the kiln, which is inclined, and at the lower end is heated to a temperature of about 1500°. The powdered materials are partially fused and pass out of the lower end of the kiln in the form of small lumps, known as *clinker*. The material is then cooled and, finally, is ground to a powder. About 3 per cent of gypsum is ground with it to retard the rate of setting. Unless some retarding agent is used, the cement may harden before it is placed in position.

During the formation of the clinker, certain chemical reactions occur. These produce, essentially, tricalcium silicate, $Ca_3SiO_5((CaO)_3.SiO_2)$; dicalcium silicate, $Ca_2.SiO_4((CaO)_2.SiO_2)$; and calcium aluminate, $Ca_3(AlO_3)_2((CaO)_3.Al_2O_3)$. The reactions occurring during the hardening of cement are very complex and not completely understood. Two kinds of reactions, however, are known to occur, namely, hydration and hydrolysis. The hydration of the compounds in cement produces

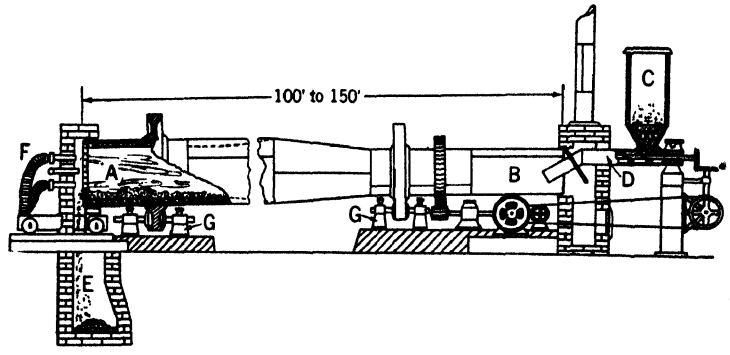


Figure 270. Cement Kiln

The raw materials are fed into the kiln (B) from the hopper (C). Powdered coal and air are blown into the lower end of the kiln through F. Clinker falls out of the kiln at A into the receiver E. The kiln is rotated by means of the gears G.

crystals. Hydrolysis produces gelatinous compounds, such as silicic acid and aluminum hydroxide, which gradually harden and firmly cement the crystals. Since all of the substances formed as the cement sets are insoluble in water, cement will harden in water, although the set occurs best in the air.

The normal annual production of Portland cement in the United States is approximately 165,000,000 barrels. The table below shows its average composition in terms of the oxides of the elements:

COMPOSITION OF PORTLAND CEMENT

Constituent *	Average percentage
Silica, SiO_2	22.5
Alumina, Al_2O_3	7.5
Ferric oxide, Fe_2O_3	3.5
Lime, CaO	62.5
Magnesia, MgO	2.5
Oxides of Sodium and Potassium (Na_2O and K_2O)	1.5

* Composition is expressed in terms of acidic and basic oxides, but it should be understood that these are combined in the form of silicates and aluminates.

MAGNESIUM

20. Occurrence

Magnesium occurs in *magnesite*, $MgCO_3$; *dolomite*, $CaCO_3.MgCO_3$; *talc*, $H_2Mg_3(SiO_3)_4$ *asbestos*, $CaMg_3(SiO_3)_4$; *meerschaum*, a hydrated magnesium silicate; and *spinel*, magnesium aluminate. Magnesium chloride and magnesium sulfate occur in sea water and in salt deposits as carnallite, polyhalite, langbeinite, and similar minerals.

21. Production of Metallic Magnesium

Magnesium is produced by several different methods. More and more of the production is coming from the sea. The magnesium ion in sea water is first precipitated as $Mg(OH)_2$ by treatment with $Ca(OH)_2$. The precipitate is removed by filtration and converted into the chloride by adding HCl. Pure magnesium chloride, actually $MgCl_2.H_2O$, is then produced by fractional crystallization; it is then dried and fused with a mixture of sodium, potassium, and sometimes calcium chlorides, and the mixture of the fused salts is electrolyzed. The iron vessel that holds the mixture acts as the cathode, and a carbon rod suspended in the bath acts as the anode. Salts of the other metals are added to lower the melting point of the bath and to make it a better conductor. Magnesium is liberated at the cathode and rises to the surface where it is protected from the air by a layer of the salts.

Magnesium is also produced by the electrolysis of a mixture containing magnesium oxide dissolved in fused magnesium fluoride to which are added fluorides of other metals, usually sodium and barium. Because of the great demands for magnesium in the production of alloys, other sources of this metal and other methods of producing it have, within recent years, come into use. Ferrosilicon is used to reduce magnesium oxide made by burning magnesite or dolomite:

$$4\ MgO + Si \longrightarrow 2\ Mg + Mg_2SiO_4$$
$$2\ (MgO.CaO) + Si \longrightarrow 2\ Mg + Ca_2SiO_4.$$

The iron of ferrosilicon plays no part in the reaction. The magnesium is distilled and condensed to separate it from the residue. On a small scale, magnesium can be produced by reducing the anhydrous chloride with sodium.

22. Properties and Uses of Magnesium

Magnesium has a density of 1.74 g. per cc. It is like silver in appearance, and is stronger than aluminum. It is relatively soft, can be cast and rolled, and is easily cut and worked by tools and lathes.

It does not react readily with oxygen at low temperatures because of the formation of a thin coating of oxide on its surface. This coat protects the metal from further oxidation. It is used in the manufacture of signal flares, star shells, incendiary

bombs, and flash light powders; to remove gases from radio tubes; to deoxidize and to remove nitrogen and sulfur from certain metals, such as copper and nickel alloys; and in the production of various magnesium alloys, which, although light, are very strong, resistant to corrosion, easily machined, and good conductors of heat. Added to aluminum it forms the alloys called *magnalium*, *duralumin*, and Dow metal which are light and possess high tensile strength. Such metals as these alloys are now widely used in airplane construction, in the pistons of motors, and elsewhere to secure lightness in bulky structures and devices without loss of strength. Magnesium is, commercially, by far the most important of the metals of this family. The producing capacity of the United States has been estimated as about 725,000,000 pounds, or more than 100 times the production of 1939.

COMPOUNDS OF MAGNESIUM

23. Magnesium Oxide and Magnesium Hydroxide

The oxide of magnesium is called *magnesia*. It is produced by burning the metal in the air or by the decomposition of the carbonate at 700–800°. The latter method is most often used, because the carbonate decomposes very readily upon heating, more readily than calcium carbonate, and produces a light, fluffy powder. The oxide reacts with water less readily and less vigorously than the oxide of calcium, which it resembles in general properties. It has a high melting point — about 2800° — and, therefore, is used to make fire brick and crucibles and as a lining of furnaces. It is also used in certain kinds of stucco, cement, and other building materials. Magnesia produced by heating magnesite at a temperature of about 1,400° is inactive, dense, and a poor conductor of heat. It is used as a heat insulator in covering hot water, steam, and hot air pipes.

A mixture of the light form of magnesium oxide with a solution of magnesium chloride sets to a hard mass. This mixture is called a *Sorel cement*, or magnesia cement. When mixed with fillers such as asbestos, sawdust, talc, or kieselguhr, this cement is used as a flooring material and as stucco. Magnesium oxide is also used in tooth powders and toilet preparations.

The hydroxide is less soluble and less basic in character than calcium hydroxide. It is precipitated when a soluble hydroxide is added to a solution containing magnesium ion. The precipitate dissolves in a solution containing ammonium ion, which reduces the concentration of the hydroxyl ion (page 331).

Milk of magnesia is the name given to a suspension of the hydroxide in water. This suspension is used in medicine as a laxative and as an anti-acid.

24. Magnesium Carbonate

Like calcium, magnesium forms a slightly soluble normal carbonate, $MgCO_3$, and a soluble bicarbonate, $Mg(HCO_3)_2$. When sodium carbonate is mixed with a solution containing magnesium ion, there is formed a light precipitate of basic magnesium carbonate,

$$3\ MgCO_3.Mg(OH)_2.3\ H_2O,$$

sometimes called *hydromagnesite*, *85 per cent magnesia*, and *magnesia alba*. It is usually made by the reaction of carbon dioxide with milk of magnesia. It is used as a heat insulator, as a filler in rubber, in dental and toilet preparations, and in medicine.

25. Magnesium Silicates

Several silicates containing magnesium are important natural products. The most important of these is *asbestos*, which because of its fibrous structure and general inert character, is used for insulation, shingles, brake bands in automobiles,

packing, fireproof theater curtains, and gaskets. Mixed with asphalt it is used in some kinds of roofing materials, and with cement it forms a resistant material that is used instead of slate or soapstone for the tops of laboratory desks, laundry tubs, etc. Most of the asbestos used in this country comes from Canada. Chemically, asbestos is a calcium-magnesium salt of metasilicic acid.

Talc and soapstone are both hydrated magnesium silicates, but the latter is harder and more compact than the former. Talc is soft and unctuous. It is used in toilet powders and in paper. Soapstone is used to make laboratory table tops, sinks, switchboards, etc. Meerschaum and serpentine are other hydrated magnesium silicates.

26. Other Compounds of Magnesium

Magnesium sulfate occurs naturally as *kieserite*, $MgSO_4.H_2O$, and *epsomite*, $MgSO_4.7\ H_2O$. The latter, in a pure form, is known as *Epsom salts*. It is found in many mineral waters, in salt deposits, and in the mother liquor left after salt is removed from sea water or from the brines of salt wells. It is used in medicine as a purgative; in weighting cotton and silk; in sizing paper; in fireproofing fabric; in compounding artificial mineral waters; and in making soaps, paints, and leather.

Magnesium chloride is found in sea water, in salt brines, and in salt deposits. One of the important minerals of the Stassfurt deposits is *carnallite* ($MgCl_2.KCl.6\ H_2O$), from which magnesium chloride may be obtained as a by-product of the recovery of potassium chloride. The salt crystallizes from aqueous solutions as the hexahydrate, $MgCl_2.6\ H_2O$. Upon heating, this hydrate does not form the anhydrous salt, but reacts to form hydrochloric acid and magnesium oxide:

$$MgCl_2 + H_2O \longrightarrow MgO + 2\ HCl\uparrow\ .$$

This reaction has been suggested as a means of producing hydrochloric acid. Magnesium oxide and magnesium chloride form the basic salt, $MgO.MgCl_2$, which is the essential principle of *Sorel cement*. This material is used to produce a substitute for tile in covering walls and floors. Magnesium chloride is also used in fireproofing wood and in the manufacture of certain disinfectants, magnesium metal, and other compounds of magnesium.

Ammonium magnesium phosphate, NH_4MgPO_4, is a slightly soluble crystalline solid, which is formed in certain tests for magnesium ion or phosphate ion in a solution. It is formed in a solution containing Mg^{++} ions when ammonium hydroxide and a solution containing a soluble phosphate are added.

BARIUM

27. Occurrence

The compounds of barium are much less abundant than those of calcium and magnesium but more abundant than those of strontium. The principal ore of barium is *barite*, $BaSO_4$, sometimes called *heavy spar*. This mineral is the source of most of the compounds of barium. *Witherite*, $BaCO_3$, also occurs in several regions. Missouri and Georgia furnish most of the barium ore used in the United States.

28. Production of the Metal

Metallic barium is usually produced by the electrolysis of fused barium chloride or by the reduction of a mixture of barium oxide and barium peroxide by aluminum in a special type of vacuum furnace that is electrically heated.

29. Properties and Uses

Metallic barium is used in the manufacture of radio tubes to remove the gases that remain after the tubes have been evacuated and to remove oxygen in the refining of copper. It is also used in several

alloys, one of the most important of which is *Frary metal*, a bearing metal that contains also lead (98%) and some calcium. An alloy of barium and nickel is used in radio tubes and in spark plugs because it readily emits electrons when it is heated.

Barium is a silvery white metal. It is almost as soft as lead. It combines readily with oxygen, even igniting spontaneously in moist air. It is much more active than beryllium, magnesium, and calcium and slightly more active than strontium.

30. Barium Oxide, Peroxide, and Hydroxide

The oxide of barium may be prepared by decomposing the carbonate, which occurs in nature as the mineral *witherite*. This decomposition is much more difficult to effect than the decomposition of calcium carbonate. A temperature of approximately 1400° must be used to produce the oxide rapidly.

$$BaCO_3 \rightleftarrows BaO + CO_2 \uparrow .$$

The reaction can be carried out at lower temperatures, by mixing finely divided carbon with the barium carbonate before it is heated. The carbon aids the reaction by converting the carbon dioxide as it is liberated into carbon monoxide.

When heated at 500°–600° in a current of air, barium oxide combines with oxygen to form *barium peroxide*, BaO_2. If the barium peroxide is then heated to 700°–800°, the reaction is reversed, and pure oxygen is liberated. This is the basis of Brin's process once used for producing oxygen. Barium peroxide may also be used to produce hydrogen peroxide (page 191).

Like quicklime, the oxide of barium is "slaked" by the addition of water. The hydroxide, $Ba(OH)_2$, is formed. The hydroxide may also be produced by treating barium carbonate with superheated steam. It dissolves to a greater extent (37 g. per liter at 18°) in water than the hydroxides of the other alkaline earth metals, and the solution (0.1N) is apparently ionized to the extent of 77 per cent of the hydroxide. It is therefore a moderately strong base. The solution, which is called *baryta water*, is used in certain analytical procedures in the chemical laboratory. When so used, it must be carefully stored out of contact with air in order that it may not absorb carbon dioxide, which reacts with the hydroxide to form the insoluble barium carbonate.

31. Barium Sulfate and Barium Sulfide

Since barium sulfate is the mineral in which barium occurs most abundantly, it is frequently used to produce other barium compounds. The sulfate is only slightly soluble even in acids. To convert it into the chloride or nitrate of barium, the sulfate must first be changed into a compound that will dissolve in solutions of HCl or HNO_3. The sulfate, first, is fused with sodium carbonate (page 462) to form barium carbonate, or it is reduced, by heating it with carbon, to barium sulfide:

$$BaSO_4 + 4\,C \longrightarrow 4\,CO + BaS.$$

The carbonate or the sulfide is then dissolved in hydrochloric or nitric acid to produce the chloride or nitrate of barium. These salts are then crystallized by the evaporation of the water from the solution.

Barium sulfide reacts with zinc sulfate to form barium sulfate and zinc sulfide, both of which are slightly soluble salts:

$$BaS + ZnSO_4 \longrightarrow BaSO_4 \downarrow + ZnS \downarrow .$$

This reaction is the basis of the production of *lithopone*, a mixture of $BaSO_4$ and ZnS, which is used in paint. In addition to possessing excellent "covering power," lithopone has certain other advantages over white lead in paint. It is not poisonous, and it is not blackened by hydrogen sulfide, which converts the white lead of "lead" paints into black lead sulfide.

Barium sulfate is used in the manufacture of white paint in a form called *per-*

manent white. It is also used as a filler in rubber, oil cloth, linoleum, and paper. Paper that has been filled with this salt is relatively heavy. Barium sulfate is opaque to X-rays and, therefore, is used in making X-ray photographs of the intestinal tract. It is insoluble and, hence, non-poisonous.

Barium sulfate is produced in the detection and quantitative estimation of either barium or sulfate ions. Because it is only very slightly soluble in water, barium sulfate is precipitated whenever barium chloride or nitrate is added to a solution containing a soluble sulfate, or when sodium or ammonium sulfate is added to a solution, containing barium ion. This precipitate is, unlike other precipitates containing barium, insoluble in hydrochloric acid. It may be separated by filtration, dried, and weighed as a quantitative measure of the quantity of sulfate ion or barium ion in the sample.

32. Other Salts of Barium

Certain other salts of barium have minor uses. The nitrate and chlorate are used to produce green colors in fireworks and signal lights of various kinds. The carbonate is used as a rat poison. The chloride is sometimes used to remove the sulfate which is present in sodium chloride as sodium or magnesium sulfate. Barium fluosilicate is used as an effective insecticide.

STRONTIUM

33. Strontium occurs in the minerals *celestite*, $SrSO_4$, and *strontianite*, $SrCO_3$. It is produced as the metal by the same method as calcium, namely by the electrolysis of its fused chloride.

Strontium hydroxide is a moderately strong base and dissolves to a considerable extent in hot water. It is used sometimes in sugar refineries to remove cane sugar from molasses. With sucrose, strontium hydroxide forms an insoluble compound which can be separated by filtration from the invert sugar and other non-crystallizing sugars of molasses. The precipitate is then treated with carbon dioxide, which precipitates the strontium as the carbonate and liberates pure sucrose.

A few compounds of strontium, including the bromide and iodide, are used in medicine. The most important use of strontium compounds is in fireworks, flares, fuses, and other lights, to which the strontium gives a red color. Strontium nitrate is most often used for this purpose.

The separation of calcium and strontium in analytical chemistry is difficult because their compounds dissolve in water to about the same extent. The most widely used method of separation involves the precipitation of strontium as the sulfate, since calcium sulfate is much more soluble than strontium sulfate. If a saturated solution of calcium sulfate is added to a solution containing Sr^{++} and Ca^{++}, there is, of course, no probability that $CaSO_4$ will be precipitated, since it is a solution of that substance that is added. This solution, however, contains a sufficient concentration of $SO_4^{=}$ ions to exceed the solubility product of $SrSO_4$, even in solutions containing only a small concentration of Sr^{++} ion.

$$\text{Solubility product} = [Sr^{++}] \times [SO_4^{=}] = 0.00000028$$

$$\text{Solubility product} = [Ca^{++}] \times [SO_4^{=}] = 0.0002$$

BERYLLIUM

34. The most important mineral containing this element is *beryl*, $Be\,Al_2\,(SiO_3)_6$. When this mineral contains chromium it is green and is called *emerald.*

Beryllium can be produced by reducing its chloride with sodium, but it is usually made by converting beryl into the chloride, which then is mixed with chlorides of the alkali metals and electrolyzed. The metal

is very hard and has a bright luster. It is difficult to produce, expensive and, therefore, is used only to a limited extent, largely in the production of alloys to which it adds lightness, hardness, and strength. Copper-beryllium alloys containing about one per cent of beryllium are used to make springs of remarkable resiliency and resistance to fatigue. An alloy containing beryllium and nickel is used in airplane motors. Beryllium is also used in some kinds of non-rusting steels.

RADIUM

35. Up to 1925, most of the radium produced in the world came from the mineral *carnotite* which was mined in Colorado and Utah. Some 150 tons of ore were required to produce one gram of radium, which was valued at $100,000. In 1925, much richer ores were found in the Belgian Congo. More recently, Canada has become an important producer. Because of the greater yield from these sources the price of radium has dropped to about $25,000 per gram. Radium is produced at the rate of about 100 g. per year, and the total quantity produced up to this time amounts to about two kilograms which in the form of radium salts is owned by university and industrial laboratories, hospitals, and clinics. These compounds, and also radon, are used in the treatment of cancer. Artificially produced radioactive isotopes are similarly used. Traces of radium bromide, or of other radioactive substances, are mixed with zinc sulfide and salts of certain metals such as copper, in the manufacture of luminous paints.

Chemically, radium and its compounds closely resemble barium and its compounds. In general, barium is slightly less active than radium, and the salts of barium are more soluble.

36. Tests for the Alkaline Earth Metals

If ammonium carbonate and ammonium chloride are added to a solution containing Mg^{++}, Ca^{++}, Sr^{++}, and Ba^{++} ions, the carbonates of calcium, strontium, and barium are precipitated and removed by filtration. The addition of NH_4^+ ions prevents the precipitation of magnesium carbonate or basic magnesium carbonate, because the ammonium ion decreases the concentration of the OH^- and $CO_3^=$ ions and prevents the solubility product of the magnesium compound from being exceeded. Magnesium can be detected by adding a solution containing the phosphate ion to the filtrate (page 478).

The residue containing the carbonates of the other three metals is dissolved in acetic acid, thus forming the acetates of calcium, strontium, and barium. From this solution barium is precipitated as yellow $BaCrO_4$ by adding a solution of potassium dichromate. This precipitate is removed by filtration. The filtrate contains strontium and calcium ions. A saturated solution of calcium sulfate is added to one portion of this solution; if strontium is present, a white precipitate of $SrSO_4$ will slowly form (page 480). If strontium is present, it is precipitated as $SrSO_4$ by adding a solution of ammonium sulfate to the second portion of the filtrate from which barium has been removed. The strontium sulfate is removed by filtration; the filtrate is made alkaline by the addition of ammonium hydroxide; and a solution of ammonium oxalate, $(NH_4)_2C_2O_4$, is added. If calcium ion is present, a white, crystalline precipitate of CaC_2O_4 is formed.

This scheme of analysis depends upon differences in the solubilities of the chromates, sulfates, and oxalates of calcium, strontium, and barium.

REVIEW EXERCISES

1. From what mineral sources are the alkaline earth metals and their compounds produced?
2. How do the hydroxides of the elements of this group compare with and how do they differ from the hydroxides of the alkali metals?
3. Compare the solubilities of the hydroxides, oxalates, sulfates, chromates, and carbonates of calcium, strontium, and barium. (See Solubility Products, Appendix.) How, in general, do the solubilities of the strontium

compounds compare with those of calcium and barium?

4. If you were to attempt to precipitate only calcium from a solution containing the three chlorides, $CaCl_2$, $SrCl_2$, and $BaCl_2$, which ion in the following list would you use? Chromate, oxalate, carbonate. Explain.
5. How would you convert the following substances one into another in the order indicated?

(*a*) $CaCO_3 \longrightarrow CaO \longrightarrow Ca(OH)_2 \longrightarrow Ca(NO_3)_2$.
(*b*) $Mg(HCO_3)_2 \longrightarrow MgCO_3 \longrightarrow MgCl_2$.
(*c*) $BaSO_4 \longrightarrow Ba(NO_3)_2 \longrightarrow BaCO_3 \longrightarrow BaCl_2$.

6. Explain why ammonium salts interfere in the precipitation of magnesium hydroxide. Would you expect ammonium salts to have a similar effect upon the precipitation of the hydroxides of calcium, strontium, and barium? Explain.
7. Why is barium sulfate almost insoluble in strong acids, while barium carbonate and barium chromate, which have approximately the same or smaller solubilities in water than the sulfate, dissolve readily even in dilute HCl?
8. The lime removed from a certain lime kiln during a day's run is 15 tons. Assuming that the rock is 95 per cent pure $CaCO_3$ and the remainder inert material, and that calcination is complete, what weight of stone is required to produce this quantity of lime and what (standard) volume of carbon dioxide is liberated?
9. Calculate the normality of saturated solutions of calcium hydroxide at 10° and 100°.
10. What substances are responsible for the hardness of water? Why are such waters objectionable?
11. Assuming equal transportation costs, 1 ton of lime can be shipped for the same price as 1 ton of calcium hydroxide (slaked lime). What weight of calcium hydroxide could be produced from this weight of lime? What is the advantage of shipping slaked lime instead of quicklime?
12. The solubility of calcium sulfate is 0.2 g. per 100 ml. of water at 18° C. What weight of soap must be used to precipitate the calcium ion in 10 liters of water, if the water contains 20 per cent as much calcium sulfate as a saturated solution and if the soap is pure sodium palmitate?
13. How does boiling affect temporarily and permanently hard waters?
14. How do the following substances react with the compounds present in hard water? Na_3PO_4, Na_2CO_3, $Ca(OH)_2$.
15. Compare the properties of magnesium and barium hydroxides.
16. In preparing lime from limestone, what is the advantage of building the kilns so that the carbon dioxide is removed rapidly?
17. In what respects does beryllium and its compounds differ from the other members of this group and their compounds?
18. How are metallic calcium and magnesium produced?
19. Refer to earlier chapters of this book and to this chapter. Make a list of as many uses of lime as you can find. These may be uses of quicklime or calcium hydroxide.
20. Using the solubility product principle, explain why limestone dissolves in water containing carbon dioxide.
21. Account for the presence frequently of calcium oxide in anhydrous calcium chloride.
22. Identify: Gypsum, plaster of Paris, permutite, milk of magnesia, magnalium, dolomite.
23. What is lithopone? How is it made and for what purpose is it used?
24. What weight of barium sulfate is contained in 1000 tons of lithopone?
25. Compare the volumes of hydrogen produced, under the same conditions, by the reaction of HCl with 10 g. each of calcium and magnesium.
26. Why can barium sulfate be precipitated from a solution of barium chloride by adding a saturated solution of calcium sulfate, while calcium sulfate cannot be precipitated by adding a saturated solution of barium sulfate to a solution of calcium chloride?
27. Barium occurs in nature as the sulfate and the carbonate. From which of these would it be easier to produce compounds, such as barium chloride and barium nitrate?
28. What is the composition of Portland cement? What reactions occur during its setting?
29. What effect, if any, would ammonium chlo-

ride have upon the solubility of calcium carbonate?

30. What is basic magnesium carbonate? How would you produce it from a solution of magnesium chloride? For what purposes is it used?

REFERENCES FOR FURTHER READING

Barium: *Ind. and Eng. Chem., News Edition,* **19,** 788 (1941); *Ind. and Eng. Chem.,* **27,** 1488 (1935); **32,** 568 (1940).

Beryllium: *Ind. and Eng. Chem.,* **28,** 1424 (1936); **30,** 501 (1938).

Calcium: *Trans. Amer. Electrochemical Society,* **66,** 63 (1934); **67,** 169 (1935); **68,** 293, 309 (1935); *Chem. and Eng. News,* **21,** 846 (1943).

Cement: *J. Chem. Ed.,* **6,** 1854 (1929); *Ind. and Eng. Chem.,* **26,** 669 (1934); **27,** 242, 638 (1935); *Chem. and Met. Eng.,* **46,** 629 (1939).

Gypsum: *J. Chem. Ed.,* **7,** 2788 (1930).

Lime: *Ind. and Eng. Chem.,* **20,** 415 (1928); *Chem. and Met. Eng.,* **27,** 347 (1922); **28,** 1066, 1088, 1112 (1924).

Magnesium: *Chem. and Met. Eng.,* **43,** 116 (1936); **45,** 478 (1938); **48,** 3–75, 9–91, 11–76, 140 (1941); **49,** 1–88 (1942); *Ind. and Eng. Chem.,* **27,** 1333 (1935); **28,** 383 (1936); **31,** 969 (1939); **32,** 1343 (1940); **33,** 932 (1941); *News Edition,* **19,** 222 (1941); **21,** 546 (1943); *J. Chem. Ed.,* **19,** 556 (1942).

Radium: *J. Chem. Ed.,* **3,** 757 (1926).

Water Softening: *Ind. and Eng. Chem.,* **16,** 621 (1924); **33,** 697, 1203 (1941); *J. Chem. Ed.,* **4,** 945 (1927); *Chem. and Met. Eng.,* **25,** 23 (1921); **27,** 1211 (1922); **28,** 862 (1923).

39

THE METALS OF THE B DIVISIONS OF GROUPS ONE AND TWO

COPPER

1. History and Occurrence

Copper was probably the first metal to be widely used by man. Its name is derived from Cyprus, an island from which it was obtained by the Romans. At first it was *cyprium*, but later it came to be called *cuprum*.

The most important deposit of native copper in the world is found in the Michigan peninsula around Houghton. The ores of copper include oxides, sulfides, and carbonates: *Chalcopyrite*, $CuFeS_2$, one of the most valuable ores; *chalcocite*, Cu_2S; *cuprite*, Cu_2O; *melaconite*, CuO; and *malachite* $Cu(OH)_2.CuCO_3$. Almost all countries produce some copper. Utah, Montana, Arizona, New Mexico, Tennessee, and Michigan produce about one-third of the two and one-half million tons of copper produced in the world each year. In recent years South America and Africa have become important producers of the metal.

2. Metallurgy

The metallurgy of copper is a fairly simple process when the metal occurs in the uncombined state. The ore is ground and some of the gangue, or earthy material, is washed away by a stream of water. The material is then heated until the copper melts, and a flux is added to form a fusible slag with the gangue. The liquid slag rises to the top and the heavier copper collects on the bottom.

Ores that contain copper in the form of the oxide, hydroxide, or carbonate may be leached with dilute sulfuric acid, which dissolves the compounds of copper, forming a solution of cupric sulfate. Dilute ammonium hydroxide may also be used. This causes the copper to pass into solution as the complex ion $(Cu(NH_3)_4^{++}$. The solutions obtained by leaching are then electrolyzed to precipitate the copper.

The sulfide ores, which are most important, must be smelted. Since these ores contain only a few per cent of copper-bearing compounds, they are first concentrated by grinding, washing with running water, and flotation. The ore is roasted to remove a portion of the sulfur, and then it is smelted in a reverberatory type of furnace. In smelting chalcopyrite, which contains a considerable amount of iron, sand is added to convert the iron into ferrous silicate, an easily fusible slag. If the ore contains an excess of silica and alumina (Al_2O_3), limestone is added as a flux. The product of the smelting furnace is a mixture of different metallic sulfides, particularly the sulfides of copper and iron. This mixture is called *matte*. It is mixed with coke and placed in a *converter*, which is made of steel and lined with magnesite brick. A blast of air is admitted near the

bottom of the converter to convert iron sulfide into the oxide which, in turn, reacts with silica to form ferrous silicate. This slag is poured off by tilting the converter. A portion of the cupric sulfide is changed at the same time, or by a continuation of the air blast, to cuprous oxide, which then reacts with the remainder of the cupric or cuprous sulfides to form free copper and SO_2:

$$2\ Cu_2O + Cu_2S \longrightarrow 6\ Cu + SO_2 \uparrow .$$

The copper is poured into molds and allowed to cool. At this stage of the process, the copper is called "blister" copper, because of the large blisters, or bubbles, formed by escaping gases as the metal solidifies.

3. Refining

Refining consists of remelting the "blister" copper in a silica-lined reverberatory furnace, where the impurities are oxidized and changed into slag. Some copper may be oxidized to cuprous oxide, which is soluble in melted copper. To prevent this occurrence, powdered coal is added to act as a reducing agent, or the melted metal is stirred with sticks of green wood. The copper is next cast into large plates and refined by electrolysis. The impure copper plates are used as anodes, and the cathodes are made of sheets of pure copper. The electrolyte is a solution of sulfuric acid. The impure copper passes into solution at the anode, and pure copper deposits on the cathode. The gold and silver in the copper anodes do not dissolve, because they have much less tendency than copper to form positive ions — they are lower in the electrochemical series. Consequently these metals, together with small quantities of palladium, platinum, and other inactive impurities, fall to the bottom of the electrolytic cell, forming "anode mud." The bath contains sodium chloride, which precipitates any silver that passes into solution as silver chloride. This mud is the source of a very important portion of the world's production of silver and gold. The zinc in the impure copper anode dissolves even more readily than copper, but the zinc ions are less readily discharged at the cathode than cupric ions and, therefore, they remain in the solution. The refined copper deposited on the cathode is about 99.95 per cent pure.

4. Properties

Copper is remarkably ductile, malleable, and flexible. The pure metal is an excellent conductor of electricity. Its color is red, when the metal is observed by light reflected from its surface, but it is green, when observed by light which passes through thin sheets. Pure copper cannot be hardened by heat-treatment as steel is hardened. Some of its alloys, however, are very hard and can be tempered.

The chemical properties of copper are those of a relatively inactive metal. It unites with oxygen, when it is heated in the air, forming CuO, and, at about 1000°, Cu_2O is formed by the dissociation of CuO:

$$4\ CuO \longrightarrow 2\ Cu_2O + O_2.$$

It dissolves in solutions of oxidizing acids, such as sulfuric and nitric acids, but in the non-oxidizing acids (HCl) it dissolves slowly and only when oxygen is present. In moist air it is soon coated with a green deposit of the basic carbonate, $CuCO_3 \cdot Cu(OH)_2$, called *verdigris*. In moist air ammonia reacts with copper to form the complex ion, $Cu(NH_3)_4^{++}$. It combines with sulfur and the elements of the halogen family more readily than with oxygen.

In its compounds copper has an oxidation number of + 1 or + 2 and in a few rare instances, + 3. In the monovalent state its ions are colorless, while divalent copper is blue. Its compounds are poisonous.

5. Uses

The most extensive use of metallic copper

is in the production of more than one thousand alloys. *Brass* and *bronze* are terms applied to many copper alloys which vary widely in the number of the metals that they contain. There are simple brasses that contain only copper and zinc; some contain lead; others contain tin, aluminum, iron, manganese, and nickel. Ordinary bronze is an alloy of tin and copper, but bronzes containing phosphorus, lead, aluminum, iron, silicon, manganese, nickel, zinc, and other elements are also well known. *Gun metal* contains copper, tin, zinc, and lead; *German silver* is an alloy of copper, zinc, and nickel; and *Britannia* metal contains copper, tin, lead, and antimony. Gold coins and jewelry contain copper and silver. Sterling silver contains 7.5 per cent of copper. Silver and nickel coins also contain copper.

Large amounts of copper are used for telephone and telegraph lines and in many electrical instruments and devices. Copper is the best conductor of the cheaper metals. The copper used for this purpose must be very pure, because impurities lower the conductivity enormously.

Copper is also used in electrotyping. After type has been set up, an impression of it is made in wax, and this is covered with graphite, which serves as an electrical conductor. The wax form is then placed as the cathode in an electrolytic cell containing cupric ions, and the copper is deposited on the letters of the wax plate. The thin metal coating is then removed from the wax and reinforced with lead which is poured, while molten, upon the back of the copper sheet. Copper is also used in making sheathing for ships; screens, gutters, and trimming for houses; rollers for printing cotton cloth; plates for making etchings and maps; and utensils used in the kitchen and in industry.

6. Oxides and Hydroxides

Copper forms two oxides: *cuprous*, Cu_2O, and *cupric*, CuO. Cuprous oxide is found in nature in the form of the mineral called "ruby copper." It may be produced in the laboratory as a reddish-brown substance by heating cupric oxide to about 1000°, by reducing cupric compounds in the presence of an alkali (Fehling's test for glucose, page 430), or by treating cuprous chloride with sodium hydroxide.

Cupric oxide is black. It is prepared by heating copper powder, wire, or foil in air or in oxygen. It is also produced when the nitrate or carbonate of copper is heated. It dissolves in acids to form cupric salts. Cupric oxide is a good oxidizing agent. When a coil of copper wire or a copper gauze is heated in the oxidizing flame cupric oxide is formed. If the copper then is dipped into a solution containing methyl alcohol, the cupric oxide oxidizes the alcohol to formaldehyde (page 420). This is one of the methods used to detect methyl alcohol. In addition to its use as an oxidizing agent, cupric oxide is used to remove the sulfur in petroleum products, to color glass and porcelain, and in the manufacture of cupric salts.

When a cuprous salt and a soluble hydroxide react, cuprous hydroxide may be produced, but it decomposes at once and completely into the oxide. Cupric hydroxide precipitates as a bright blue, gelatinous mass when a soluble hydroxide is added to a cold solution of a cupric salt, but decomposes when slightly heated. It is soluble in solutions containing ammonia, with which cupric ion combines to form a very weakly ionized complex ion:

$$Cu^{++} + 4\ NH_3 \rightleftarrows Cu(NH_3)_4^{++}.$$

Bordeaux mixture contains cupric hydroxide and calcium sulfate. It is made by adding slaked lime to a solution of cupric sulfate, and is used in the form of a spray as a fungicide and insecticide.

7. Cuprous Salts

Cuprous chloride is a white, slightly sol-

uble salt. It can be prepared by reducing cupric chloride with metallic copper in the presence of hydrochloric acid.

$$(Cu^{++} + 2\ Cl^-) + Cu \longrightarrow 2\ CuCl\ \downarrow .$$

Cuprous chloride dissolves in an excess of HCl to form the compound $H^+CuCl_2^-$.

Cuprous sulfide, Cu_2S, may be prepared by heating cupric sulfide or a mixture of copper and sulfur, in the absence of air, and by reducing cupric sulfide by means of hydrogen.

$$2\ CuS \longrightarrow Cu_2S + S$$
$$2\ Cu + S \longrightarrow Cu_2S$$
$$2\ CuS + H_2 \longrightarrow Cu_2S + H_2S.$$

Cupric ion, Cu^{++} reacts with iodide ion, I^-, to form cuprous iodide and with cyanide, CN^-, ion to form cuprous cyanide:

$$2\ Cu^{++} + 4\ I^- \longrightarrow 2\ CuI + I_2$$
$$2\ Cu^{++} + 4\ CN^- \longrightarrow 2\ CuCN + (CN)_2.$$

8. Cupric Salts

Cupric ion is blue. Its salts, in general, are more soluble and more stable than the corresponding cuprous compounds. In aqueous solution the blue color of cupric compounds is the color of the hydrated ion, $Cu(H_2O)_4^{++}$. Cupric hydroxide dissolves in a concentrated solution of sodium hydroxide to form dark blue $Cu(OH)_4^=$ ions. Both normal and basic cupric salts can be prepared. Most of the salts are prepared from the oxide, carbonate, or the free metal. They are usually blue, yellow, or green.

Cupric sulfate is the most important commercial salt of copper. It is prepared by treating the oxide or carbonate with sulfuric acid, by the oxidation of cupric sulfide, or by treating granulated copper with sulfuric acid. Commercially, it is prepared in the refining of silver (page 489) or by the oxidation of sulfide minerals, such as chalcopyrite, which contain copper. The pentahydrate, $CuSO_4.5\ H_2O$, crystallizes from aqueous solution as blue crystals called *blue vitriol* or *blue stone*. Other hydrates are known. The anhydrous salt, which is prepared by heating any of the hydrates, is white.

Cupric sulfate has a number of uses. It is used in the preparation or manufacture of other copper compounds, Bordeaux mixture (page 487), Fehling's solution, insecticides, germicides, fungicides, paint pigments, and artificial silk. Its solution is used in the refining of copper by electrolysis, in electroplating, in electrotyping, and in certain electrochemical cells (page 452). It is sometimes used in very small amounts to destroy the algae which grow in municipal water supplies and which give the water a disagreeable odor and taste.

Cupric sulfide, CuS, a black compound, is one of the least soluble sulfides. It is produced when hydrogen sulfide is passed into a solution containing a cupric salt, and because of its very small solubility product it is precipitated in solutions containing high concentrations of hydrochloric acid (page 363). It occurs as the mineral called *covellite*.

The cupric ion forms complex ions with ammonia, cyanide ion, chloride ion, and with several organic radicals. Concentrated solution of cupric chloride and bromide are yellowish green and brown, respectively, because of the presence of complex ions, such as $CuCl_4^=$. As the solutions are diluted they become blue because of the formation of $Cu(H_2O)_4^{++}$ ions.

Other common cupric salts are

Basic carbonate,	$(CuCO_3)_2.Cu(OH)_2$, azure (blue)
	$CuCO_3.Cu(OH)_2$, malachite (green)
Chloride,	$CuCl_2.2\ H_2O$ (green)
Bromide,	$CuBr_2$ (dark brown)
Nitrate,	$Cu(NO_3)_2.6\ H_2O$ (blue)
Acetate,	$Cu(C_2H_3O_2)_2.H_2O$ (dark green)

SILVER

9. History and Occurrence

Because it occurs as the native metal, silver has been known since very early times. The Latin name *argentum* means "white." The alchemists associated the metal with

the moon, and even now the name *lunar caustic* for silver nitrate is a remnant of this association.

Native silver is seldom pure; it is alloyed with gold, copper, or mercury. It occurs, sometimes, as large masses or nuggets, but more often it is found as flakes embedded in layers of rock. Small deposits of *cerargyrite* or horn silver, AgCl, occur, but the principal compounds in which silver is found are sulfides. The most important of these is *argentite* or *silver glance*, Ag_2S, but others, which contain arsenic or antimony, as well as silver, are also of considerable value. A large amount of the silver produced comes from the refining of copper, lead, and nickel, since silver sulfide is often associated, in small amounts, with the sulfides of these metals. The principal silver-producing countries are the United States, Canada, and Peru. In the United States the principal silver-producing states are Utah, Idaho, Arizona, and Montana.

10. Metallurgy

Several methods are used to recover silver from its ores. The general principles involved in the processes may be described under the following heads:

(1) *Parke's Process.* This process is widely used to recover silver from lead and copper ores. In addition to serving as a source of silver, this process is also a means of purifying lead and copper. When silver ores are treated by this process, they are mixed with lead ores before they are smelted in a furnace, and the product of the smelter is an alloy of lead and silver. The Parke's process deals directly with this alloy or with impure lead obtained in the smelting of lead ores. The alloy is melted in large kettles, and about 1 per cent of its weight of zinc is added and stirred with it. The zinc is added as a solvent for the silver, which is much more soluble in zinc than it is in lead. Zinc also dissolves gold and copper readily. Since zinc is lighter than lead, and since the two metals do not mix, the zinc rises to the top and brings with it most of the silver, gold, and copper originally present in the lead. As the mass cools, this layer forms a crust upon the surface of the molten lead. It is removed by large skimmers, and is then heated in a retort to distill the zinc, which is used again. The residue remaining in the retort contains silver, gold, and copper. The silver is purified by electrolysis or by the process of cupellation (see below).

(2) In the process used for *anode mud* (page 485) the more active metals are dissolved in dilute sulfuric acid. The residue of insoluble, less active metals is first dried and later is heated with a mixture of some oxidizing agent, such as sodium or potassium nitrate, sodium carbonate, and sand. This treatment is intended to convert the base metals first into oxides and then into slag (silicates), which can be separated readily from the silver and other precious metals.

(3) *Leaching Processes.* Ores containing silver sulfide are sometimes roasted to produce silver sulfate, and the product is leached with water, in which silver sulfate is soluble. The silver is precipitated and recovered from this solution by adding copper. Cupric sulfate (page 487) is a valuable by-product of this process.

One of the most important methods of recovering silver from its ores depends upon the solubility of the metal and many of its compounds in solutions of the alkali cyanides (NaCN or KCN). Complex cyanides, such as $NaAg(CN)_2$, are produced. This method of dissolving silver is applicable to ores containing silver chloride or small scattered particles of metallic silver, if the ores are finely pulverized in a stamp mill before they are treated with a solution of the cyanide. Silver is recovered from the cyanide solutions by adding zinc shavings or powdered aluminum to displace the silver.

(4) *Amalgamation.* Ores containing metallic silver or silver chloride may be treated with mercury to form an amalgam, which is separated from the earthy material of the ore and distilled in a retort. Silver remains in the retort, while the mercury is distilled, condensed, and used again. The metallic silver of the ore alloys (amalgamates) with the mercury directly, while the silver chloride is first converted by the mercury into metallic silver and mercurous chloride.

11. Refining

(1) *Electrolytic process.* Pure silver is used as the cathode, impure silver as the anode, and a solution of silver nitrate and nitric acid as the electrolyte. Silver dissolves at the anode and is deposited as loose crystals on the cathode.

(2) *Cupellation.* An alloy of silver and lead is heated in a shallow hearth furnace, in which the hearth is made of a porous material, such as cement. A current of air blows over the hearth and oxidizes lead and other impurities. The oxides thus formed are brushed off or removed by vaporization and by absorption in the lining of the furnace. The silver, still containing gold, copper, and small amounts of other metals, is cast into ingots of *doré bullion.* Gold is separated from silver by electrolysis or by treating the bullion with hot, concentrated sulfuric acid, which does not affect gold but changes silver and other metals that may be present into soluble sulfates. The gold is recovered from the residue, or "mud," and the silver is displaced from the solution by copper:

$$(2\,Ag^{++} + SO_4^{=}) + Cu \longrightarrow (Cu^{++} + SO_4^{=}) + 2\,Ag\downarrow .$$

12. Properties and Uses of Silver

Silver is a white, heavy metal. It is somewhat harder than gold and somewhat softer than copper. It is an excellent conductor of electricity and heat and is one of the most malleable and ductile of the metals. It alloys readily with almost all of the heavy metals, and although some pure silver may be used in jewelry and other ornaments, alloys of silver are most often used for this purpose as well as for coins, tableware, etc. These alloys are harder and more durable than pure silver.

Chemically, silver is classed as one of the least active metals. It is attacked more readily by sulfur than by any other element. Sulfur and many sulfur-compounds produce a black coat of silver sulfide upon the surface of any article made of silver. Silver is attacked by the halogens, but the action is slow and usually affects only the surface, because the silver halide which is formed protects the metal from further action. It dissolves in the oxidizing acids, such as HNO_3, and H_2SO_4, to form salts, $AgNO_3$ and Ag_2SO_4, but it does not dissolve in acids by displacing hydrogen, and it is not soluble in solutions of alkalies. The solubility of the metal in solutions of the alkali cyanides has already been mentioned:

$$8\,(Na^+ + CN^-) + O_2 + 2\,H_2O + 4\,Ag \longrightarrow 4\,(Na^+ + OH^-) + 4\,(Na^+ + Ag(CN)_2^-).$$

Metallic silver has a number of uses. Because of its slowness to tarnish and pleasing appearance, it is used to electroplate cheaper metals in the manufacture of tableware and many ornaments. Almost all mirrors are made by depositing reduced silver upon glass. Its use to make coins, jewelry, silver nitrate, and the silver halides has been mentioned previously. Coinage silver contains 10 per cent, and sterling silver 7.5 per cent of copper, which increases the hardness. In almost all of its compounds silver has an oxidation number of + 1, but a few compounds are known in which the number is + 2 or + 3.

13. Silver Oxide, Ag_2O

Whenever a soluble hydroxide is added to a solution containing a silver salt, the

hydroxide of silver, which we might expect to form, decomposes very rapidly, except at low temperatures, to form the oxide, Ag_2O. Despite this behavior, silver hydroxide must exist to a slight extent in mixtures containing the oxide and water, because the solution is strongly enough alkaline to change the color of red litmus to a pronounced blue.

Like the oxides of many of the heavy metals, silver oxide is not very stable. When it is heated, even at 200°–250°, the decomposition is rapid. Silver oxide in combination with certain substances of a protein nature is used as an antiseptic. Argentic oxide is a black compound. It is produced by the action of ozone upon silver.

14. Compounds of Silver and the Halogens

Of the four halides of silver, only silver fluoride, AgF, is readily soluble. The fluoride is prepared by treating the oxide of silver with hydrofluoric acid. The other silver halides can be prepared in a similar manner and also by simple precipitation reactions, in which a soluble chloride, bromide, or iodide is added to a solution of a silver salt:

$$(2\ Ag^+ + SO_4^=) + 2\ (Na^+ + Cl^-) \longrightarrow (2\ Na^+ + SO_4^=) + 2\ AgCl\downarrow .$$

$$(Ag^+ + NO_3^-) + (Na^+ + I^-) \longrightarrow (Na^+ + NO_3^-) + AgI\downarrow .$$

$$(Ag^+ + NO_3^-) + (Na^+ + Br^-) \longrightarrow (Na^+ + NO_3^-) + AgBr\downarrow .$$

These three silver halides form curdy precipitates. Freshly prepared silver chloride is white; silver bromide is pale yellow; and silver iodide has a brighter yellow color. All three salts are sensitive to light and are used in photography (page 491).

Silver chloride dissolves in a solution containing ammonia, forming the complex ion $Ag(NH_3)_2^+$. It also forms the complex ions, $AgCl_3^=$, $Ag(CN)_2^-$ and $Ag(S_2O_3)_2^=$. The tendency of silver salts to dissolve is explained by the very slight ionization of the complex ions. Whether or not all of the silver salt dissolves depends upon the quantity of cyanide, thiosulfate, chloride, or ammonia added, and also upon the solubility of the silver salt; the less soluble (in water) silver iodide does not dissolve in ammonium hydroxide, for example, while silver chloride dissolves readily.

15. Silver Nitrate

Silver nitrate, sometimes called *lunar caustic*, is used to make other compounds of silver. It is prepared by dissolving silver in nitric acid:

$$3\ Ag + 4\ (H^+ + NO_3^-) \longrightarrow 3\ (Ag^+ + NO_3^-) + 2\ H_2O + NO.$$

The solid salt is used, in the form of sticks, to cauterize wounds. Its use for this purpose depends upon the strong oxidizing powers of silver nitrate and upon the precipitation of protein compounds by silver ion. The pure salt is not affected by light but when placed upon the skin, black metallic silver is deposited by the action of reducing agents. Similar deposits of silver are produced when a solution of the salt is placed upon cloth. For this reason a solution of silver nitrate is used either alone or as an ingredient in marking inks.

PHOTOGRAPHY

16. Photographic Plates and Films

Modern photography depends essentially upon the effect which light produces when it falls upon a silver halide:

$$2\ AgBr \rightleftarrows 2\ Ag + Br_2.$$

The photographic plate or film consists of a glass plate or a film made of cellulose nitrate or acetate. One side is covered with a light-sensitive coating of gelatin in which there is a colloidal suspension of the silver halide. In the camera a lens focuses upon the plate the light which is

reflected from the object to be photographed. When the shutter of the camera is opened, this light strikes different portions of the gelatin film with different intensities. The light from dark objects, which reflect feebly, is less intense than that reflected from white or brighter parts of the subject before the camera. It is thought there may be some slight decomposition of the silver bromide into silver and bromine, but no visible deposit of silver is produced. Instead, the silver bromide exposed to light is sensitized. Since the effect of the light upon the silver halide varies with the intensity of the light an invisible image is produced upon the plate or film.

17. Developing

The decomposition of the silver halide is not completed by the brief exposure, but those portions most affected by the light are most easily reduced when the entire plate is treated with a reducing agent. This treatment is called *developing*, and the reducing agent is the developer. For this purpose a solution of pyrogallol, hydroquinone, or some other good reducing agent of a similar character is used in the presence of sodium carbonate. The developer may also contain a *preservative*, such as sodium sulfite, and a *retarder*, usually potassium bromide, or an accelerator, usually sodium carbonate. In this developing solution, the silver halide is reduced to metallic silver; those portions of the plate which have been affected by the most intense light are more completely reduced and, consequently, show darker deposits of metallic silver. The portions of the plate which have not been exposed to light are not affected by the developer.

18. Fixing

Before it can be exposed to the light, the developed plate or film must be treated in a fixing bath, which is a solution of sodium thiosulfate (page 371). This solution dissolves all of the silver halide which has not been reduced:

$$AgBr + 2\,(2\,Na^+ + S_2O_3^=) \longrightarrow [3\,Na^+ + Ag(S_2O_3)_2^=] + (Na^+ + Br^-).$$

The plate is then washed and dried. It is now the *negative*. In it the directions are reversed to those in the subject, and the dark portions of the subject are represented by the light portions of the negative, on which no silver has been deposited.

19. Printing

The negative is used to make the *prints* or positives. A sheet of paper which is covered with a gelatin suspension of silver halide (bromide or chloride, usually) is placed behind the negative, which is exposed to the light, usually an artificial light. The effect is the same as in the making of the negative. The portions of the plate or film which are free of silver permit the full intensity of the light to act upon the silver halide of the paper. Those portions upon which silver is deposited permit less light to act upon the paper, the intensity depending upon the thickness of the silver deposit. After exposure, the print is developed and fixed in the same manner as the negative. Most printing papers are coated with a suspension of silver bromide or a mixture of the bromide and chloride. If silver chloride alone is used, no developer is needed, because the image instead of being latent, is immediately visible without the use of a developer. Such papers are used in making *proofs*. After exposure, the excess of unaffected silver chloride is removed in the fixing bath, and the paper is washed in a solution of a gold or platinum salt. Since it is higher in the electrochemical series, the silver replaces either gold or platinum from the solutions of their salts, and these metals are deposited on the paper in its place. If gold is used, the proof is reddish brown in color; and if a platinum bath is used, it has a lustrous, gray, metallic color.

20. Sensitizers

The sensitivity of a silver halide to light may be increased remarkably by the use of *sensitizers*, which are usually dyes. These are effective because they absorb wave lengths of radiations which have little effect directly upon the silver halides. Plates or films containing such dyes are described as *panchromatic*. By the use of sensitizers better pictures can be made, for example, in mist and fog, which are more readily penetrated by infrared radiation than by ordinary light.

GOLD

Gold was probably the first metal used by man. Its rarity, pleasing appearance, softness, and durability made gold highly desirable for jewelry, ornaments, and even for the decoration of buildings. Its occurrence in the native state permitted primitive peoples to obtain it in moderate quantities before there was any knowledge of metallurgical processes. Throughout the history of man, gold has played an important part as a standard of value and a medium of trade.

21. Occurrence

Gold is found in nature almost always in the free state. It sometimes occurs as nuggets, but more frequently as small flakes scattered in veins of quartz or in deposits of sand. Nuggets weighing as much as 190 pounds have been found. Native gold usually contains some silver, platinum, and related metals. It is present in small quantities in the sulfide-ores of metals, such as copper and lead, and the tellurides of gold and silver occur as mixed crystals in the mineral called *sylvanite*. The chief gold producing regions of the world are Africa, which supplies about 40 per cent of the world's production, the United States (about 12 per cent), Canada (13 per cent), Europe and Asia (about 20 per cent each), Mexico, Australia, and Central America.

22. Mining and Metallurgy

In the gold rush days of California, gold was obtained by *panning*. This method was used to recover the gold found in alluvial sands. The material was placed in shallow pans and washed with water; the flakes of gold collected on the bottom of the pan. *Placer mining* made use of the same principle on a larger scale. The deposits were placed in long troughs, and the sand was carried away by a stream of water. The gold particles settled to the bottom of the troughs and were caught and held there by small cleats. These methods later gave way to *hydraulic* mining, in which powerful streams of water are directed against the sand, which is washed into sluices in which the gold is collected by settling, and the lighter material is washed away.

The gold which occurs in quartz veins is recovered by one of the following processes. These processes may be used, also, on alluvial deposits. First of all the quartz ore must be pulverized in a stamp mill.

(1) *Amalgamation.* The use of mercury in the recovery of gold has been practiced for almost 2500 years. Gold dissolves in mercury, forming an amalgam which is easily separated from quartz, soil, and other materials. The pulverized ores are made to flow in streams of water over copper plates, whose surfaces are amalgamated. The gold dissolves in the mercury and the amalgam is scraped off the plates. In sluice or "placer" mining, mercury to form the amalgam is sometimes placed between the cleats in the bottom of the trough. To separate the gold from the mercury, the mixture is placed in a retort, and the mercury is distilled.

(2) *The Cyanide Process.* This process has made possible the recovery of gold from very low grade ores, from material

that has already been worked over by panning or by sluice or placer mining, and from the discarded materials of the amalgamation process. The ore is treated with a dilute solution of sodium or potassium cyanide in the presence of air, and gold is converted into a soluble complex cyanide by the following reaction:

$$4\,Au + 8\,(Na^+ + CN^-) + O_2 + 2\,H_2O \longrightarrow 4\,(Na^+ + OH^-) + 4\,(Na^+ + Au(CN)_2^-).$$

The gold is finally recovered from this solution by adding zinc to precipitate it or by electrolysis.

23. Physical Properties of Gold

Gold is the most malleable and ductile of all the metals. Gold foil only 0.00001 mm. in thickness can be made by rolling the metal. Pure gold is yellow. The yellow gold used in coinage and in jewelry is alloyed with copper. This alloy has a redder color than pure gold. It is also harder. Gold alloys with a green tint are produced by adding silver or cadmium. White gold contains silver, or, sometimes, palladium or nickel. The purity, or fineness, of gold is expressed in carats, which indicate the number of parts of gold in 24 parts of the metal. Thus, a 14-carat (yellow) gold ring contains 41 per cent of copper (10/24), and an 18-carat ring contains 25 per cent of copper. The gold used in United States gold-coins is 21.6 carat; this is 90 per cent gold. Gold-plated jewelry and ornaments are made by electroplating gold on copper from a solution of sodium or potassium aurocyanide ($NaAu(CN)_2$). Alloys containing more than 18-carat gold are too soft for most uses. Gold is easily prepared in the colloidal state by reducing gold salts in solution or by the Bredig arc method (page 226).

24. Chemical Properties and Compounds of Gold

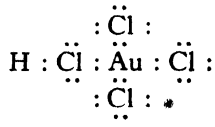
Chemically, gold is an inactive metal. It is not attacked by oxygen or by common acids, such as HCl, HNO_3, or H_2SO_4. It reacts with chlorine to form auric chloride, $AuCl_3$, at temperatures above 150°. It also reacts slowly with bromine and with iodine. Fluorine scarcely attacks it at ordinary temperatures, but the reaction is somewhat more pronounced at higher temperatures. It dissolves in aqua regia and in chlorine water to form auric chloride, or chloroauric acid, $HAuCl_4$. When heated with alkalies, such as KOH, the oxide is converted into soluble alkali aurates, e.g., $KAuO_2$ or $KAu(OH)_4$, and in acids forms auric salts, such as $AuCl_3$. Gold forms compounds in which it is monovalent, but these *aurous* compounds tend to change spontaneously in solution into *auric* compounds and metallic gold:

$$6\,(Au^+ + Cl^-) + 3\,HOH \longrightarrow Au_2O_3 + 6\,(H^+ + Cl^-) + 4\,Au.$$

When heated, the auric compounds decompose to give either metallic gold or the corresponding aurous compounds:

$$AuCl_3 \longrightarrow Cl_2\uparrow + AuCl.$$

Gold forms many complex compounds. Both aurous chloride and auric chloride dissolve in an excess of hydrochloric acid; aurous chloride forms chloroaurous acid, $HAuCl_2$, and auric chloride forms chloroauric acid, $HAuCl_4$. The formation of complex ions by the sharing of electrons is illustrated by the following formula for chloroauric acid:



ZINC

Zinc has been known as a pure metal and as a constituent of brass for a very long time. It was certainly one of the first metals to be produced from its ores by simple metallurgical processes. In early

times, however, not pure zinc but an alloy of copper and zinc (brass) was produced by smelting ores containing both metals.

25. Occurrence and Metallurgy

The occurrence of zinc in nature is limited to deposits in scattered localities on the earth's surface. The most important ores are *sphalerite*, ZnS; *smithsonite*, $ZnCO_3$; *willemite*, Zn_2SiO_4; *franklinite*, $ZnFe_2O_4$, with iron and manganese replacing some of the zinc; *zincite*, ZnO; and *calamine*, $Zn_2H_2SiO_5$. In the United States, the chief zinc-producing localities are in Oklahoma, Missouri, Kansas, New Jersey, Wisconsin, Montana, Utah, Idaho, Colorado, Tennessee, and New Mexico. The normal, annual production of the United States is 550,000 tons.

The older metallurgical treatment of zinc ores consists of roasting the sulfide or igniting the carbonate to form the oxide and then reducing the oxide by carbon. The ore is first crushed and then concentrated by flotation (page 231). After roasting, or ignition, the concentrated material is heated with coal in earthenware retorts. Condensers are placed over the mouths of the retorts, and as the zinc is produced by reduction, it distills and is condensed in these receivers. If the temperature of the condenser is above 419.4° (the melting point of zinc), the metal is collected in the liquid state and can be drawn off and allowed to solidify in molds. Zinc dust, containing 5 per cent or more of zinc oxide, first collects in the receivers, when the temperature is low. The zinc that comes from the molds is called *spelter*. It contains, in addition to zinc, small amounts of iron, cadmium, lead, arsenic, and carbon. Some of these impurities can be separated by redistilling the spelter in a vacuum, or in an



Figure 271. Zinc Furnace

Zinc ore is reduced in the retorts and the vapor is condensed to liquid zinc in the condensers, the ends of which are seen projecting from the furnace. The gas that burns at the ends of the condensers is carbon monoxide.

(Courtesy of United States Steel Corporation)

atmosphere of hydrogen to prevent oxidation.

Zinc oxide is also reduced by carbon in an electric furnace built in the form of a tower forty feet high and about six feet in diameter. The current passes through a mass of zinc oxide and coke, the resistance of which produces heat that promotes the reaction and vaporizes the zinc. The zinc vapor is condensed in an earthenware condenser placed on the top of the furnace.

More recent metallurgical practice involves, first, the leaching of the roasted ore with a solution of sulfuric acid. This gives a solution of zinc sulfate from which the zinc is recovered by electrolysis.

26. Physical Properties

Freshly polished zinc has a white metallic luster, but because of tarnishing its more familiar appearance is blue-gray. At ordinary temperatures, it is hard, crystalline, and brittle. If heated to 100°–150°, it becomes malleable enough to be rolled into thin sheets and can be drawn into wire. Above 200°, it loses this property and becomes brittle again. This behavior indicates the existence of allotropic forms of the metal. Granulated or *mossy* zinc is made by pouring melted zinc slowly into water. Zinc melts at 419° and boils at 930° C.

27. Chemical Properties

When freshly polished zinc is exposed to moist air, the surface is soon coated with a basic carbonate, $Zn(OH)_2.ZnCO_3$. When heated above 600°, zinc burns in air with a bluish, white flame to form ZnO. Zinc also undergoes combustion, when the dust or very small particles are heated with sulfur. It does not displace hydrogen from cold or boiling water, but it does displace hydrogen from steam, if strongly heated. Pure zinc reacts very slowly with dilute hydrochloric and sulfuric acids, because hydrogen collects on the surface, forming a protective layer. Ordinary, commercial zinc dissolves readily in dilute acids, because it contains metals like iron and copper as impurities (page 454). Zinc dissolves, also, in solutions of strong bases, liberating hydrogen and forming *zincates*. This behavior indicates that zinc has non-metallic as well as metallic properties.

28. Uses of Zinc

We are most familiar with zinc as the protecting covering on *galvanized* iron. The surface of the iron is coated with zinc by electroplating, by dipping the iron sheet into melted zinc, or by covering the surface of the iron with a spray of melted zinc. *Sherardized* iron is produced by covering the iron with a mixture of zinc dust and zinc oxide and heating it in a revolving drum. Zinc forms an alloy on the surface of the iron that is very durable. The protective action of the zinc covering is explained, in part, by the exclusion of air from the surface of the iron. Zinc, itself, resists corrosion because a thin but firmly attached layer of basic zinc carbonate is formed on the surface of the zinc exposed to the air, and this coating protects the metal from further action by oxygen. When a scratch is made through the zinc, or the layer of zinc becomes broken in any way, the zinc further protects the iron by acting as the more active metal of the couple. The zinc corrodes, while the iron remains unaffected for a time.

Zinc is also used in manufacturing many alloys: brass, Babbitt metal (page 383), German silver, etc. It is also used in batteries and dry cells (page 453); in separating silver and gold from lead (page 516); and in weather-stripping, gutters, cornices, etc. It has many uses in the laboratory as a reducing agent.

29. Zinc Oxide and Zinc Hydroxide

Zinc oxide is a white powder at ordinary temperatures. It turns yellow when heated, but becomes white again as it cools. It is

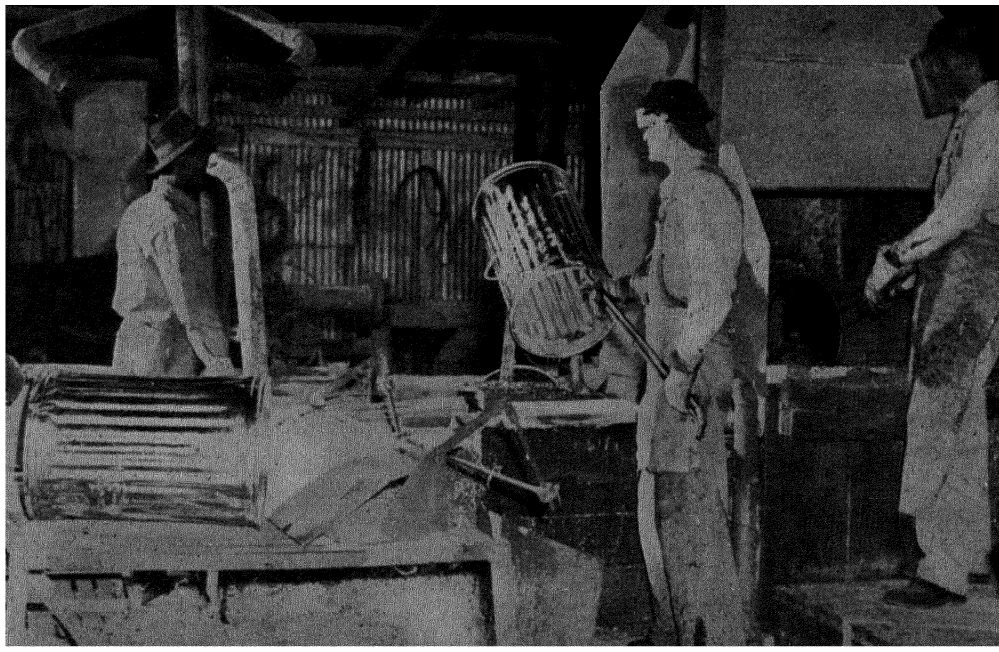


Figure 272. Galvanizing Garbage Cans

The steel cans are dipped into molten zinc. The process is known as hot-dipped galvanizing.
(Courtesy of United States Steel Corporation)

made by burning metallic zinc; by heating the basic carbonate, $Zn(OH)_2.ZnCO_3$; or by roasting the sulfide-ores of zinc. It is used as a paint pigment called *zinc white*. Since zinc sulfide is also white, paints containing zinc oxide (instead of white lead) do not darken, when they are exposed to an atmosphere containing hydrogen sulfide. One of the important uses of zinc oxide is in the manufacture of automobile tires (page 413) and other rubber goods. It is also used in manufacturing glass and enamels, and in medicine for the preparation of ointments. Mixed with zinc chloride (saturated solution) it sets to form a hard mass that is used as a cement.

Zinc hydroxide[1] may be precipitated by adding a soluble hydroxide to the solution of a zinc salt. The precipitate dissolves in an excess of sodium hydroxide or potassium hydroxide, because $Zn(OH)_2$ is amphoteric:

$$Zn(OH)_2 + 2\ (Na^+ + OH^-) \longrightarrow (2\ Na^+ + ZnO_2^=) + 2\ H_2O.^1$$

It dissolves in acids to form zinc salts:

$$Zn(OH)_2 + 2\ (H^+ + Cl^-) \longrightarrow (Zn^{++} + 2\ Cl^-) + 2\ H_2O.$$

It dissolves readily in solutions containing ammonia because of the formation of a very slightly ionized complex ion, $Zn(NH_3)_4^{++}$:

The zinc ion exists in aqueous solutions as the hydrated ion, $Zn(H_2O)_4^{++}$. This ion reacts with water to form hydrogen (hydronium) ion and causes solutions of zinc salts to be acidic:

[1] The compound precipitated is probably hydrated — i.e., $Zn(H_2O)_2(OH)_2$ — but for convenience and because the quantity of water contained in the compound is not known definitely we use the simple formula $Zn(OH)_2$.

[1] The actual composition may be better represented as $Na_2Zn(OH)_4$ ($Na_2ZnO_2.2\ H_2O$).

$$Zn(H_2O)_4^{++} + H_2O \longrightarrow H_3O^+ + Zn(H_2O)_3OH^+.$$

30. Zinc Chloride, $ZnCl_2$

Zinc salts are prepared by treating zinc or zinc oxide with the appropriate acid. To produce zinc chloride, an excess of hydrochloric acid is used. The resulting solution is evaporated to dryness, and the residue is fused to remove the last traces of water. The excess of acid is used to prevent hydrolysis during evaporation. The chloride is also produced by the direct reaction of zinc and chlorine. In the absence of the acid, zinc chloride hydrolyzes to produce the basic chloride, ZnOHCl, or the oxychloride, Zn_2OCl_2. Zinc chloride is used to preserve wood; in manufacturing parchment and wall board; and to clean the surfaces of metals before soldering. This last use depends upon the ability of the solution of zinc chloride to dissolve the oxides of other metals, because of the acid that it contains as the result of hydrolysis. Zinc chloride acts upon cellulose — wood, paper, and similar materials — to form a gelatinous mass.

31. Zinc Sulfate, $ZnSO_4$

This salt is prepared by roasting ores containing zinc sulfide. Some zinc sulfate is produced by oxidation. This is dissolved by leaching the material with water and is recovered by crystallization. The heptahydrate, $ZnSO_4.7\ H_2O$, which crystallizes from solutions, is called *white vitriol*. It is used in medicine, as a mordant in dyeing, and in the manufacture of lithopone (page 479).

CADMIUM

32. Occurrence and Metallurgy

Cadmium occurs as the sulfide, CdS, in the mineral called *greenockite*. Almost all of the ores of zinc, and especially the sulfide and carbonate ores, contain some cadmium. The ratio of zinc to cadmium in these ores is about 200 to 1. During the reduction of zinc oxide, metallic cadmium is also produced and distills over with the zinc. Since cadmium is the more easily reduced and, also, is the more volatile of the two metals, the first of the zinc to be condensed contains most of the cadmium. If the first of the distilled zinc is redistilled, and if this process of fractional distillation is repeated a number of times, cadmium can be recovered in a fairly pure form. It can also be separated from zinc during the refining of the latter by electrolytic methods since it has a lower electrode potential.

33. Properties and Uses

Cadmium greatly resembles zinc. It is silverwhite with a slight tinge of blue. It is softer, more ductile, and more malleable than zinc. It becomes brittle when heated. The metal is used in electroplating iron and steel articles, such as wire, tools, automobile parts, etc., to protect them against rusting. It appears to be better suited for this purpose than zinc, and is used, also, to some extent in place of nickel. It is sometimes used to plate articles that are later plated with silver. It is also used in some antifriction metals, and in several alloys of low melting point (page 397). Alloyed with silver it is said to retard tarnishing. Its alloy with gold has a greenish tinge.

34. Chemical Properties and Compounds

Cadmium oxide is brown. It is produced by the same methods as zinc oxide (page 496). The hydroxide, $Cd(OH)_2$ does not act as an acid in solutions of strong bases, but it dissolves in an excess of ammonium hydroxide to form $Cd(NH_3)_4(OH)_2$. Cadmium also forms a complex cyanide ion, $Cd(CN)_4^{=}$, and complex halide ions, $CdCl_4^{=}$ and $CdI_4^{=}$.

All the stable and familiar compounds of cadmium are those in which the metal has a valence of two. The chloride, $CdCl_2$, crys-

tallizes from solutions as the dihydrate and the sulfate as $(CdSO_4)_3.8\ H_2O$. The sulfate and also metallic cadmium are used in manufacturing standard electrochemical cells for use in scientific work. The sulfide, CdS, is used as a yellow paint pigment. It is less soluble than zinc sulfide and is usually precipitated in analytical procedures with the copper group (page 363) in a moderately acid solution.

MERCURY

Mercury was known before the beginning of the Christian era and was an important substance in the practices of the alchemists. It is sometimes called *quicksilver*. Its principal ore is *cinnabar*, HgS, but it also occurs in the native state and as amalgams of silver and gold. The chief producing localities of the world are located in Italy, Spain, California, and Oregon.

35. Metallurgy

The ores of mercury are of low quality and must be concentrated by flotation. The concentrate is then roasted in the air. The sulfur of the ore is converted into sulfur dioxide and the mercury is set free:

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

Mercuric oxide does not form, because it decomposes upon heating. Since mercury is volatile, it distills as rapidly as it is produced, and the vapor is easily condensed. The metal is purified, first, by filtering it through chamois skin or soft leather, and then by washing it in a dilute solution of nitric acid or mercurous nitrate. The mercury is made to flow in a fine stream through the solution of the acid, which oxidizes most of the metals that occur as impurities in the mercury and changes them into soluble compounds. The mercury can also be purified by distillation under reduced pressure.

36. Properties and Uses

Mercury is a silver-white, liquid metal, which freezes at − 38.9° and boils at 357° C. It is an excellent conductor of electricity. With many metals it forms alloys called *amalgams*. Its use in recovering gold by forming an amalgam with that metal has already been described. Sodium amalgam, which is much less active than sodium itself, is often used as a reducing agent. The amalgams of silver, gold and tin are used in making dental fillings. Its liquid state, high density, and low vapor tension fit it for use in barometers, thermometers, and similar instruments.

Mercury vapor does not conduct the electric current when it is cold, but it does conduct when the vapor is heated by producing an arc in the tube containing the vapor. The tube is filled with light rich in ultra-violet radiation. If the tube is made of silica (quartz), the ultra-violet rays are transmitted through the walls and may be used in treating certain diseases and as illumination in photographic work. Mercury vapor lamps are also used as a source of light in factories and in street signs. A mercury vapor tube containing one iron electrode and one of mercury, acts as a current rectifier. This device causes the current to be conducted in one direction only and consequently is used to change an alternating current (A.C.) into a direct current (D.C.).

37. Chemical Properties

Mercury lies toward the bottom of the electrochemical series and is displaced from its compounds by most of the metals. Corresponding to its position in the electrochemical series, mercury does not combine readily with oxygen, and does not displace hydrogen from acids. Like copper, it dissolves in oxidizing acids, such as HNO_3, to form salts. The element forms two series of compounds. These are called *mercurous* and *mercuric* compounds, respectively. Both

series of compounds are fairly stable under ordinary conditions, but most of the compounds of mercury decompose to form free mercury at high temperatures. Reducing agents, such as stannous chloride, usually reduce mercuric ion to mercurous ion and, if an excess of the reducing agent is used, finally to free mercury:

$$2\,(Hg^{++} + 2\,Cl^-) + (Sn^{++} + 2\,Cl^-) \longrightarrow Hg_2Cl_2\downarrow + (Sn^{+4} + 4\,Cl^-)$$

$$Hg_2Cl_2 + (Sn^{++} + 2\,Cl^-) \longrightarrow 2\,Hg + (Sn^{+4} + 4\,Cl^-).$$

This reaction is used frequently in the detection of mercury in analytical chemistry.

The halides of mercury appear, by conductivity measurements and otherwise, to be only slightly ionized in solution, probably because of the formation of such complex ions as $HgCl_4^{=}$. This is true also of the salts of zinc and cadmium, especially of the latter.

Mercurous chloride is represented by the formula Hg_2Cl_2 instead of HgCl; two mercurous ions are combined to form the ion Hg_2^{++}. The mercury atom contains two electrons in the valence shell and the shell next to this contains 18 electrons. In the mercurous ion the valence shell still contains an electron, which is in a more or less unstable state. Greater stability is attained when two mercurous ions share their odd electrons: $(Hg{:}Hg)^{++}$.

38. Mercurous Compounds

Mercurous oxide, Hg_2O, is produced when a mercurous salt is treated with an alkali, such as NaOH. It is not a stable substance. At ordinary temperatures it decomposes slowly, and at 100° it decomposes rapidly to form free mercury and mercuric oxide:

$$Hg_2O \longrightarrow Hg + HgO.$$

Mercurous oxide is not amphoteric as shown by its failure to dissolve in an excess of NaOH.

Mercurous sulfide, Hg_2S, resembles the oxide. It decomposes under ordinary conditions into free mercury and mercuric sulfide:

$$Hg_2S \longrightarrow Hg + HgS.$$

Mercurous chloride, Hg_2Cl_2, is the most important salt of the mercurous ion. Since it is only slightly soluble, it may be made by adding a soluble chloride to a solution of mercurous nitrate. It is also prepared by heating mercuric chloride with free mercury:

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2.$$

This reaction is slightly reversible, and the reverse reaction is accelerated in the sunlight. Mercurous chloride is a white crystalline salt, which is only slightly soluble in water, and which sublimes, when heated, without melting. It is the substance known in medicine as *calomel*.

Mercurous nitrate, $HgNO_3$, and *mercurous sulfate*, Hg_2SO_4, are prepared by the action of concentrated nitric or sulfuric acid upon an excess of mercury. If an excess of the acid is used, the mercuric salts are formed. The nitrate is fairly soluble in water, but the sulfate is only slightly soluble. Both salts hydrolyze to form basic salts.

39. Mercuric Compounds

When a solution of a base is added to a cold solution of a mercuric salt, a yellow precipitate of *mercuric oxide*, HgO, is formed instead of mercuric hydroxide, which decomposes immediately even at ordinary temperatures. If the yellow mercuric oxide is heated, it changes into a red variety of the same compound. The red form is prepared directly by heating mercuric nitrate:

$$2\,Hg(NO_3)_2 \longrightarrow 2\,HgO + 4\,NO_2 + O_2,$$

or by heating mercury in air. The red and yellow colors of the oxide appear to be due to differences in the state of division of the substance rather than to different struc-

tures. When it is heated, mercuric oxide decomposes into the two elements, mercury and oxygen. It is slightly soluble in solutions of NaOH or KOH, because of weakly acid properties.

40. Mercuric Chloride, $HgCl_2$

This salt is commonly called bichloride of mercury or corrosive sublimate. It can be produced by heating mercury in an atmosphere of chlorine, or by heating a mixture of sodium chloride and mercuric sulfate:

$$HgSO_4 + 2\ NaCl \longrightarrow Na_2SO_4 + HgCl_2 \uparrow .$$

Mercuric chloride is easily recovered from the mixture in a pure state, because it is volatile and sublimes. It is only moderately soluble in water, and the solution is a poor conductor of electricity, probably because the chloride is converted into the complex compound, $HgHgCl_4$. Mercuric chloride is very poisonous. A solution of mercuric chloride (about 1 part in 1000) is widely used as an antiseptic. The iodide, HgI_2, exists in two forms, scarlet and yellow. The yellow form is stable above 128°. Mercuric iodide dissolves in an excess of KI to form the complex, K_2HgI_4. A solution of this complex and KOH is called *Nessler's reagent*, which is used in detecting and estimating ammonia in various solutions and in water supplies.

41. Ammonia Compounds

Ammonia combines with mercuric salts to form compounds analogous to the hydrates and which may be called *ammoniates:*

$$HgCl_2 + 2\ NH_3 \longrightarrow HgCl_2.2\ NH_3.$$

It also reacts with mercuric salts in a manner that resembles the reaction of water in hydrolysis:

$$HgCl_2 + HOH \longrightarrow HgOHCl + HCl$$
$$HgCl_2 + HNH_2 \longrightarrow HgNH_2Cl + HCl$$
$$HgNH_2Cl + HNH_2 \longrightarrow Hg(NH_2)_2 + HCl.$$

A reaction of this kind, which involves ammonia instead of water, is called *ammonolysis*, and the products of the reaction are an acid (HCl) and an *ammono base* or an *ammonobasic* salt ($HgNH_2Cl$). Mercurous chloride forms the same ammonobasic salt as mercuric chloride and liberates free mercury, when it is treated with ammonia:

$$Hg_2Cl_2 + NH_3 \longrightarrow HgNH_2Cl + Hg + HCl.$$

This reaction is frequently used in the detection of mercury in its univalent (mercurous) state.

42. Mercuric Sulfide

As precipitated by passing hydrogen sulfide into a solution of a mercuric salt, mercuric sulfide is a black, amorphous, very nearly insoluble substance. A red crystalline form of the sulfide is made by heating a mixture of mercury and sulfur, or by grinding the two elements together and adding a warm solution of potassium sulfide. This red form is called *vermillion* and is used as a paint pigment. Mercuric sulfide is slightly soluble in a solution of sodium or potassium sulfide.

43. Summary

The metals of the *B* division of group two are distinctly different from the metals of the *A* division of the group, but the differences are not as pronounced as they are in group one. Furthermore, the first elements of group two (beryllium and magnesium), resemble the elements of the *B* division almost as closely as they resemble those of the *A* division. This is not true of the first two elements of group one. Mercury resembles the other elements in the group very little; it is more like the noble metals of group one as regards its position in the electrochemical series and the ease with which its compounds are decomposed and its ions are reduced. Zinc and cadmium lie above hydrogen in the electrochemical series but they are not as strongly electropositive as calcium, strontium, and barium. Their hydroxides are stable but are not as strongly basic as those of calcium, strontium, and barium. Zinc hydroxide is amphoteric, and in its acidic character it resem-

bles the hydroxide of beryllium. In their action upon water, zinc, cadmium, and mercury more clearly resemble beryllium and magnesium than they resemble the metals of the *A* division of their group.

All the elements in the group have an oxidation number of + 2. Mercury resembles copper, silver, and gold in forming, also, a series of compounds in which its oxidation number is + 1. Zinc, cadmium, and mercury differ especially from the other members of the group in their tendency to form complex ions.

REVIEW EXERCISES

1. Outline the steps involved in the metallurgy of the sulfide ores of copper.
2. What principles are involved in the separation of copper from gold, silver, and lead by the electrolytic refining process.
3. Suggest a method for determining the percentage of silver in a silver ring.
4. Write equations showing the different states of equilibrium which are set up when solid silver chloride is mixed with water and a solution of ammonia is added.
5. Name the respects in which copper, silver, and gold differ from the alkali metals.
6. Describe the chemical reactions which are involved in the metallurgy of gold by (1) amalgamation, and (2) by the use of cyanides.
7. Starting with a piece of solid gold and a ring made of copper, how would you electroplate the ring with the gold?
8. From their atomic structures explain the valences of copper and gold. Why do the alkali metals have no valence other than positive one?
9. How would you bring about the following transformations?

$Ag_2S \longrightarrow Ag_2SO_4$; $CuCl_2 \longrightarrow CuCl$;
$CuSO_4 \longrightarrow Cu(NH_3)_4^{++}$; $AgNO_3 \longrightarrow Ag_2O$;
$Au \longrightarrow HAuCl_4$; $Ag \longrightarrow Ag_2SO_4$;
$HgCl_2 \longrightarrow Hg$; $ZnCl_2 \longrightarrow Na_2ZnO_2$.

10. Compare the properties of gold, silver, and copper.
11. Describe the chemical reactions involved in the Parke's process for the production of silver.
12. Why does pure zinc dissolve more slowly in dilute sulfuric acid than the impure, commercial product?
13. Using the principles of the solubility product and ionic equilibria explain why CdS, CuS, and HgS can be precipitated by H_2S in a dilute hydrochloric acid solution, while ZnS is not precipitated under the same conditions.
14. Briefly outline the occurrences, metallurgy, properties, and uses of zinc, cadmium, and mercury.
15. Give methods which could be used in preparing the following compounds and state the purposes for which each substance is used: CdS, ZnO, $HgCl_2$, HgS.
16. Write a balanced equation to show the precipitation of silver from a solution of potassium argentocyanide ($KAg(CN)_2$) by metallic zinc.
17. Why is a solution of mercurous nitrate suitable for use in removing many of the metals which occur as impurities in mercury?
18. Name and describe one important chemical property of each of the following: $Hg(OH)_2$, AgBr, Ag_2O, $AuCl_3$, $HgCl_2$, HgO.
19. Describe the electrolytic method of refining copper.
20. In what respect do the elements of the *B* division of group two differ (chemically) from the *A* elements of this group?
21. What is "galvanized" iron and how is it made?
22. What is an amalgam?
23. Identify: Anode mud, bullion, brass, German silver, Bordeaux mixture, photographic negative, blister copper, zinc spelter, blue vitriol, calomel.
24. What is the meaning of the following terms as they are used in photography: Negative, exposure, positive, developing, fixing.
25. What would be the effect if the exposed film were placed in the fixing bath, by accident, before it was placed in the developer? What would be the effect if it were placed in the developer after having been removed from the camera in the light?
26. What is the weight of gold in an 18-carat ring that weighs 20 g.?
27. A portion of a sterling silver spoon was dis-

solved in nitric acid and the silver was precipitated as silver chloride. The dried precipitate weighed 2.734 g. What did the sample of the spoon weigh?

28. A hydrate of cupric sulfate contains 36.04 per cent of water. What is the formula of the hydrate?
29. What weight of chalcopyrite is required to produce sufficient cupric oxide to oxidize 1 g. of carbon to carbon dioxide?
30. What is the weight of a block of copper having the dimensions, in feet, of $1\frac{1}{2} \times 1 \times 2$?
31. Suggest tests that could be used to distinguish $HgCl_2$ from Hg_2Cl_2; $ZnCl_2$ from $CdCl_2$; AgI from AgCl; CuS from HgS; CuO from HgO; CuS from As_2S_3. More than one reaction may be required in each test.

REFERENCES FOR FURTHER READING

Davis, W., *The Story of Copper.* New York: The Century Company, 1924.

Cadmium: *Ind. and Eng. Chem.*, **22,** 119 (1930); *Chem. and Met. Eng.*, **23,** 1257 (1921); **48,** 147 (1941).

Copper: *J. Chem. Ed.*, **6,** 413 (1929); **8,** 829 (1931); **21,** 137 (1944).

Gold: *J. Chem. Ed.*, **15,** 507 (1938).

Mercury: *J. Chem. Ed.*, **5,** 419 (1928); *Chem. and Met. Eng.*, **47,** 644 (1940); *Ind. and Chem. Eng., News Edition*, **19,** 787 (1941).

Photography: *J. Chem. Ed.*, **7,** 420, 882, 1154 (1930); **23,** 595 (1946).

Zinc: *J. Chem. Ed.*, **10,** 600, 682 (1933); **11,** 33, 111 (1934); **13,** 60 (1936); *Chem. and Met. Eng.*, **16,** 554 (1917); **24,** 245 (1921); **25,** 754 (1921); **29,** 660 (1923).

40

ALUMINUM

1. The Elements of Group Three

Group three contains twenty-three elements, but only two of these (boron and aluminum) are very well known. The others are rare and, for the most part, not very important as judged by their uses or the uses of their compounds. Boron has been described in a preceding chapter, and some of the other elements of the group will be discussed in the last chapter.

2. History of Aluminum

Aluminum was first prepared in 1825 by Oersted (Denmark), who reduced aluminum chloride with metallic potassium. In 1854, Deville (France) produced aluminum by using sodium as a reducing agent. This led to improvements in methods of producing metallic sodium and to lowered prices for aluminum.

The modern process of producing this metal was discovered by Charles M. Hall in 1886, who started his work on the project while a student in Oberlin College. The name *aluminium*, as the metal was once called, or *aluminum*, as it is now called, is derived from the word *alum*.

3. Occurrence

Aluminum is the most abundant metal and the third most abundant of the elements. The most common occurrence of the metal is in clay, which is largely hydrated aluminum silicate. It is also present in slate and shale, and many other natural silicates. None of these materials serve as an important source of aluminum, however, because they are difficult to reduce and contain many impurities that are difficult to remove. The most important ore of aluminum is *bauxite*, a mixture of hydrated aluminum oxide, $Al_2O_3.2\ H_2O$ or $Al_2O_3.H_2O$, and iron oxide. *Cryolite*, Na_3AlF_6, is also used in the production of aluminum. Other minerals containing the element are *corundum*, Al_2O_3; *emery*, Al_2O_3 and the black oxide, Fe_3O_4, of iron; *garnet*, a mixed orthosilicate of iron, aluminum, calcium, and magnesium; and *turquoise*, which contains a basic aluminum phosphate. The oxide, with small amounts of the oxides of other metals, occurs as *ruby*, *sapphire*, *topaz*, and *oriental amethyst*.

4. Metallurgy

Metallic aluminum is produced by Hall's process (Figure 273), which involves the electrolysis of a solution of aluminum oxide in fused cryolite. The cryolite was once obtained almost entirely from Greenland, but most of it is now manufactured. Bauxite, from which the oxide is produced, comes from Arkansas and Georgia or from South America.

Electrolysis is carried out in an iron tank. The inside walls of the tank are coated with

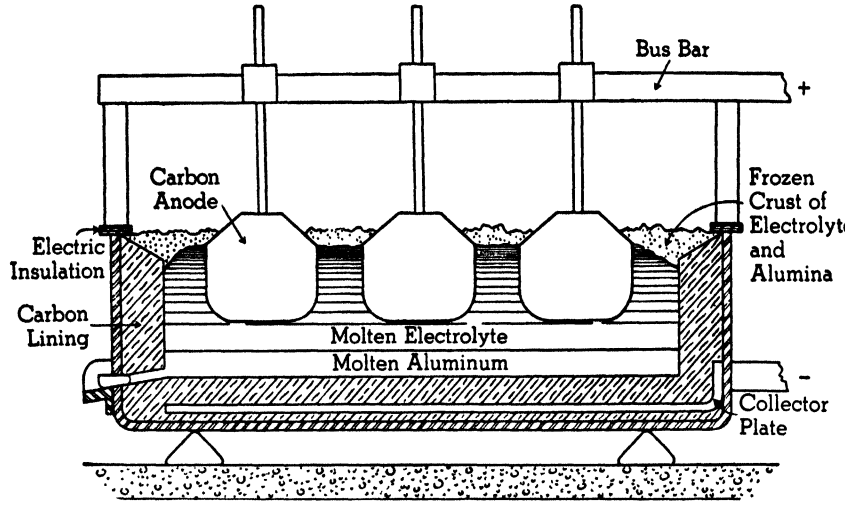


Figure 273. The Electrolytic Preparation of Aluminum
(Courtesy of Aluminum Company of America)

a mixture of coke and tar, which is carbonized more or less completely by baking, thus giving the walls of the tank a lining of carbon. This lining serves as the cathode of the cell. The anodes are carbon rods (Figure 273), which are lowered until they touch the bottom of the tank. An arc is thus produced, and this liberates sufficient heat to melt the cryolite. When the cryolite has melted, the aluminum oxide is added, and the anodes are raised. Further additions of the oxide are made as electrolysis proceeds. Oxygen is liberated at the anode. The aluminum liberated at the cathode is in the liquid state, since the cell is operated at a temperature above its melting point (660°). It is drawn off from the bottom of the cell.

Very pure aluminum oxide must be used in the electrolytic cell. The ore is heated under pressure with a solution of sodium hydroxide in which Al_2O_3 dissolves to form sodium aluminate. The insoluble, nonamphoteric impurities, such as Fe_2O_3, are removed by filtration. The filtrate is cooled, and water is added to precipitate hydrous aluminum oxide (aluminum hydroxide), which is then separated by filtration and heated to expel water, leaving pure Al_2O_3.

The aluminum made by this process is more than 99 per cent pure. Very nearly pure aluminum (99.98 per cent) can be made by refining the metal by a special electrolytic process. Aluminum was first produced in significant quantities during the last decade of the nineteenth century. In 1900, the United States produced about 7,000,000 pounds. The annual production of new aluminum in the United States now amounts to several hundred thousand tons.

5. Physical Properties and Uses

Aluminum becomes very brittle when heated to 150° or higher, but at lower temperatures it is ductile and malleable. The metal is not easily soldered or cast, and it tends to adhere to tools used in machining it. It melts at 600° and boils at 1800°. It has a high tensile strength, and can be hardened by cold-rolling and drawing. It is a good conductor of heat and of electricity. As an electrical conductor its specific conductivity is not as high as that of copper, but its lower density makes it more desirable than copper for electrical power transmission cables, and weight for weight, it is the better conductor of the two. It alloys readily with many metals, such as copper,

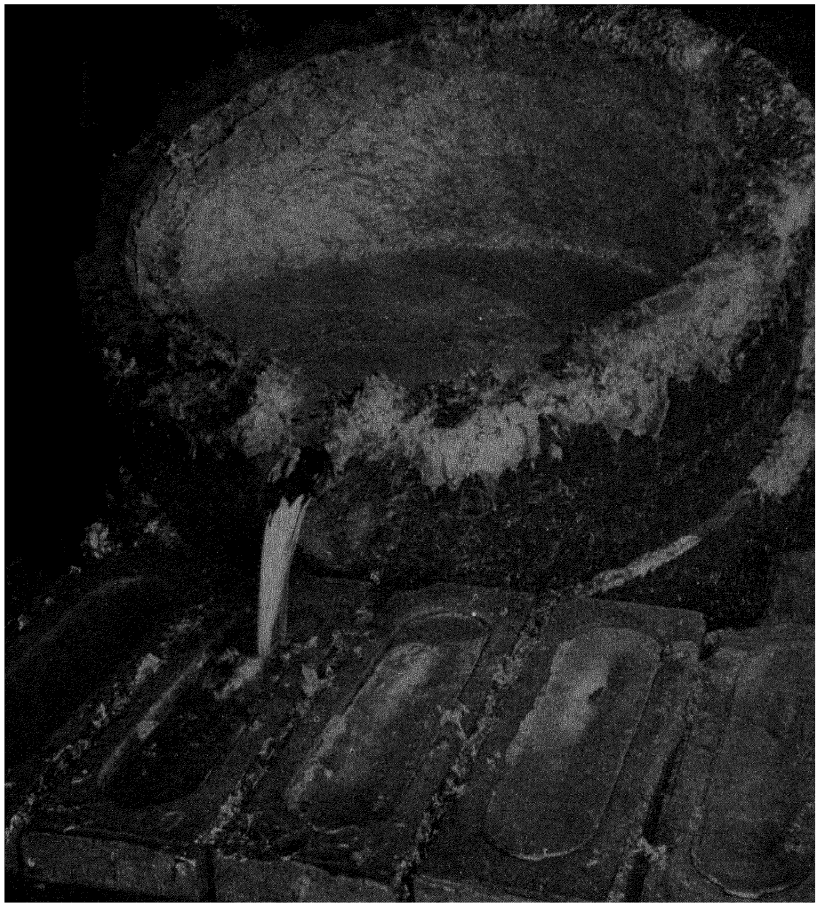


Figure 274. Pouring Molten Aluminum from Ladle into Pig Molds
(Courtesy of Aluminum Company of America)

iron, magnesium, nickel, tin, and zinc. Its freshly exposed surface is silvery white in color, but the metal soon becomes covered with a thin, tenacious coat of the oxide, which produces a dull, white luster.

The uses of aluminum depend upon the low density, high tensile strength, and durability of the metal or its alloys. It is used as a structural material in the construction of automobiles, railway cars, airplanes, street cars, furniture, and even buildings. Its most familiar use is in kitchen utensils. Thin sheets of aluminum are used, in place of tin foil, as wrapping for foods and other products, in electrical condensers, as an insulator to reflect heat, in mirrors, as tinsel, in flashlight bulbs, and for many other purposes. Powdered aluminum is mixed with oil to make "silver paint." Aluminum wire and cable, also aluminum-covered steel cable, are used in constructing transmission lines. Aluminum is used to remove the oxygen from iron and steel, thus preventing the formation of blow-holes in the castings. It is also used to reduce the oxides of certain metals in the thermite process (page 459) of welding.

Two of the important alloys of aluminum are *magnalium* and *duralumin*. The former contains 10 to 30 per cent of magnesium, and the latter contains about 4 per cent of copper and about 0.5 per cent each of

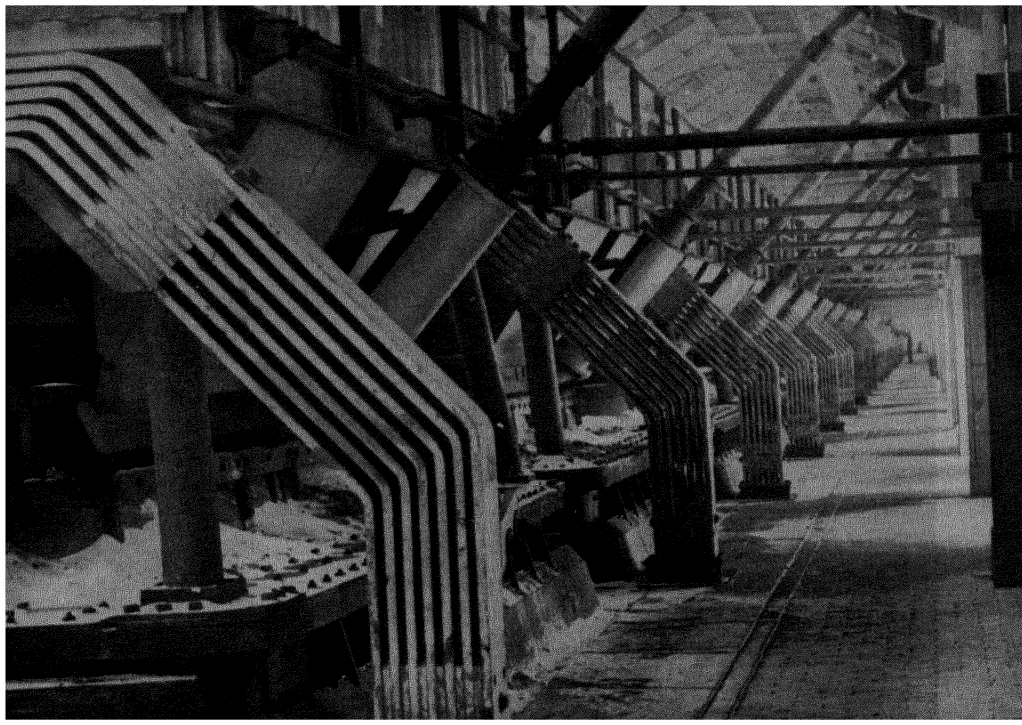


Figure 275. Line of Electrolytic Cells in Which Aluminum Oxide is Reduced in Making Aluminum
(Courtesy of Aluminum Company of America)

manganese and magnesium. These alloys have a tensile strength which is about twice that of aluminum, itself, and, at the same time, are almost as light as the pure metal. Other aluminum alloys contain small percentages of zinc, nickel, and certain other metals. Generally speaking, the alloys do not resist corrosion as well as the pure metal. In some instances, therefore, alloys are covered by thin sheets of pure aluminum to prevent corrosion.

6. Chemical Properties

Aluminum reacts with the oxygen of the air, at ordinary temperatures, only until a covering of the oxide is produced, but at high temperatures the metal burns with a very brilliant flame. It does not decompose water, although it is relatively an active metal, because of the deposition of the oxide or hydroxide upon the surface. It dissolves readily in hydrochloric acid, somewhat less readily in sulfuric acid, and is passive or inactive toward nitric acid, which may be shipped in aluminum containers. Aluminum dissolves, also, in concentrated solutions of bases, such as sodium and potassium hydroxide, liberating hydrogen and forming aluminates (page 70). Aluminum combines directly with sulfur, nitrogen, carbon, and the halogens, when it is heated in their presence. Its ordinary compounds are either aluminum salts, such as $AlCl_3$, or aluminates, such as Na_3AlO_3.

The composition of the compound usually called *aluminum hydroxide* is uncertain. It is sometimes assigned the formula $Al(H_2O)_3(OH)_3$, because this formula agrees with a coordination number of 6 for aluminum (page 344), and because it is useful in

explaining certain reactions of aluminum hydroxide. We have, therefore, used this formula for aluminum hydroxide in the discussion that follows.

7. Aluminum Oxide and Hydroxide

A precipitate of aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is most easily prepared by adding a moderate amount of an alkali to a solution of an aluminum salt. If an excess of the base is added, aluminum hydroxide fails to precipitate, because it reacts as an acid:

$$(Al(H_2O)^{+++} + 3\,Cl^-) + 3\,(Na^+ + OH^-) \longrightarrow Al(H_2O)_3(OH)_3\downarrow + 3(Na^+ + Cl^-) + 3\,H_2O.$$

$$Al(H_2O)_3(OH)_3 + (NA^+ + OH^-) \longrightarrow (Na^+ + Al(H_2O)_2(OH)_4^-) + H_2O.$$

When dehydrated by heating, the $Al(H_2O)_2OH_4^-$ ion forms the AlO_2^- ion by the loss of four molecules of water. When $Al(H_2O)_3(OH)_3$ reacts as an acid, as the reaction above shows, a proton is given up by one of the molecules of water attached to aluminum to an OH^- ion from sodium hydroxide.

Aluminum hydroxide acts as a base with acids:

$$Al(H_2O)_3(OH)_3 + 3(H^+ + Cl^-) \longrightarrow (Al(H_2O)_6^{+++} + 3\,Cl^-).$$

It is, therefore, an amphoteric substance.

A solution of aluminum chloride, aluminum sulfate, or a compound of similar nature contains the hydrated aluminum ion, $Al(H_2O)_6^{+++}$ as shown in the equations above. This ion can react with water,

$$Al(H_2O)_6^{+++} + H_2O \longrightarrow Al(H_2O)_5(OH)^{++} + H_3O^+,$$

and, therefore, solutions of aluminum salts are acidic in nature.

The salts of aluminum hydroxide and the weak acids are hydrolyzed very strongly. Such salts as aluminum sulfide, Al_2S_3, exist only in the dry state. If the sulfide is made by the direct combination of aluminum and sulfur, and the salt is then placed in water, it is converted completely into hydrogen sulfide and aluminum hydroxide:

$$Al_2S_3 + 9\ HOH \longrightarrow 2\ Al(H_2O)_3(OH)_3 + 3\ H_2S.$$

In a similar manner the carbonate, acetate, and other salts of weak acids are hydrolyzed and form precipitates of aluminum hydroxide, when they are dissolved in water. This behavior of aluminum salts has many useful applications. Cloth which is soaked in a solution of aluminum acetate becomes impregnated with the precipitated aluminum hydroxide produced by hydrolysis. This precipitate fills the spaces between the threads, renders the fabric more nearly waterproof, and gives it a smooth and nonabsorbent surface. It may be used, also, as a mordant, since it absorbs the dyestuff and holds it fast in the cloth. Paper may be sized in a similar manner. The precipitated hydroxide gives a surface to the paper which is less absorbent and smoother, and which carries ink in a more satisfactory way than unsized paper. The use of aluminum sulfate in the purification of water has been mentioned in another chapter (page 187). This use, also, depends upon the hydrolysis of an aluminum salt.

The oxide prepared by the gentle ignition of the hydroxide is soft and readily soluble in acids and bases. If it is made by ignition at a high temperature, it is much harder and is insoluble in acids and bases. This product is known under several names, e.g., *Alundum*. It is produced by heating the precipitated hydroxide or bauxite in an electric furnace until a portion of the material fuses. It is then ground to a powder and used as an abrasive and as a refractory (fire-resisting brick). Very hard, crystalline forms of aluminum oxide occur in nature. One of these, *corundum*, is essentially aluminum oxide and the other, called *emery*, contains magnetite in addition to Al_2O_3. Both are used as abrasives in grinding and polishing tools and many parts of machines, such as the valves and piston rings of automobile engines. Impure, crystalline corundum also occurs naturally as some of the most valuable gems. Ruby is corundum containing the oxide of chromium, Cr_2O_3. The blue sapphire contains the oxides of titanium, iron, cobalt, and chromium. Artificial rubies and sapphires are now produced in quantities that run into the millions of carats. These have approximately the same composition and appearance as the natural stones, but may be distinguished from them by certain characteristics of the tiny bubbles that appear in the stones; those in the natural gems are round, while those in the artificial ones are flattened. The imitations found in very cheap jewelry are merely red or blue glass.

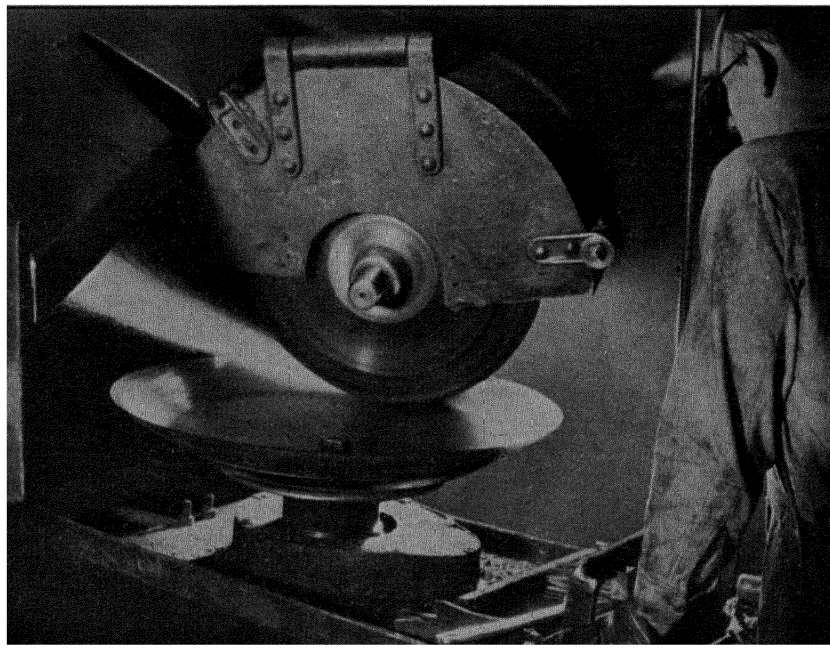


Figure 276. Polishing Cultivator Disks with a Wheel Coated with an Aluminum Oxide Abrasive, Alundum
(Courtesy of Norton Company)

8. Aluminum Chloride

Anhydrous aluminum chloride is made by the direct action of chlorine upon aluminum. The principal commercial process, however, involves the action of chlorine upon bauxite mixed with coal. The vapor density of the anhydrous compound indicates that the formula is Al_2Cl_6.

Anhydrous aluminum chloride is purified by sublimation. In the pure state it is not a conductor. It combines with water very readily:

$$Al_2Cl_6 + 12\ H_2O \longrightarrow 2\ (Al(H_2O)_6^{+++} + 3\ Cl^-).$$

It is used as a reagent and as a catalyst in many organic reactions. One of the processes used in cracking petroleum oils, for example, employs aluminum chloride as the catalyst. Its catalytic action, like the reaction with water, is probably explained by the rather unusual capacity of aluminum to share pairs of electrons belonging to atoms of other molecules which have such electron-pairs to share.

The iodide, bromide, and fluoride resemble the chloride of aluminum in many ways, but aluminum fluoride is ionic in its pure state.

9. Aluminum Sulfate, $Al_2(SO_4)_3$

Aluminum sulfate is prepared by treating bauxite or clay with sulfuric acid. With clay the acid reacts as follows;

$$H_2Al_2(SiO_4)_2.H_2O + 3\ (2\ H^+ + SO_4^=) \longrightarrow (2\ Al^{+++} + 3\ SO_4^=) + 2\ H_2SiO_3 + 3\ H_2O.$$

The aluminum sulfate is recovered by filtering the solution, in which the silicic acid is insoluble. The filtrate is then evaporated and crystals of $Al_2(SO_4)_3.18\ H_2O$ are formed. This substance is now used for many purposes in place of alum.

Alum is the term most often used in referring to the *double salt* $K_2SO_4.Al_2(SO_4)_3.24\ H_2O$. It is made by mixing potassium

sulfate and aluminum sulfate in equal molecular proportions, and dissolving them in water. The solution is then allowed to evaporate, and crystals of alum are formed. Other alums may be made in a similar manner. Instead of potassium sulfate, the sulfate of ammonium, of another alkali metal, or of other univalent metals, such as silver or thallium, may be used. Aluminum may be replaced by chromium, iron, manganese, or other trivalent metals in other alums. As an example of one of these alums, we may mention the double salt of cesium sulfate and ferric sulfate, $Cs_2SO_4.Fe_2(SO_4)_3.24\ H_2O$. This is *cesium iron alum*. An alum is a *double salt*. Such salts should be distinguished from complex salts, such as $Cu(NH_3)_4SO_4$, K_2HgI_4, and $NaAg(CN)_2$, which contain complex ions, such as $Cu(NH_3)_4^{++}$. Double salts ionize in aqueous solutions to produce simple ions. Thus, a solution of $K_2SO_4.Al_2(SO_4)_3$ contains K^+, Al^{+++}, and $SO_4^{=}$ ions.

Alum and aluminum sulfate are used in fire extinguishers (page 305), and in purifying water (page 187). Anhydrous sodium aluminum sulfate is used in some baking powders. These uses depend upon the hydrolysis of the aluminum salt. In baking powders, the acid formed by this reaction is the important substance. This is true, also, in the old style of fire extinguishers. In extinguishers of the foam type (page 305) and in the purification of water, the formation of slightly soluble aluminum hydroxide is important.

10. Aluminum Silicates: Ceramics

Many of the most important silicate rocks contain aluminum (page 390). The weathering of these rocks results in the disintegration of the complex silicates which they contain. The thawing and freezing of water in the rocks, and the chemical action of water and carbon dioxide convert these compounds into potassium carbonate, sand, and clay. The following reaction explains the weathering of potassium feldspar:

$$\underset{\text{(feldspar)}}{K_2O.Al_2O_3.6\ SiO_2} + H_2CO_3 + H_2O \longrightarrow K_2CO_3 + \underset{\text{(sand)}}{4\ SiO_2} + \underset{\text{(clay)}}{Al_2O_3.(SiO_2)_2.2\ H_2O}.$$

Pure clay, which has the formula shown above, is white and is called *kaolin*. Ordinary clay contains compounds of iron and of other metals, which give it a yellow or reddish-yellow color. Kaolin is used to make porcelain and china. These materials usually contain feldspar, which melts easily and cements the parts of the clay article together, making it a semi-vitrified body. Impure clays are more easily fused because they contain oxides of iron, calcium, magnesium and other metals which form easily melted silicates with sand. Such clays are used to make brick, tile, and stoneware, such as crocks, jars, and jugs. Stoneware is usually glazed to give it a less porous surface by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate and sodium aluminum silicate, which melt readily and cover the entire surface. When the article cools, the covering solidifies, producing a compact, smooth, waterproof surface. Porcelain and chinaware are usually glazed with feldspar.

The use of clay in making pottery and other ceramic articles depends upon the plasticity of the paste which is made of clay and water. When soaked in water the clay progressively hydrates, and the paste becomes more plastic. When the clay is heated the water of hydration is lost, and a hard, rock-like mass is formed.

Fire brick is made from *fire clay*, which does not soften until it is heated to a temperature above 1500°. Fire clay resembles kaolin and is purer than ordinary clay. Bricks made from this clay are used as refractories in building glass-pots, kilns for firing procelain, crucibles for melting metals, furnaces, etc. The bricks are fired or baked at a high temperature and are harder,

more dense, and less porous than ordinary bricks which are made from clays containing larger percentages of impurities.

REVIEW EXERCISES

1. What are the principal occurrences of aluminum in nature? From what natural materials is aluminum produced?
2. Describe the process by which metallic aluminum is produced.
3. Why can metallic aluminum not be prepared in the same manner as metallic copper or metallic zinc?
4. Suggest some method, consisting of a series of reactions, that might be used to produce metallic aluminum from clay? Why is this method not practical?
5. Write equations to show (1) the amphoteric character of aluminum hydroxide and (2) the hydrolysis of aluminum acetate.
6. Assuming an efficiency of 60 per cent, what weight of crystalline aluminum sulfate could be produced from one ton of pure kaolin?
7. What weight of pure "potash" alum could be prepared from the weight of aluminum sulfate made from the clay (see preceding problem)?
8. What is a double salt? Give examples of double salts and salts containing complex ions and point out the differences between them.
9. What is the general chemical composition of an alum?
10. Why does a precipitate consisting of aluminum hydroxide form when hydrogen sulfide is passed into an alkaline solution containing aluminum chloride?
11. Identify the following: Emery; kaolin; bauxite; porcelain; Alundum; ferric alum; magnalium.
12. What is the origin of clay?
13. The hydroxides of both zinc and aluminum dissolve in NaOH, but only zinc hydroxide dissolves in NH_4OH. Why?
14. What must be the source of the oxygen that is liberated at the anode during the production of aluminum by electrolysis (page 504)?
15. In what ways is aluminum chloride like the salts of metals and in what ways is it different from them?
16. Given a sample of metal that may be aluminum, silver, or zinc. Outline a series of reactions, or tests, that could be used to determine which of these three metals it is.

REFERENCES FOR FURTHER READING

Bureau of Standards, Circular No. 76 (1919), *Aluminum and Its Alloys*, Washington, D.C.: Government Printing Office.

Aluminum Alloys: *Ind. and Eng. Chem.*, **27,** 745 (1935).

Aluminum in Industry: *Ind. and Eng. Chem.*, **26,** 1231 (1934); **30,** 35 (1938); *J. Chem. Ed.*, **7,** 233 (1930); **23,** 399 (1946); *Chem. and Met. Eng.*, **37,** 428 (1930); **43,** 64 (1936); **48,** 9–106 (1941); *Chem. and Eng. News*, **21,** 2018 (1943).

Bauxite: *Chem. and Met. Eng.*, **49,** 1–147 (1942); *Ind. and Eng. Chem., News Edition*, **19,** 248 (1941).

Ceramics: *J. Chem. Ed.*, **9,** 795 (1932).

Gems, natural and artificial: *J. Chem. Ed.*, **8,** 1015 (1931); **11,** 323 (1934); **21,** 133 (1944); **23,** 418 (1946).

General: *J. Chem. Ed.*, **7,** 233 (1930).

41

TIN AND LEAD

TIN

1. Occurrence

It is estimated that about 0.00001 per cent of the earth's crust is tin. The Romans called the element *stannum*, and it is from this Latin name that our present symbol, Sn, for tin is derived. The most important ore of this metal is the mineral *cassiterite*, SnO_2, which is found in the Malay States, Bolivia, the Dutch East Indies, Spain, China, England, and Australia. Cassiterite is a heavy mineral, and for this reason it is often found as gravel in the beds of streams which have removed the mineral from the deposits in which it occurred originally. A considerable portion of the tin that is recovered comes from alluvial deposits of this kind. This tin is known as "stream tin." There are only a few deposits of the mineral in North America, and these are not important. The world's annual production is, normally, about 250,000 tons.

2. Metallurgy

Cassiterite ores are of low grade and must be concentrated before they are treated for the recovery of the metal. The usual method of concentration is a flotation process, in which the heavy particles of the ore settle and the lighter, worthless portions are carried to the top in the froth. The concentrated ore is roasted to remove sulfur and arsenic and to convert zinc, iron, and copper into their oxides. It is then washed with a solution of hydrochloric or sulfuric acid, which changes the oxides of all of the metals, except tin, into soluble chlorides or sulfates. The tin concentrate is then smelted in a reverberatory furnace with pulverized coke or hard coal, which reduces the oxide of tin to the free metal. Some of the tin remains in the slag as a silicate, and some is carried away in the dust from the furnace. The slag and dust are smelted again. The tin which is set free during smelting is drawn off from the bottom of the furnace. The metal is purified by one of several methods. It may be stirred, while molten, with green poles (page 485). It may be heated in a furnace with a sloping hearth; the tin which melts at a low temperature flows toward the bottom of the furnace, leaving slag and other less fusible materials at the top. Purification may also be accomplished by a process called *tossing*. This consists of pouring the melted tin from large ladles. The impurities, which are less fusible and which consequently solidify before the tin, are left in the ladles as the liquid tin is poured off. The purified metal is cast into large blocks and is called *block tin*. More highly refined tin is obtained by electrolysis, using impure tin anodes, pure tin cathodes, and a bath of fluosilicic acid (H_2SiF_6) and sulfuric acid.

Tin is recovered by several different methods from scrap tin plate, such as that used in making cans, pails, and other utensils. One of these processes involves the action of dry chlorine upon the tin coating of the plate. Chlorine converts the tin into stannic chloride, which is a volatile liquid, that can be distilled, but chlorine has no effect, if it is dry, upon the iron which lies beneath the layer of tin.

3. Properties

Tin has two solid allotropic forms. These are designated as *alpha* and *beta* tin, and they are also called *gray* and *white* tin, respectively. The transition temperature, at which one form changes into the other, is 18° C.; white, or beta, tin is the stable form above that temperature. The white variety of tin is a malleable metal, which melts at 232° C. and boils at 2260°. When cooled to 18° or lower, gray tin is formed slowly, and this is brittle and easily crumbled. Articles made of tin are, consequently, likely to disintegrate in cold weather. The change slowly progresses from some point of origin and produces an effect called "tin disease."

4. Uses

White tin can be rolled into thin sheets, or tin-foil, which is used for wrapping foods and other products. The metal is very resistant to corrosion and, for this reason, is used to make "block tin" pipes for conveying distilled water and other liquids. It is also used to coat sheets of iron, copper wire, etc. Tin plate is made by dipping sheets of iron in melted tin or by the electrode position of tin upon iron.

Tin is also used to produce many alloys: White metal, tinsel, bronze, bell metal, Britannia metal, gun metal and many others. The compositions of four of its most important alloys are shown in the table below:

Solder: Sn(50), Pb(50)
Pewter: Sn(80), Pb(20)
Type metal: Sn(5), Pb(80), Sb(15)
Rose's metal; Sn(23), Pb(27), Bi(50).

5. Chemical Properties

Tin is not attacked by air and moisture at ordinary temperatures, but at higher temperatures, it is coated with a layer of oxide. When it is heated in the air above its melting point, it is slowly oxidized, and at very high temperatures (1500°–2000°) it burns with a white flame. The metal reacts more readily with chlorine and the other halogens than it does with oxygen. Dry chlorine converts it into stannic chloride. It also combines directly with sulfur when heated with that element. It reacts only slowly with dilute hydrochloric acid to form stannous chloride, $SnCl_2$, and hydrogen. It also reacts slowly with dilute sulfuric acid to liberate hydrogen, but it reduces the concentrated acid, liberating sulfur dioxide. Dilute nitric acid acts upon tin to form stannous nitrate, $Sn(NO_3)_2$, and at the same time nitrogen is reduced. Concentrated nitric acid oxidizes tin very vigorously to the insoluble beta metastannic acid, which probably must be regarded as a hydrous oxide of tin, $SnO_2.nH_2O$, but it is sometimes represented by the formula H_2SnO_3.

Tin is also attacked by hot solutions of sodium hydroxide and other alkalies, in which it dissolves, forming stannites, such as Na_2SnO_2 or $NaHSnO_2$, and liberating hydrogen. This behavior of tin is similar to that of aluminum and zinc, and shows that stannous hydroxide is amphoteric in nature.

6. Stannous Oxide, SnO, and Stannous Hydroxide, $Sn(OH)_2$

Stannous oxide is a black or green powder, depending upon the method of production. It is prepared by heating stannous hydroxide or stannous oxalate, SnC_2O_4.

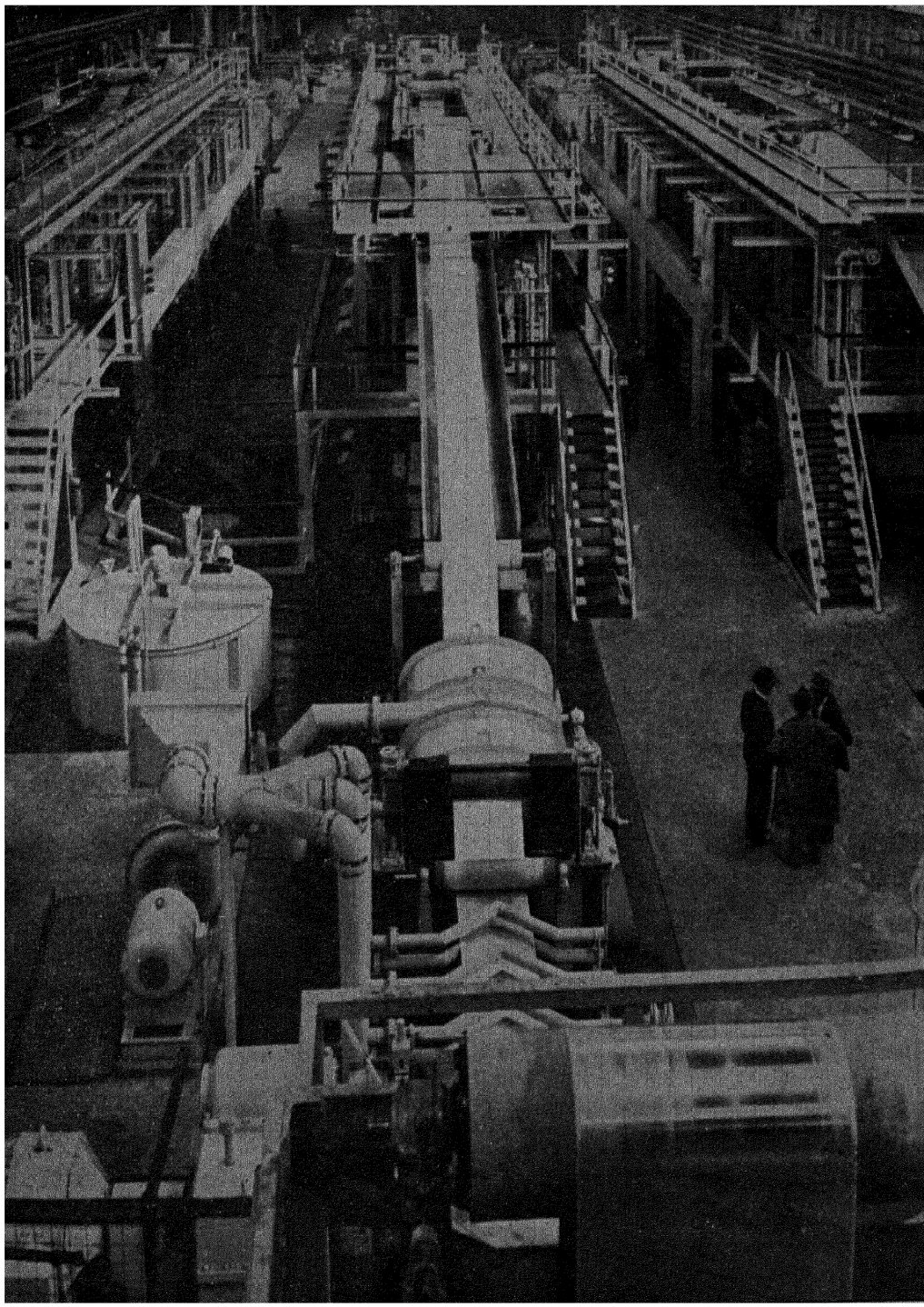


Figure 277. Electrotinning Steel Sheets

Steel sheets are coated with a layer of tin by electroplating. Three continuous lines are shown. The baths in which the electroplating occurs are shown in the upper background. *(Courtesy of Du Pont Company)*

$$SnC_2O_4 \longrightarrow SnO + CO + CO_2.$$

It burns in the air, when it is heated, and forms stannic oxide.

Stannous hydroxide cannot be prepared in the pure, dry state. It may be precipitated by adding an alkali hydroxide to a solution of a stannous salt:

$$(Sn^{++} + 2\ Cl^-) + 2\ (Na^+\ OH^-) \longrightarrow Sn(OH)_2 \downarrow + 2\ (Na^+ + Cl^-).$$

The precipitate dissolves in an excess of the alkali, forming sodium stannite.

$$H_2SnO_2 + 2\ (Na^+ + OH^-) \longrightarrow (2\ Na^+ + SnO_2^=) + 2\ H_2O.$$

It also dissolves in acids, forming salts like $SnCl_2$. The hydroxide, therefore, is amphoteric.

Like the corresponding compounds of zinc (page 496) and aluminum (page 507) the compound that we have represented above as stannous hydroxide, $Sn(OH)_2$, is probably the hydrous oxide, $SnO.nH_2O$. Sodium stannite is sometimes represented by the formula $NaSn(OH)_3$ or $NaHSnO_2.H_2O$. We have used the formula corresponding to $Sn(OH)_2$ for convenience.

7. Stannous Chloride, $SnCl_2$

A solution of this salt can be prepared by dissolving tin in concentrated hydrochloric acid. The anhydrous salt is prepared by passing hydrogen chloride over the metal. When a solution of stannous chloride is evaporated, crystals of $SnCl_2.2\ H_2O$ form. When heated, this hydrate liberates hydrochloric acid by the hydrolysis of $SnCl_2$, which is converted into the basic salt, Sn(OH)Cl. Stannous chloride is widely used as a reducing agent, because of the tendency of tin to pass into the quadrivalent condition. It reduces mercuric chloride to mercurous chloride (page 499) and ferric chloride to ferrous chloride. These and similar reactions are frequently employed in analytical chemistry. It is used in dyeing as a mordant, in weighting silk, and in the manufacture of tin-coated metallic articles, such as pins.

8. Stannic Oxide, SnO_2

Stannic oxide is a white powder when cold and yellow when hot. It is prepared by burning tin or stannous oxide at a high temperature, or by igniting stannic hydroxide. It is used in the manufacture of opaque glass and white enamel ware. An iron article, such as a kettle, is coated with a mixture of stannic oxide, powdered glass, and water. It is then dried and heated at a temperature that will fuse the ingredients of the mixture, which form a resistant, white porcelain-like covering on the iron base.

When a solution of stannic chloride is treated with a limited quantity of sodium hydroxide, or some other alkali, a white, gelatinous precipitate is produced. This is called *alpha stannic acid*, which, because of the composition of salts corresponding to it, is assigned the formula $H_2Sn(OH)_6$, which is equivalent to $SnO_2.4\ H_2O$, the hydrous oxide. It reacts with sodium hydroxide as follows:

$$H_2Sn(OH)_6 + 2\ (Na^+ + OH^-) \longrightarrow (2\ Na^+ + Sn(OH)_6^=) + 2\ H_2O.$$

The compound Na_2SnO_3, called *sodium metastannate*, is formed by fusing SnO_2 with NaOH. When hydrated, it is equivalent to $Na_2SnO_3.3\ H_2O$ or $Na_2Sn(OH)_6$. Alpha stannic acid reacts with hydrochloric acid as follows:

$$H_2Sn(OH)_6 + 6\ (H^+ + Cl^-) \longrightarrow (2\ H^+ + SnCl_6^=) + 6\ H_2O.$$

Stannic chloride is not formed by this reaction, because it is almost completely hydrolyzed,

$$SnCl_4 + 6\ H_2O \longrightarrow H_2Sn(OH)_6 + 4\ (H^+ + Cl^-),$$

and because of conversion of Sn^{++++} ions by Cl^- ions into the slightly ionized complex ion, $SnCl_6^=$.

Alpha stannic acid differs from the beta

form in that the latter dissolves in sodium hydroxide and other alkali hydroxides but not in acids.

9. Stannic Chloride, $SnCl_4$

Pure stannic chloride resembles carbon tetrachloride in some ways. It is a nonconductor, and only in solution does it show any salt-like properties. The anhydrous compound is a liquid which boils at 114° and freezes at −30°. With water it forms a crystalline hydrate, which has the formula $SnCl_4.5\ H_2O$. It forms a complex acid with hydrogen chloride, H_2SnCl_6. This substance is called *chlorostannic acid*. Its ammonium salt, $(NH_4)_2SnCl_6$, is used as a mordant in dyeing. Stannic chloride hydrolyses in water and in moist air to form alpha stannic acid which is precipitated in the fibers of fabrics to weight them, as in the case of silk, or to act as a mordant in dyeing.

10. Stannous and Stannic Sulfides

Like the sulfides of arsenic and antimony, dark brown stannous sulfide and yellow stannic sulfide dissolve in solutions of the alkali and ammonium sulfides to form *thiostannates*. Stannous sulfide must be oxidized, however, by the use of a polysulfide, and forms thiostannate rather than thiostannite ion:

$$SnS_2 + (2\ NH_4^+ + S^=) \longrightarrow (2\ NH_4^+ + SnS_3^=).$$

These reactions are important in the separation of tin from other metals whose sulfides do not react with ammonium sulfide.

LEAD

11. Occurrence

Lead was produced and used by the Egyptians, Babylonians, and Romans. The symbol, Pb, of the element comes from the Latin name *plumbum*. The most important ore of lead is *galena*, PbS, which is found in association with sulfide minerals of zinc, silver, copper, arsenic, antimony, bismuth, and tin and with other minerals, such as quartz, fluorite, and barite. *Cerussite*, $PbCO_3$, and *anglesite*, $PbSO_4$, are also of some importance. The United States and Mexico produce approximately one half of the world's supply of lead. Spain, Australia, Canada, and Germany are the other principal producing countries. Most of the lead produced in the United States comes from Missouri, Idaho, and Utah. The United States produces about 425,000 tons, each year.

12. Metallurgy

The lead ore is crushed, concentrated by flotation, and then roasted in a furnace to remove a part of the sulfur. During the roasting the sulfides of iron, zinc, and copper are changed into oxides. The lead sulfide is partially converted into lead monoxide, PbO, and lead sulfate, $PbSO_4$:

$$3\ PbS + 5\ O_2 \longrightarrow PbSO_4 + 2\ PbO + 2\ SO_2.$$

Some of the lead sulfide remains unchanged. This material is then mixed with fresh lead ore, iron ore (Fe_2O_3), carbon, and limestone, and heated in a small blast furnace. Air is forced in at the bottom of this furnace. The limestone is added as a flux for the silica which is present in the ore. Several reactions occur, but the principal one is the reduction of lead monoxide by carbon or carbon monoxide:

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

The lead is drawn off from the blast furnace as lead *bullion*. This contains some silver, gold, bismuth, zinc, copper, arsenic, antimony, and other metals. The other products of the furnace are the slag, which is worthless, and a *matte*, which consists of the sulfides of copper, lead, iron, and other metals. The matte is treated again in the blast furnace to remove lead and the silver and gold which it contains.

13. Refining

Lead bullion is hard because it contains

alloys of lead with other metals. The more easily oxidized metals are separated by melting the bullion in a reverberatory furnace in the presence of air. Arsenic, zinc, antimony, copper, and some of the lead are changed to oxides, which float on the melted lead and are removed by skimming. The lead is then drawn off and further purified by one of the following methods:

(1) *Parke's Process.* The lead is melted with a small amount of zinc, which does not mix with it. The zinc layer dissolves silver, gold, and copper and floats on the heavier layer of lead. When the top layer cools, it forms a crust, which is easily skimmed off. The lead must be treated with zinc three or four times to remove the other metals. The small amount of zinc which is not removed by skimming is separated from the lead by changing it into the oxide. This is accomplished by blowing air and steam into the melted mass.

(2) *The Betts Process.* This is an electrolytic process of refining. Anodes are made of the lead bullion, and these are suspended in a bath of fluosilicic acid and lead fluosilicate, $PbSiF_6$. The lead dissolves from the anodes and is deposited on cathodes made of sheets of pure lead. The process is very much like the electrolytic refining of copper. The anode mud contains silver, gold, and bismuth. The more active metals, such as iron and zinc, dissolve but remain in the solution.

14. Physical Properties

Lead is a heavy, soft, malleable metal of low tensile strength. A freshly cut surface is brightly lustrous, but this is soon covered in the air with a coat of dull gray material containing the basic carbonate, lead monoxide, and particles of lead. It melts at 327.5°. When heated to a temperature slightly below its melting point, it becomes softer and more plastic. In this condition it can be made into lead pipes, wire, and rods. It is only a moderately good conductor of electricity.

15. Uses

Lead has a few properties that make it suitable for a number of uses. It is soft and easily melted; hence, it is easily molded and worked. It is chemically not very active and, therefore, does not corrode easily under conditions that cause many of the more active metals to wear away rapidly. Its use in the chambers of sulfuric acid plants has already been mentioned. It is also used to make pipes and troughs for the conveyance of liquid wastes, traps for sinks, etc. It is used as a lining in pipes, tanks, sinks, and other apparatus and containers whose outside walls are made of less resistant metals; as a covering or sheath for telephone and other electrical cables; to make the plates of storage batteries; in the manufacture of white lead and other compounds of lead; and in the production of many alloys, some of which are pewter, shot, solder, type metal, and fuse metal.

16. Chemical Properties

Lead is directly above hydrogen in the electromotive series. This means that it is a slightly active metal. Its activity in reactions with most reagents is further decreased, because most of the compounds formed in these reactions are insoluble and therefore, form layers that act as protective coverings for the metal. It does not react noticeably with cold water and only very slightly with hot water. When lead pipes are used for the conveyance of hard water, the pipes become coated with a layer of lead carbonate and lead sulfate. If soft water containing dissolved oxygen flows through the pipe, lead hydroxide, $Pb(OH)_2$, is formed. The hydroxide is somewhat soluble in water and, like all lead compounds, is poisonous. Hence, lead pipes are not suitable for the conveyance of drinking water. Dilute hydrochloric and sulfuric acids attack lead only slightly, because of the formation of insoluble compounds that protect the metal. Sulfuric

acid solutions containing more than 77 per cent of H_2SO_4 act upon lead more rapidly than the dilute acid, since lead sulfate is somewhat soluble in concentrated sulfuric acid, and, therefore, does not protect the metal. Nitric acid dissolves lead, forming lead nitrate and liberating nitric oxide or nitrogen dioxide (cf. copper, page 349). Many of the weak acids, such as hydrosulfuric, carbonic, and acetic, act upon the metal.

The most familiar compounds of lead are those in which the metal is bivalent. The hydroxide, $Pb(OH)_2$, is amphoteric, but it is more basic than acid in nature. The salts of bivalent lead, if soluble, are moderately hydrolyzed in solution, often forming basic salts. Lead also forms a series of compounds in which it is quadrivalent. Among these are lead dioxide, PbO_2, and the plumbates, of which sodium plumbate, $Na_2Pb(OH)_6$, or $Na_2PbO_3.3\,H_2O$, is an example. All soluble lead compounds are poisonous.

17. Oxides and Hydroxides of Lead

Lead monoxide, PbO, exists in two forms, a buff or yellowish-red, rhombic crystalline variety and a red, tetragonal crystalline variety called *massicot*. The latter is the stable form above 490°. The buff variety is known as *litharge*. It can be produced by heating lead in the air, but the commercial product is made, largely, during the refining of lead and silver. It is used in making lead glass, in manufacturing rubber goods, storage batteries, glazes for pottery, and paints. It is used as a "drier" for linseed oil in paints, where it probably acts as a catalyst for the oxidation of linseed oil. A mixture of litharge and glycerine is used by plumbers as a rapidly hardening cement.

Lead dioxide, PbO_2, is produced by the action of vigorous oxidizing agents, such as chlorine, sodium hypochlorite, or calcium hypochlorite, in an alkaline solution of a lead salt:

$$Pb(OH)_2 + (Na^+ + ClO^-) \longrightarrow PbO_2 \downarrow + (Na^+ + Cl^-) + H_2O$$

and by the action of nitric acid upon red lead, Pb_3O_4:

$$Pb_3O_4 + 4\,(H^+ + NO_3^-) \longrightarrow PbO_2 \downarrow + 2\,(Pb^{++} + 2\,NO_3^-) + 2\,H_2O.$$

It is a brown powder. It is used in storage batteries; in making the "striking" surface on boxes of safety matches; and in many reactions involving oxidation, such as the preparation of potassium permanganate from manganese dioxide, or the liberation of chlorine from hydrochloric acid.

Lead monoxide and the corresponding hydroxide, $Pb(OH)_2$, which is precipitated when an alkali is added to a solution of a lead salt, are soluble in acids and in bases. *Plumbous* salts, such as $PbCl_2$, are formed with acids, and *plumbites* are formed in solutions of bases:

$$H_2PbO_2 + 2(Na^+ + OH^-) \longrightarrow (2\,Na^+ + PbO_2^{=}) + 2\,H_2O.$$

As compared with stannous hydroxide, $Pb(OH)_2$ is a slightly stronger base.

Lead dioxide dissolves slightly in concentrated solutions of sodium or potassium hydroxides forming *plumbates;* e.g., $Na_2Pb(OH)_6$, or $Na_2PbO_3.3\,H_2O$. Towards acids, the dioxide is almost inert as regards basic properties. It reacts slowly with nitric acid, but lead is reduced to the bivalent state, and oxygen is liberated. Under ordinary conditions, it oxidizes hydrochloric acid to liberate chlorine.

18. Red Lead, Pb_3O_4

Red lead, or *minium*, is not an oxide but a compound of two lead oxides, PbO and PbO_2. This compound, Pb_2PbO_4, may be called *plumbous plumbate*, $(PbO)_2.PbO_2$. It is a red powder and is produced by heating the monoxide in the air at temperatures between 425° and 450°. It is used in glass-making and as a paint pigment, especially

in paint which is applied as the first coat for structural iron and steel.

19. Lead Nitrate, $Pb(NO_3)_2$

This is the salt of lead which is commonly employed in the laboratory to prepare solutions containing the ion, Pb^{++}. It is prepared by the action of nitric acid upon lead or lead monoxide. It is used in matches, and in the preparation of other lead compounds. When the crystals of the salt are heated, lead monoxide is produced by decomposition. It is soluble in water, but hydrolysis produces a slightly soluble basic nitrate, except in the presence of an excess of acid.

20. Lead Acetate, $Pb(C_2H_3O_2)_2$

Lead monoxide dissolves in acetic acid to form plumbous acetate, which crystallizes as the hydrate, $Pb(C_2H_3O_2)_2.3\ H_2O$. This salt of lead has a sweet taste and is called *sugar of lead*. It is used in preparing ointments for the treatment of certain skin diseases and in the dyeing and printing of cloth. It is very poisonous.

21. Lead Halides

The halides of lead, of which lead chloride is the most familiar, are prepared by the action of the hydro-halogen acids upon lead monoxide or by precipitation reactions between plumbous ion and the halide ions. They are slightly soluble in cold water and somewhat more soluble in hot water. In the detection of lead in a solution which contains other metals, lead chloride is precipitated along with the chlorides of silver and mercury (*-ous*) by the addition of a soluble chloride. The lead chloride of the residue is then removed by dissolving it in hot water, in which silver and mercurous chlorides do not dissolve appreciably. The lead ion may then be detected in the solution obtained by washing the residue with hot water by adding sodium or potassium chromate, which precipitates the lead as yellow lead chromate, $PbCrO_4$.

22. Paints; White Lead

This substance is the basic carbonate of lead, $Pb(OH)_2.2\ PbCO_3$. It is best known as a substance used to provide the *body* of paints. Paints are made by grinding an insoluble, heavy, durable substance in linseed oil, hemp oil, or tung oil. The body must possess good "hiding" power in covering the surface to which the paint is applied. White lead is one of the most widely used substances for this purpose, but lithopone and titanium dioxide are also used. Coloring materials are added to form paints of the desired color or shade; these are called *pigments*. Many paints also contain certain fillers, such as calcium or barium sulfate, kaolin, or calcium carbonate.

The oil used in paints must dry, or harden, when exposed to the air, to form a durable, flexible coating on the painted surface. The drying process involves oxidation, which is accelerated by heating the oil with *dryers*, such as the oxides of lead and manganese.

White lead is usually made by the *Carter* or by the *Old Dutch* process. The latter has been used for several centuries. In this process the lead is cast in the form of thin, perforated disks, called "buckles." These disks are stacked in earthenware vessels containing a shallow layer of dilute acetic acid. The vessels are stacked in tiers in a large room and covered with spent tanbark, which ferments, liberating carbon dioxide and producing heat, which vaporizes the acetic acid. White lead is produced by the action of acetic acid vapor, carbon dioxide, water, and oxygen upon the lead. The process requires three or four months for completion. We may think of the following equations as representing the changes which occur:

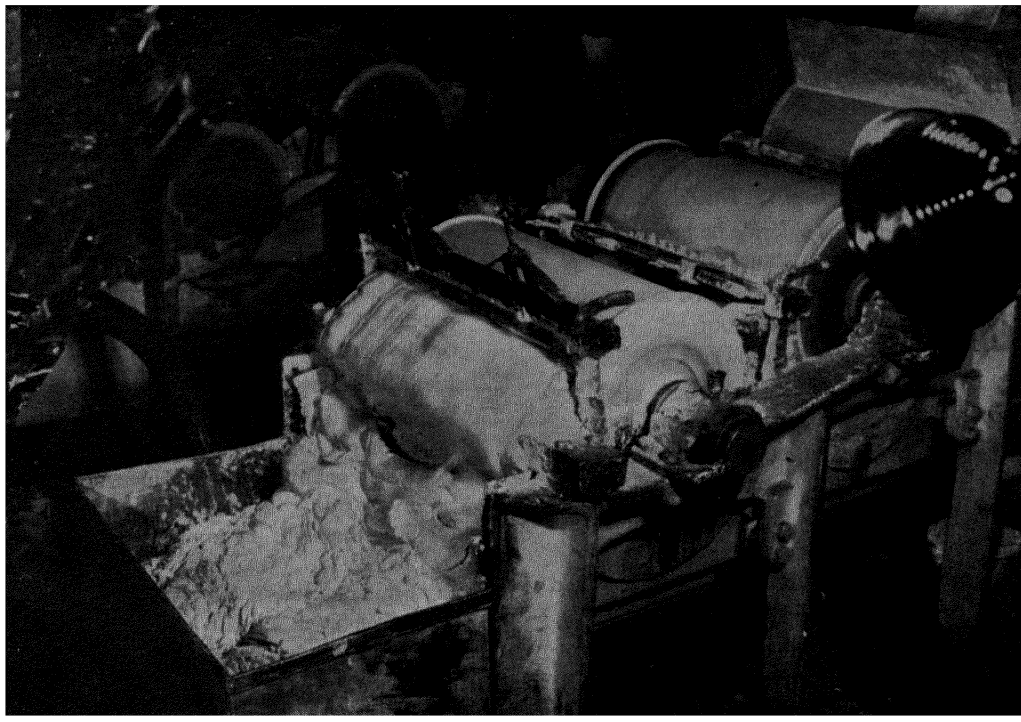


Figure 278. Grinding White Lead and Oil in the Manufacture of Paint
(Courtesy of Eagle Picher Company)

$$4\ Pb + 8\ HC_2H_3O_2 + 2\ O_2 \longrightarrow 4\ Pb(C_2H_3O_2)_2 + 4\ H_2O$$

$$Pb(C_2H_3O_2)_2 + HOH \longrightarrow Pb(OH)(C_2H_3O_2) + HC_2H_3O_2$$

$$3\ Pb(OH)(C_2H_3O_2) + 2\ H_2CO_3 \longrightarrow (PbCO_3)_2.Pb(OH)_2 + 3\ HC_2H_3O_2 + H_2O.$$

The Carter process produces white lead more rapidly than the Old Dutch process. Melted lead is atomized by a blast of compressed air. This finely divided material is then placed in revolving wooden drums, which also contains acetic acid and carbon dioxide. The reactions are completed in about two weeks.

23. Other Compounds of Lead

Lead chromate, $PbCrO_4$, is used as yellow paint pigment, which is called *chrome yellow*. *Lead sulfate*, $PbSO_4$, is used to some extent as a paint pigment. *Sublimed white lead* is a mixture of lead sulfate, lead monoxide, and zinc oxide. It is produced by heating galena and is used as a pigment. *Lead arsenate*, $Pb_3(AsO_4)_2$, is used as an insecticide. *Lead sulfide*, PbS, is precipitated by hydrogen sulfide from solutions containing the lead ion in the presence of moderate concentrations of hydrochloric acid. In qualitative analysis it is precipitated, therefore, in the group that contains copper and mercury. *Lead tetraethyl*, $Pb(C_2H_5)_4$, is used in making "ethyl" gasoline. It is made by treating an alloy of sodium and lead with ethyl bromide.

REVIEW EXERCISES

1. Describe the methods which are used in the production of tin from cassiterite.
2. How is tin recovered from tin plate scrap or waste, such as tin cans?

3. How does stannic chloride differ from ordinary salts, such as sodium chloride?
4. Stannic sulfide, SnS_2, dissolves in a solution of ammonium sulfide, $(NH_4)_2S$. Can you suggest the reason for this behavior?
5. Write equations to show the reactions which occur when tin is treated with a boiling solution of (1) HNO_3 and (2) NaOH.
6. How can stannous chloride be prepared from (1) tin and (2) from stannic chloride?
7. In what way is tin not as effective as zinc in protecting the surface of iron?
8. What is the condition known as *tin disease?*
9. Suggest chemical reactions which could be used to distinguish between tin and lead.
10. What is one objection to the use of white lead in paints?
11. Outline the essential steps in the production of lead from galena.
12. Identify: Lead bullion, chrome yellow, red lead, sugar of lead, and white lead.
13. Describe the Old Dutch process for the manufacture of white lead.
14. Make a list of representative compounds of lead and tin.
15. Enumerate the uses of tin, lead, and their compounds.
16. Why does dilute sulfuric acid have little effect upon lead?
17. A sample of pure white lead evolved 100 ml. (standard) of carbon dioxide when it was treated with an acid. What was the weight of the sample?
18. A solution containing mercuric chloride was treated with sufficient stannous chloride to completely reduce the mercuric ion to metallic mercury. If the mercury resulting from the reaction weighed 1.4 g. and the volume of the solution was 400 ml., what was the concentration of the mercuric chloride in the solution?
19. The iron, in a sample of iron ore weighing 10 g., was completely converted into ferric chloride, $FeCl_3$, which then was reduced to $FeCl_2$ by $SnCl_2$. If 1.5 g. of $SnCl_2$ was used, what was the percentage of iron in the ore?
20. What weight of $PbSO_4$ can be produced by the oxidation of 100 g. of PbS?
21. A sample of PbO weighing 100 g. is first converted into red lead and then into PbO_2 with the help of nitric acid. What weight of PbO_2 can be produced?
22. Identify litharge, massicot, and red lead.
23. Write equations for the following reactions:
    (*a*) Litharge dissolves in sodium hydroxide.
    (*b*) The reaction of lead dioxide with sodium hydroxide.
    (*c*) Tin dissolves in concentrated sulfuric acid.
    (*d*) Stannous sulfide dissolves in ammonium polysulfide.
    (*e*) The reaction of lead dioxide with nitric acid.

REFERENCES FOR FURTHER READING

Alloys of Tin and Lead: *Ind. and Eng. Chem.*, **28,** 1406 (1936).

Lead: *Ind. and Eng. Chem.*, **23,** 108 (1931); **27,** 1133 (1935); **31,** 1439 (1939).

Paint: *J. Chem. Ed.*, **5,** 515, 682, 836 (1928); **10,** 529 (1933); **11,** 487 (1934).

Tin: *Ind. and Eng. Chem.*, **23,** 1113 (1931); **32,** 1162 (1940); *Chem. and Met. Eng.*, **19,** 526 (1918).

Tin Plate: *Ind. and Eng. Chem.*, **15,** 423 (1923); Detinning: *Chem. and Met. Eng.*, **32,** 40 (1925).

White Lead and Paints: *J. Chem. Ed.*, **2,** 1151 (1925); **7,** 515, 682 (1930).

42

CHROMIUM AND MANGANESE

CHROMIUM

1. Occurrence

This element is the most abundant metal of group six. Its most important ore is *chromite*, $Fe(CrO_2)_2$. It also occurs in small amounts with aluminum in igneous rocks; as the mineral *crocoite*, $PbCrO_4$; and in some precious stones (page 507). About one half of the world's supply of chromite comes from Rhodesia. Almost all of the ore now used in the United States is imported. Our normal yearly requirement is 250,000–300,000 tons.

2. Metallurgy

To prepare compounds of chromium, chromite ore is fused with sodium carbonate in the presence of air. The iron is oxidized to Fe_2O_3 and the chromium is converted into sodium chromate, which is dissolved in water and recovered as crystals by evaporation. Other compounds of the element may be prepared from the sodium chromate thus produced. When chromite is reduced by carbon in an electric furnace, an alloy of chromium and iron, called *ferrochrome*, is produced. This is used in making chromium steels. The metal can also be deposited electrolytically on iron or copper electrodes from a solution containing chromic acid and chromium sulfate.

3. Physical Properties and Uses

Chromium is a very hard, crystalline, silvery white metal. It melts at 1615°. It is used to electroplate many articles made of other metals because of its resistance to corrosion, its hardness, and its lasting bright luster, which resembles the color of platinum. It is also used to make several alloys. The most important of these are the chromium steels, which are made by adding ferrochromium to melted steels. These steels contain from 1 up to 20 per cent of chromium. They are hard, strong, and tough, and resistant to corrosion and tarnishing. Such steels are used to make bearings, valves, cutlery, armor plate, shells, safes, bank vaults, and high-speed tools. Stainless steel, which is used in making cutlery, contains 12 to 14 per cent of chromium. Alloys of iron with chromium and nickel are used in apparatus that must withstand corrosive action in the chemical manufacturing industries. *Nichrome* (nickel, chromium, and iron) and *chromel* (nickel and chromium) are used in the form of wire as electrical resistance in making the heating units of small electrical furnaces and small heaters. *Stellite*, which is used in making cutting tools, contains chromium, tungsten, and cobalt.

4. Chemical Properties

Chromium does not tarnish in the air at ordinary temperatures, but it burns, when heated to a high temperature, producing the oxide, Cr_2O_3. When heated to redness it liberates hydrogen from steam. Like iron, aluminum, nickel, and to a lesser extent several other metals it has an *active* and a *passive* state. Chromium, after it has been dipped in concentrated nitric acid or chromic acid, or exposed to the air for some time, does not react with nitric, hydrochloric or sulfuric acid, and does not displace other metals that lie below it in the electrochemical series from solutions of their salts. The passive state is not permanent. It may be changed to the normal, active condition by allowing the metal to stand in solutions of the acids, by heat, or even by a shock or a jar, or by contact with the active form of the metal. The passive state may be caused by a protective film of oxide on the surface of the metal. The active metal dissolves in the non-oxidizing acids to produce chromous salts and to liberate hydrogen:

$$2\,(H^+ + Cl^-) + Cr \longrightarrow (Cr^{++} + 2\,Cl^-) + H_2.$$

It dissolves slightly in sodium hydroxide and other alkalies to form chromites and hydrogen. Chromium lies between zinc and cadmium in the electrochemical series.

The oxidation number of chromium in its compounds is + 2, + 3, or + 6. In its divalent state, the element is basic, in the trivalent state amphoteric, and in the hexavalent state acidic. The oxides, hydroxides, acids, and typical salts are shown in the table below.

THE COMPOUNDS OF CHROMIUM

Oxide	Hydroxide	Properties of hydroxide	Salts	Color of the ions
CrO	$Cr(OH)_2$	basic	$CrCl_2$, chromous chloride	blue
Cr_2O_3	$Cr(OH)_3$ or H_3CrO_3 or $HCrO_2$	basic and acidic	$CrCl_3$, chromic chloride; $NaCrO_2$ or $NaCr(OH)_4$, sodium chromite	green-violet; green-black
CrO_3	H_2CrO_4 or $H_2Cr_2O_7$	acidic	Na_2CrO_4, sodium chromate; $Na_2Cr_2O_7$, sodium dichromate	yellow; red

5. Chromous Compounds, Cr^{++}

Chromous hydroxide, $Cr(OH)_2$, is basic. It is readily oxidized in the air. Solutions of the chromous salts are prepared by dissolving the metal in acids or by reducing solutions of chromic salts with chromium or zinc:

$$2\,(Cr^{+++} + 3\,Cl^-) + Cr \longrightarrow 3\,(Cr^{++} + 2\,Cl^-).$$

Chromous compounds are of little practical importance.

6. Chromic Compounds

The oxide, Cr_2O_3 is formed when the metal is heated in the air, when a dichromate is heated with sulfur,

$$Na_2Cr_2O_7 + S \longrightarrow Na_2SO_4 + Cr_2O_3,$$

or when ammonium dichromate is ignited,

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4\,H_2O.$$

It is the most stable of the three oxides. It has a green color and is used as the pigment called *chrome green.* It is also used to color glass and ceramics, to which it imparts a green or blue color. It also has some use as a catalyst. When the hydroxide is prepared by precipitation it acts as a green gel and resembles aluminum hydroxide. It dissolves in acids to form chromic salts:

$$Cr(H_2O)_3(OH)_3 + 3\,(H^+ + Cl^-) \longrightarrow (Cr(H_2O)_6^{+++} + 3\,Cl^-).$$

It also dissolves in alkali hydroxides to form chromites, and similar compounds are formed when Cr_2O_3 is fused with the oxides of metals.

$$Cr(H_2O)_3(OH)_3 + (Na^+ + OH^-) \rightleftharpoons (Na^+ + Cr(H_2O)_2(OH)_4^-) + H_2O.$$

$$Cr_2O_3 + CaO \longrightarrow Ca(CrO_2)_2.$$

The compound $Cr(H_2O)_6Cl_3$ is the same as $CrCl_3$, except that it shows the hydration of the chromium ion. In the second equation, sodium chromite is represented as $NaCr(H_2O)_2(OH)_4$ or, if we omit the water molecules combined with

chromium, this would be $NaCr(OH)_4$ which, in turn, is equivalent to $NaCrO_2$, $2\ H_2O$.

The hydroxide is precipitated again when the solution of the alkali hydroxide is boiled. This effect is the result of the hydrolysis of sodium chromite. Chromite, $Fe(CrO_2)_2$, one of the ores of chromium, is ferrous chromite. Other chromites occur in nature.

Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24\ H_2O$, is the most important chromic salt. It is used as a mordant, in tanning leather, in printing cotton cloth, and in waterproofing certain materials.

7. Chromic Chloride

The chloride of trivalent chromium crystallizes from solutions as $CrCl_3.6\ H_2O$. The anhydrous chloride is produced by the action of chlorine upon metallic chromium at elevated temperatures and is finally recovered by sublimation. It is reddish-violet in color. A violet-colored solution results when the chloride is dissolved in cold water, but, upon boiling, the color changes to green and, when the solution is evaporated, green crystals of $CrCl_3.6\ H_2O$ are obtained. It appears that the change in color is the result of a change from one compound to another, both compounds having the same empirical formula. The blue compound is probably $Cr(H_2O)_6Cl_3$ and the green compound, $[Cr(H_2O)_4Cl_2]^+Cl^-.\ 2\ H_2O$. It will be noted that in each of these compounds the central chromium atom has a coordination number of 6, but in the second compound the six atoms and groups surrounding the chromium atom consist of four molecules of water and two atoms of chlorine. It is found that only one atom of chlorine — the one outside the group of six — is a free ion, because silver ion (from silver nitrate) will precipitate only one chloride ion of the three in the compound, whereas all three chloride ions of the blue compound are immediately precipitated.

8. Chromic Acid and the Chromates

Salts of chromic acid, H_2CrO_4, are produced by heating chromite, Cr_2O_3, or chromic salts, with an alkali hydroxide or carbonate in the presence of air. The reaction of chromite and sodium carbonate is

$$8\ Na_2CO_3 + 7\ O_2 + 4\ Fe(CrO_2)_2 \longrightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2,$$

and for sodium hydroxide and sodium chromite,

$$4\ NaOH + 4\ NaCrO_2 + 3\ O_2 \longrightarrow 4\ Na_2CrO_4 + 2\ H_2O.$$

The trioxide, CrO_3, is produced as scarlet needle-like crystals, when sulfuric acid is added to a concentrated solution of potassium dichromate, $K_2Cr_2O_7$.

$$(2\ K^+ + Cr_2O_7^=) + (2\ H^+ + SO_4^=) \longrightarrow (2\ K^+ + SO_4^=) + H_2O + 2\ CrO_3.$$

When dilute sulfuric acid is added to a yellow solution of potassium chromate, the color changes to red or orange, and upon evaporation, crystals of potassium dichromate separate.

$$2\ (2\ K^+ + CrO_4^=) + (2\ H^+ + SO_4^=) \rightleftarrows (2\ K^+ + SO_4^=) + H_2O + (2\ K^+ + Cr_2O_7^=).$$

The dichromates are used as oxidizing agents in many reactions. They are also used in tanning leather; the dichromate is first reduced to a compound of trivalent chromium, and the chromic hydroxide which is formed by hydrolysis is precipitated in the leather. Dichromates are also used in photography. Lead chromate, $PbCrO_4$, and barium chromate, $BaCrO_4$, are used as yellow pigments.

Potassium chromate is used in the dyeing industry and in the manufacture of certain inks. Potassium dichromate is used in medicine, in tanning, in bleaching and purifying certain oils, and as a laboratory reagent. Basic lead chromate, $PbO.PbCrO_4$, is a red pigment.

MANGANESE

9. Occurrence and History

Manganese is the only well known element of Division *A* of group seven. Its most important ore is *pyrolusite*, MnO_2, which is mined in Russia, Africa, India, and Brazil. A small amount is produced in Georgia and in a few of the western states. It also occurs in the form of other oxides or hydrated oxides; *braunite*, Mn_2O_3; *manganite*, MnO(OH); and *hausmannite*, Mn_3O_4. The name *manganese* is derived from a Latin word which means *magnet*. Compounds of the element are found in many minerals containing iron.

10. Preparation of the Metal; Its Physical Properties and Uses

Pure manganese has no commercial use and is difficult to prepare. It can be liberated from the dioxide or from other oxides by reduction with carbon in the electric furnace. The product contains carbon. More nearly pure manganese can be made by using powdered aluminum as the reducing agent. Usually, alloys of iron and manganese are produced instead of the pure metal. These are made by the simultaneous reduction of manganese and iron ores in a blast furnace and are called *ferromanganese* and *spiegeleisen*. The former contains about 75 per cent of manganese and the latter about 10. These alloys are used in the production of steel either to remove impurities, such as oxygen and sulfur, or to make manganese steels, which contain from 10 to 15 per cent of manganese. These steels are very hard, but are more easily rolled and forged than manganese-free steels. They are used wherever there is likely to be extensive wear, e.g., in steel rails and in the gears and other parts of machines. More than 90 per cent of the manganese ore produced in the world goes to make steel.

Manganese is a reddish-gray metal and in a very pure state is softer than iron, which it resembles in many of its physical and chemical properties. It melts at 1260°. If it contains carbon, it is very hard and brittle.

In addition to its alloys with iron, manganese forms a number of important alloys with the nonferrous metals. *Manganese bronze*, which contains copper, manganese, tin, and zinc, is especially resistant to the corrosive action of sea water and is used, for this reason, in propeller blades of steamships.

11. Chemical Properties and Compounds

Like iron, manganese is readily oxidized in the air. The presence of small amounts of carbon makes it more resistant to oxidation. It reacts slowly with water to liberate hydrogen and dissolves in acids, forming salts such as $MnCl_2$. The element forms five oxides and five corresponding series of compounds. Only the salts in which manganese has an oxidation number of + 2, e.g., $MnCl_2$ and $MnSO_4$, or + 7, e.g., $KMnO_4$, are of much importance.

The five oxides, their properties, and examples of the corresponding salts are shown in the table below.

COMPOUNDS OF MANGANESE

Oxide	Hydroxide or acid	Properties	Salts	Color of ion
MnO	$Mn(OH)_2$	basic	$MnCl_2$ manganous chloride	pink
Mn_2O_3	$Mn(OH)_3$	basic	$MnCl_3$ manganic chloride	violet
MnO_2	$Mn(OH)_4$ H_2MnO_3	amphoteric (relatively inert)	$MnCl_4$ $CaMnO_3$ calcium manganite	green
MnO_3	H_2MnO_4	acidic	Na_2MnO_4 sodium manganate	green
Mn_2O_7	$HMnO_4$	acidic	$NaMnO_4$ sodium permanganate	purple

12. Manganous Compounds

Yellow manganous oxide, MnO, is produced by reducing MnO_2 with hydrogen. Manganous hydroxide is produced as a

white precipitate when a soluble base is added to the solution of a manganous salt, e.g., $MnCl_2$. This hydroxide dissolves in acids but not in bases. In the air it is rapidly oxidized to Mn_2O_3, which is brown. Manganous chloride, $MnCl_2$, and the sulfate, $MnSO_4$, are the most important manganous compounds. Most manganous salts are pink in color.

13. Manganic Compounds

In its trivalent state manganese forms the hydroxide $Mn(OH)_3$ and corresponding manganic salts. These salts are very slightly stable and are easily reduced to manganous compounds. The hydroxide dissolves in acids but not in bases. The most important manganic salt is the alum, $K_2SO_4.Mn_2(SO_4)_3.24\ H_2O$.

14. Tetravalent Manganese

The most important compound of tetravalent manganese is the dioxide, MnO_2, which frequently occurs as the hydrated oxide, $MnO_2.H_2O$, sometimes represented as $MnO(OH)_2$ or as H_2MnO_3. The dioxide is relatively inert toward acids and bases. It does dissolve in cold concentrated hydrochloric acid to give a solution of $MnCl_4$, but at higher temperature, manganese is reduced to Mn^{++}, and chlorine is liberated. The dioxide does not dissolve readily in solutions of alkalies. Manganites can be produced by fusing the dioxide with the oxides of certain metals. These salts correspond to the purely hypothetical acid, H_2MnO_3. Calcium manganite, for example, is $CaMnO_3(CaO.MnO_2)$ or $CaMn_2O_5(CaO.2\ MnO_2)$.

The dioxide is used as a decolorizer of glass, as a component of dry cells, in manufacturing black glass and enamels, and as a drier in varnish.

15. Manganates (Hexavalent Manganese)

When any manganese compound, e.g. MnO_2, is fused with potassium or sodium hydroxide or carbonate in the presence of potassium chlorate, lead dioxide, or some other vigorous oxidizing agent, a green mass is obtained:

$$3\ MnO_2 + 6\ NaOH + KClO_3 \longrightarrow 3\ Na_2MnO_4 + KCl + 3\ H_2O.$$

The green compound is an alkali manganate, e.g., Na_2MnO_4. When water is added, this substance dissolves and is changed into permanganate and manganese dioxide. This reaction is more pronounced in the presence of acids.

$$3\ (2\ Na^+ + MnO_4^=) + 2\ (2\ H^+ + SO_4^=) \longrightarrow 2\ (Na^+ + MnO_4^-) + MnO_2 + 2\ (2\ Na^+ + SO_4^=) + 2\ H_2O$$

16. Permanganates (Heptavalent Manganese)

The most familiar and important compound of heptavalent manganese is potassium permanganate, $KMnO_4$. It is prepared as described in the preceding section of this chapter. A solution of the free acid, $HMnO_4$, is prepared by treating lead dioxide and a manganous salt or manganese dioxide with a solution of hot nitric acid:

$$2\ MnO_2 + 3\ PbO_2 + 6\ (H^+ + NO_3^-) \longrightarrow 3\ (Pb^{++} + 2\ NO_3^-) + 2\ HMnO_4 + 2\ H_2O.$$

The solution of the acid is pink. This reaction is sometimes employed in the detection of manganese.

In previous chapters, many examples of the use of potassium permanganate as an oxidizing agent have been mentioned (page 256). In an acid solution the manganese is reduced to manganous ion, Mn^{++} by such reducing agents as SO_2, $H_2C_2O_4$, $FeSO_4$, and H_2S. In an alkaline solution the manganese is reduced to MnO_2 or to a hydrated form of this oxide.

Potassium permanganate is used, also, in dyeing; as a disinfectant; as a bleaching agent; and in medicine for the treatment of snake bites, ivy poisoning, etc.

REVIEW EXERCISES

1. Construct a table showing the characteristic compounds of chromium and contrast these with the compounds of sulfur.
2. Describe the occurrences of chromium in nature, the methods of producing it from its ores, and its uses.
3. What is ferrochrome and for what purpose is it used?
4. Starting with the most abundant ore of chromium outline a method by which potassium dichromate can be produced. Write all equations for the reactions.
5. A sample of potassium dichromate was added to a solution containing HCl. Assuming that the reaction was complete, what weight of the dichromate was added, if the volume of the chlorine liberated was 150 cc. (standard)?
6. Write a balanced equation to show the reaction of potassium dichromate with hydrogen sulfide in an acid solution (H_2SO_4), if the sulfur is liberated as the free element.
7. In which of its compounds does manganese most closely resemble chlorine?
8. How would you prepare potassium permanganate from manganese dioxide?
9. What are pyrolusite, spiegeleisen, nichrome, stellite?
10. Describe the reasons for adding manganese and chromium to steel.
11. In which of their compounds do chromium and manganese act most as metals?
12. Write equations for the following reactions:
    (*a*) Chromium hydroxide is precipitated by adding sodium hydroxide to a solution of chromium chloride, $CrCl_3$.
    (*b*) Chromic hydroxide dissolves in an excess of sodium hydroxide.
    (*c*) A solution of potassium chromate is treated with sulfuric acid.
    (*d*) Manganese dissolves in hydrochloric acid.
    (*e*) Chromic chloride, $Cr(H_2O)_6Cl_3$, hydrolyses.
    (*f*) Manganic chloride, $MnCl_3$, is treated in solution with sodium hydroxide.
    (*g*) $CaMnO_3$ reacts with HCl.

REFERENCES FOR FURTHER READING

Evans, U. R., *Metals and Metallic Compounds*, vol. II, page 301.

Chromium: *Ind. and Eng. Chem.*, **19,** 773 (1927); **28,** 1381 (1936); *Chem. and Met. Eng.*, **30,** 149, 627 (1924); **32,** 692 (1925); **33,** 434 (1926).

Manganese: *Ind. and Eng. Chem.*, **32,** 1168 (1940).

Passive State of Metals: *J. Chem. Ed.*, **10,** 108 (1933).

43

METALS OF GROUP EIGHT

1. Introduction

The elements of group eight consist of three series, or triads, of metals: (1) Iron, cobalt, and nickel; (2) ruthenium, rhodium, and palladium; and (3) osmium, iridium, and platinum. Each of these series lies in the middle of one of the long periods of elements in the periodic classification. The metals of the first triad are much more abundant and important than those of the second and third. They are also relatively active metals, while the others are noble metals similar to platinum. Iron, cobalt, and nickel have very similar properties. The other six members of the group are also closely related to one another and are commonly grouped together as the *platinum family*.

IRON

2. History and Importance

The symbol, Fe, of the element and the names of its compounds, *ferrous* and *ferric*, are derived from the Latin name *ferrum*. The iron first used by man was probably of meteoric origin. Primitive methods of smelting iron ores consisted of mixing the ores with charcoal and covering over a pile of this material with clay. A hole was left at the top and one at the bottom to produce a draft. The charcoal was ignited and some of it burned to liberate heat. Carbon dioxide was first formed, and later was reduced to carbon monoxide, which acted as the reducing agent on iron oxide. The production and use of iron on a large scale began about 1620, when the ores of the metal were first reduced by means of coal.

Iron is the most widely used and important metal. Its importance depends upon three factors: (1) The ores of the metal are abundant, contain large percentages of iron, and are found in many parts of the world; (2) the metal is easily and cheaply produced from its different ores; and (3) the properties of the metal can be varied over a wide range by different methods of treatment or by the addition of other substances, thus producing metal which is adapted to many widely different uses. To most persons the name metal is almost synonomous with iron, and the most casual observer knows that more iron is used than all of the other metals together.

3. Occurrence

The principal ores of iron are *hematite*, Fe_2O_3; *limonite*, $(Fe_2O_3)_2.3\ H_2O$; *magnetite*, Fe_3O_4, or $FeO.Fe_2O_3$; *siderite*, $FeCO_3$; and *pyrite*, FeS_2, sometimes called fool's gold because of its yellow color. Hematite the most important of these ores. It is responsible for the red color of sandstones and soils. Iron compounds occur in almost

all rocks and soils and are responsible for much of the coloring of many formations. Iron compounds are also found with the chlorophyll of plants and in the hemoglobin of the blood. Iron appears to be necessary for the proper functioning of these substances and for life itself.

The Lake Superior region furnishes more than 80 per cent of the ore mined in the United States. The second most important iron-ore mines in this country, at the present time, are in the region around Birmingham, Alabama. The other principal producing countries are France, Great Britain, Germany, Russia, Belgium, Sweden, and Japan.

METALLURGY OF IRON AND STEEL

4. The Blast Furnace

Iron ores are reduced in a blast furnace (Figure 279). This is a steel tower, about 90 feet in height, and 20–22 feet in diameter at the widest point. It is lined with fire brick, and the walls of the lower part of the furnace are cooled by water which circulates through blocks or tubes made of bronze and embedded in the walls. The furnace tapers toward the top and toward the bottom. The lower constriction in the size of the tower is necessary to provide a support for the charge, when the materials near the bottom of the furnace melt. A blast of hot air is blown into the furnace (near the bottom) through pipes called *tuyeres*. The charge consists of suitable proportions of ore, coke, and limestone. This material is dumped from cars into the top of the furnace through a trap called a *bell*, which prevents the furnace from remaining open at the top, thus causing a strong draft which would remove the gases in the furnace too rapidly and also lower the temperature. The gases which escape through a pipe at the top contain carbon monoxide and, therefore, have some value as fuel. They are burned to heat the air which is blown into the furnace through the tuyeres and to supply the energy required for the operation of machinery in other parts of the plant.

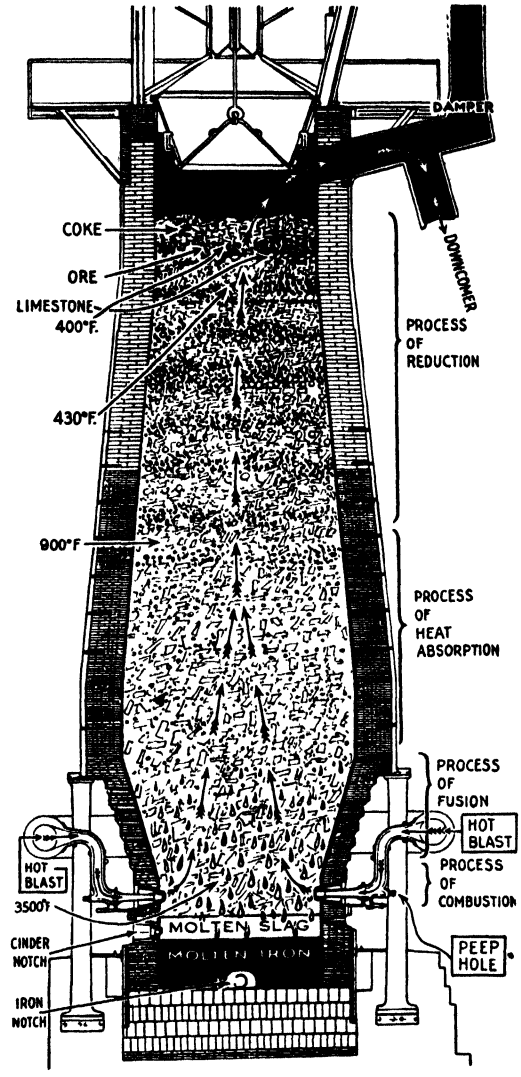


Figure 279. Cross Section Diagram of a Blast Furnace
(Courtesy of United States Steel Corporation)

Coke is added for two purposes. Its combustion in the lower part of the furnace provides the heat required for the process and to melt the iron and slag which are produced. It also acts as the reducing agent or produces carbon monoxide, which acts in this capacity.

The limestone is added as a flux. Most iron ores contain silica and clay which must

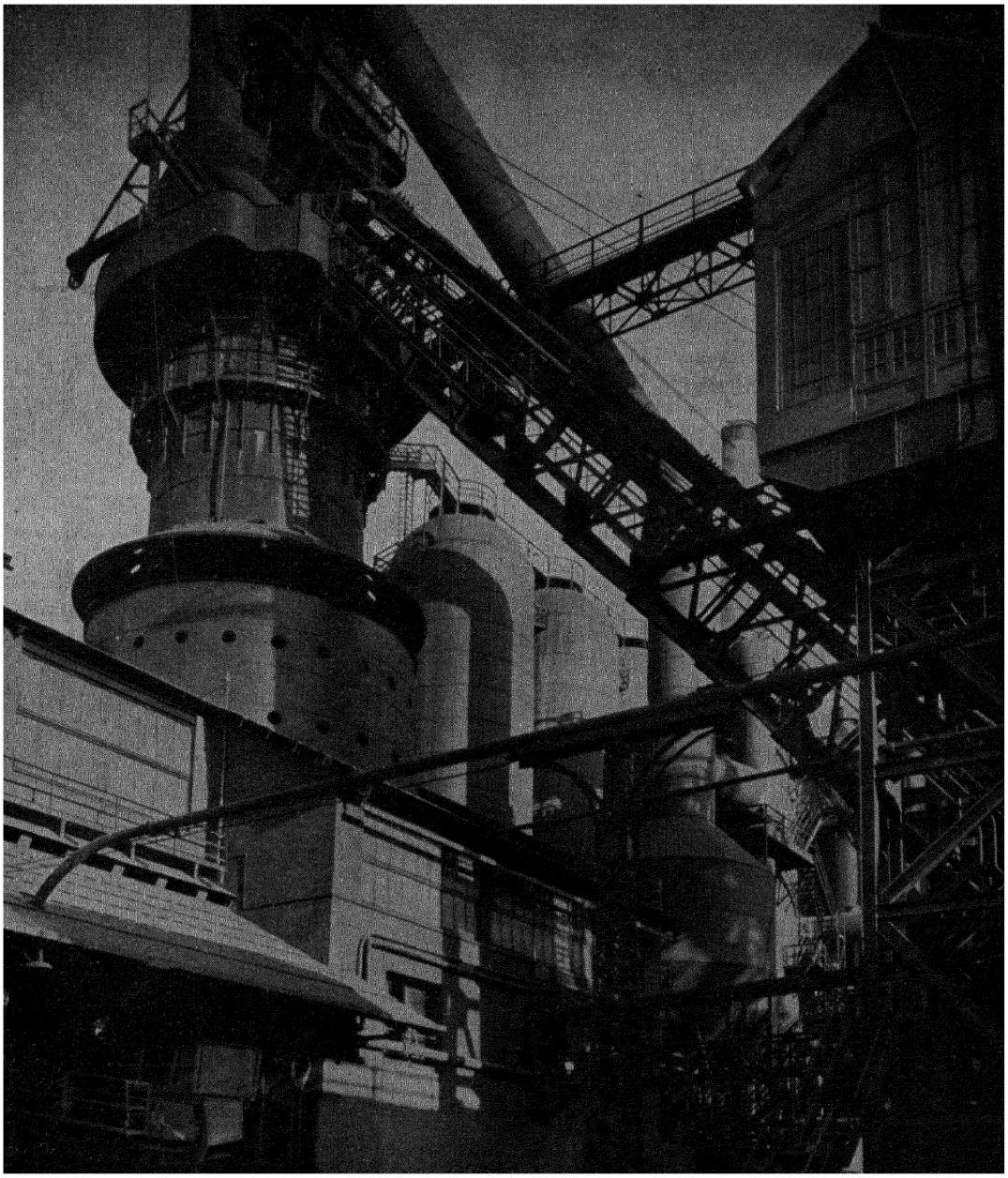


Figure 280. Blast Furnaces
(Courtesy of Ford Motor Company)

be separated from the iron. The limestone reacts with these substances to produce a slag, which is drawn off, as it collects, through a conduit. This slag is important because (1) it collects on top of the iron and provides a protection against oxidation, which otherwise would be very rapid; and (2) the liquid slag provides a medium in which the melted iron, which is produced in small drops, may collect into a single mass.

The melted iron collects in the lowest part of the furnace, which is called the *crucible*. It is drawn or tapped off from the crucible at 6-hour intervals. The narrow portion of the furnace above the crucible is called the *bosh*.

5. Reactions in the Blast Furnace

The air which enters the furnace at the bottom of the bosh burns some of the fuel, forming carbon dioxide. The temperature at this point is about 1600°. At the top of the bosh, where the temperature is about 1300°, the limestone is decomposed, forming CaO and liberating more CO_2. Here and at lower levels, the lime and silica react to form slag. Here, too, some of the iron ore which has escaped reduction in the upper part of the furnace is reduced by the direct action of carbon. The carbon dioxide passes with other gases up through the charge, and slightly above the top of the bosh it is reduced to carbon monoxide, which acts as the reducing agent in the upper portions of the furnace. The reactions are summarized below:

$$C + O_2 \longrightarrow CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$CO_2 + C \longrightarrow 2\,CO$$
$$Fe_2O_3 + 3\,C \longrightarrow 3\,CO + 2\,Fe$$
$$Fe_2O_3 + CO \longrightarrow 2\,FeO + CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2.$$

The iron which is drawn off as a liquid from the crucible is run off into large buckets for transportation to the steel mill or into molds or troughs and cast into forms called "pigs." Pig iron is then used as the starting material in the production of all varieties of iron and steel. It contains 3 to 4.5 per cent of carbon and varying small amounts of silicon (about 2 per cent), manganese, phosphorus, and sulfur. It must be refined before it can be used for almost all purposes, since it has a very low tensile strength and is brittle. The production of pig iron fluctuates from year to year with the periods of prosperity and depression in the business world. The producing capacity of the United States is estimated at about 98,000,000 tons. A single blast furnace produces 500–1000 tons of iron per day.

6. Cast Iron

This is the nearest relative of pig iron. It is made by melting pig iron in a *cupola furnace* with scrap iron of somewhat better quality than the pigs themselves. The furnace is much smaller than a blast furnace but has about the same design. Coke is added as the fuel and some additions, such as ferromanganese, may be made. The liquid iron is cast in sand molds, in which it is cooled gradually. The product is called *gray cast iron*. It always contains more than 2 per cent of carbon and variable amounts of silicon and manganese with smaller amounts of sulfur, phosphorus, and other elements. It cannot be welded, rolled, or forged and has a small tensile strength. It is used largely in making articles which can be made by casting instead of forging or machined. These articles include such things as the parts of stoves and steam radiators.

The carbon contained in gray cast iron is present largely as a carbide, Fe_3C, called *cementite* which decomposes and liberates carbon as graphite as the iron cools slowly; graphite is responsible, in considerable measure, for the color and other properties

of the metal. *Chilled* or *white cast iron* is made by rapidly cooling the iron, or at least the surface portions, while it is in the molds. This variety of cast iron contains carbon in the form of cementite rather than graphite. It is very hard and brittle, and possesses excellent wear-resistance. *Malleable cast iron* is made by heating white cast iron for 50 to 70 hours at a red heat and then allowing it to cool gradually. Most of the carbon in this product is present as small particles of graphite. This variety of cast iron is slightly more desirable for use in making the parts of heavy machines and certain kinds of tools and agricultural implements. It is slightly malleable and fairly strong, but it cannot be welded or forged. Because of other elements that it contains, cast iron has a relatively low melting point and, therefore, can easily be cast in different forms.

7. Wrought Iron

This is a fairly pure form of iron which is made by burning out most of the impurities that occur in the product of the blast furnace. The process is carried out in a *puddling* furnace, which is a small reverberatory furnace (Figure 281). The heat is reflected from the roof upon the charge, which consists of pig iron on top and a layer of iron oxide on the bottom. The iron melts and the impurities are oxidized by the oxide. The carbon and sulfur are removed as carbon dioxide and sulfur dioxide. Silicon and phosphorus are changed into oxides, which react with oxides of iron and manganese or with limestone, which is added as a flux, to produce a slag. The pure iron which is formed, as the impurities are removed, has a higher melting point than pig iron, and the mass consequently becomes less fluid. It is raked together by means of a "rabble" and removed from the furnace in large balls. These are hammered or rolled to remove the slag. The product contains 0.2 per cent or less of carbon. It is fibrous and is softer and stronger than cast iron but not as strong as steel. It is malleable and ductile. It is used to make articles which can be hammered into shape while red hot. Plowshares, anchors, and horseshoes are examples.

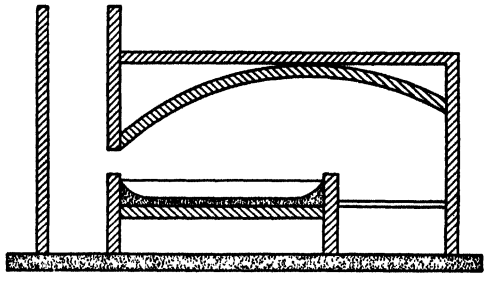


Figure 281. Puddling Furnace

Iron that is 99.9 per cent pure is produced from wrought iron. It melts at 1535°, is very soft, and is used in the manufacture of certain iron compounds. Nearly pure iron, about 99.95 per cent, is produced electrolytically.

STEEL

The term steel is a name which is applied to many widely different alloys of iron. It is made from pig iron by burning out the impurities and later adding constituents such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce steels which possess specific properties and which are suited for specific uses. Steels usually contain between 0.1 and 1 per cent of carbon. Hence, a large part of the carbon contained in pig iron must be removed in the production of steel. Phosphorus, silicon, and sulfur, which are especially objectionable, because they make steel brittle, must also be removed. The two most generally used methods of making steel are the *Bessemer* and the *Open-Hearth* processes.

8. The Bessemer Process

This process depends essentially upon

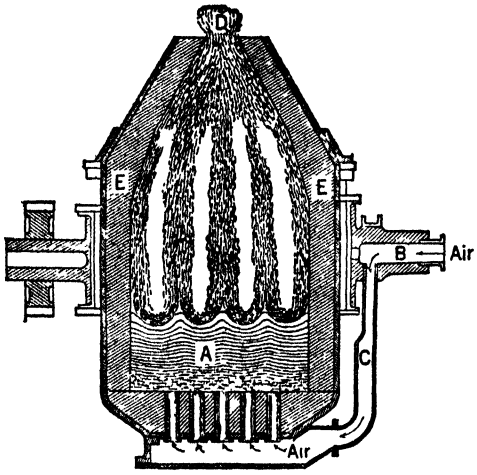


Figure 282. The Bessemer Converter

Air enters the converter through the trunnion (B). Gases resulting from the combustion of impurities escape at D and the molten steel collects at A.

the use of an air blast in burning the impurities out of pig iron. The reaction is carried out in a large egg-shaped crucible (Figure 282) called a Bessemer converter. The crucible is made of steel and, in the United States, is usually lined with silica brick. The silica constitutes an "acid" lining, which will react with basic oxides that are produced by the oxidation of the impurities but not with the oxides of phosphorus or sulfur. Hence, the *acid* Bessemer process is suited only to the production of steels from pig iron containing inappreciable quantities of these two elements.

The converter is built on a trunnion so that it may be tipped over to receive the charge of melted iron from the blast furnace, or to deliver the finished product into large ladles. A converter holds from 15 to 25 tons of steel. Air is forced under a pressure of about 30 pounds through a hollow trunnion and through holes in a false bottom of the converter into the melted iron. The oxidation of silicon, carbon, and other impurities liberates considerable heat, and during the "blow" the flames and sparks are shot out of the mouth of the crucible with a dazzling, blinding brilliance. The air blast is continued for 10 to 20 minutes until the character of the flame indicates that the carbon is completely oxidized. Carbon, manganese, chromium, and other elements are then added to give a product of the desired composition. These elements usually are added in the form of iron alloys such as ferromanganese. To remove oxygen which may remain in the steel, or which may become trapped in it as the metal is poured, deoxidizers are also added prior to pouring. Aluminum, ferromanganese, or ferrosilicon are used for this purpose. If not removed, the gas forms small bubbles which weaken the steel. The converter is tilted and the charge is poured into large ladles and then into large molds, where it solidifies to form ingots. The ingots are rolled to make rails and beams of structural steel or hammered into other forms.

9. The Open-Hearth Process

The furnace used in this process is shown in Figure 283. A charge consisting of pig iron, scrap iron covered with rust, and limestone is placed in the furnace. The hearth of the furnace is made, usually, of a basic material, such as limestone, dolomite, or magnesite. A hearth made of silica brick is used in the acid open-hearth furnace to make steel from iron which contains very little phosphorus or from scrap steel. Heat is provided by burning fuel gas, an oil spray, or powdered coal over the charge. The fuel and air enter through preheaters. The air

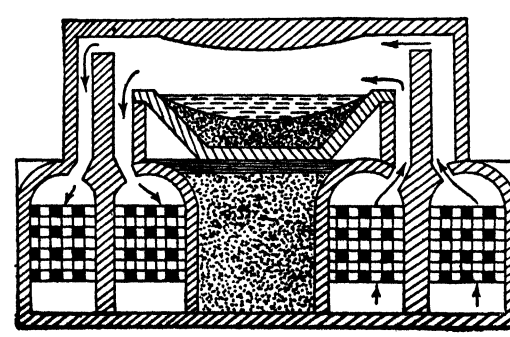


Figure 283. The Open-Hearth Furnace

is preheated by passing through a brick-work chamber before it enters the furnace If a gas is used as fuel it may be preheated in a similar manner. The hot gases which are produced during the oxidation of the carbon, sulfur, and certain other impurities pass off through another brick-work chamber. The directions of the entering gases and the gaseous products are reversed frequently so that each chamber is alternately heated and serves, in its turn, to preheat the air. The carbon is removed from the iron as carbon dioxide, while the phosphorus, sulfur, and silicon are converted first into oxides, and then into fusible compounds by interaction with lime or magnesia. This material collects as slag on the surface of the steel and is easily removed. The furnace makes about 50 tons of steel at one time. The process requires about 8 hours for each charge.

Near the end of the reaction deoxidizers are added. Because the process is very slow, the steel can be analyzed from time to time, and the operation can be stopped when the analysis shows that the desired carbon content has been reached. Just before the steel is poured, the required and

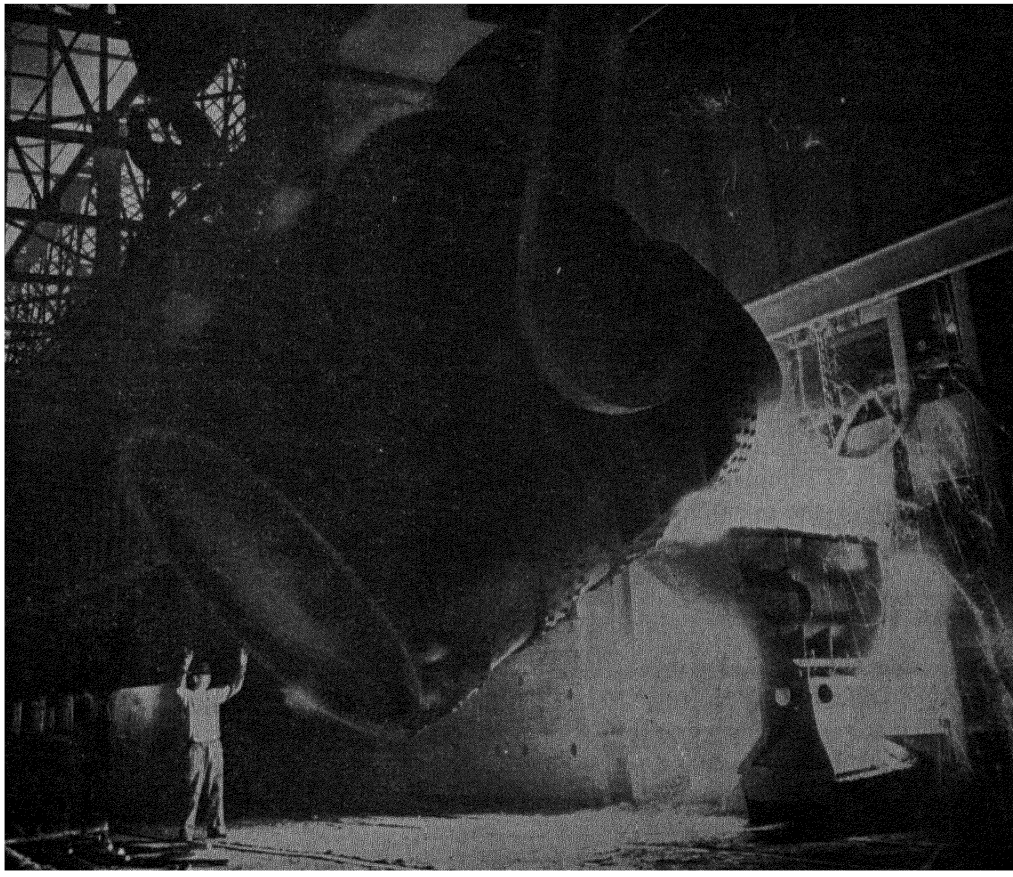


Figure 284. Open-Hearth Furnace

A charge of pig iron is poured into the furnace which already contains a charge of partially melted steel scrap. The ladle shown contains about 100 tons of metal.

(Courtesy of United States Steel Corporation)

calculated amounts of manganese, chromium, and other elements are added.

After the removal of the slag, molten steel is *poured* by allowing it to run into *ladles* (actually large buckets). Sometimes oxygen scavengers and elements that form alloy steels are added to the charge in the ladles. From the ladles the steel is poured into molds to form ingots. Blowholes, produced largely by carbon monoxide, may form as the ingots solidify. These can be prevented by adding scavengers that combine with oxygen and thus prevent the formation of carbon monoxide. Blowholes are also removed by rolling and drawing.

Slightly more than 90 per cent of the steel made in the United States is produced by the basic open-hearth process. Open-hearth steel is uniform in structure and is less likely to contain flaws than Bessemer steel. Some steel is produced in electric furnaces, which operate on the same principles as the open-hearth furnaces, except for the use of electricity as a source of heat.

The Duplex Process is a combination of the Bessemer and Open-Hearth processes. Iron is first treated in an acid Bessemer converter until some of the carbon and all of the silicon and manganese are oxidized. It is then placed in a basic open-hearth furnace in which the oxidation of carbon and phosphorus is completed. This process is faster than the open-hearth process alone.

10. Crucible Steel

High-grade steel, containing up to 1.5 per cent of carbon, is made by melting wrought iron or steel made in the Bessemer converter or in the open hearth furnace, in large crucibles. The required amounts of carbon and other elements (chromium, manganese, tungsten, etc.) are added and allowed to dissolve in, or alloy with, the iron. The steel made in this manner has a uniformly high quality but must be made in small units. It is used mainly in the manufacture of tools, and other articles, such as springs, files, razor blades, and knives.

11. Hardening and Tempering Methods

Steel ingots, after they have solidified, are placed in a soaking pit. Here they are kept at red heat for some time in order that the strains and stresses produced during solidification may be relieved. Afterwards, while still hot, the steel goes to the rolling mill where it is rolled, i.e., worked into different shapes by passing it through steel rollers. Some may be drawn into wire or rod, and some may be forged.

The properties of iron and steel depend, to a considerable extent, upon the physical state of the iron and upon the condition of the carbon. At ordinary temperatures, the stable form of iron is soft. This is called *alpha iron* or *ferrite*. At temperatures above 900°, this modification of iron changes to *gamma iron*, which consequently is the form of iron in steels that are heated to high temperatures. This form of iron dissolves carbon up to about 1.5–2 per cent and when rapidly cooled, crystallizes to give a solid solution of *cementite*, Fe_3C, and gamma iron. This solution is called *austenite*. Steel of this composition is made by quenching the hot metal in water or oil. The composition remains unchanged during the cooling, since the change to alpha iron and the changes involving carbon do not have time to occur completely.

If steel is cooled slowly, after being heated for some time above 900°, the alpha modification of iron is produced, and the carbon is deposited for the most part as crystals of cementite. This variety of steel is softer, more pliable, and has a higher tensile strength than steel which has been cooled rapidly.

If steel which has been cooled rapidly is reheated to temperatures between 200° and 600°, some of the solid solution of cementite and iron is broken up into separate crystals of the two substances. At the same time,

mechanical strains resulting from rapid cooling are also relieved. By varying the temperature, the length of the period of heating, and the rate of cooling, these changes may be made to occur to different extents, and steels possessing varying degrees of hardness can be produced.

Case-hardened steel is made by heating low-carbon steel in closed containers with powdered carbon and later quenching it in oil. The steel takes up some of the carbon on its surface, thus producing a metal which has a thin layer of hard high-carbon steel on its surface and a core of strong, pliable, low-carbon steel. Steel treated in this manner is used to make axles, car wheels, and other articles that must be hard to resist wear and, at the same time, somewhat flexible to prevent breaking when subjected to sudden strains and shocks. A similar variety of steel is made by heating the metal in an atmosphere of ammonia. In this case the surface is hardened by the formation of iron nitride.

12. Alloy Steels

The simplest steels contain small percentages of carbon and manganese. In order that steels may be produced that are hard and, at the same time, strong instead of brittle, chromium, nickel, manganese, vanadium, molybdenum, silicon, tungsten, and uranium are added. For every ton of steel produced about 30 pounds of non-ferrous metals are added or used as coatings. By varying the number and percentages of these elements steel possessing practically any set of properties may be produced. Some of the important features of these steels are summarized in Table 25.

IRON AND ITS COMPOUNDS

13. Properties of Pure Iron

Pure iron is scarcely ever prepared on a commercial scale and is not well known even in the laboratory. It may be made by reducing pure ferric oxide with hydrogen. Wrought iron comes the nearest of the commercial forms of iron to possessing the properties of the pure metal. Pure iron melts at about 1530°, wrought iron at about 1500°, and pig iron at about 1100°. The pure metal has a silvery white luster, and is malleable, ductile, and relatively soft. It possesses much stronger magnetic properties than any of the commercial forms of iron. Two of its allotropic modifications, alpha iron and gamma iron, have been mentioned in connection with the tempering of steel (page 534). In addition

TABLE 25. ALLOY STEELS

Element	Percentage	Properties of Steel
Silicon	1–2	Hard; strong
	12–15 (duriron)	Resistant to corrosion, acids, etc.
Cerium	70	Pyrotechnic, emits sparks when scratched.
Nickel	1.5–4	Strong, resistant to corrosion, tough, low coefficient of expansion.
Nickel-Chromium	1–1.5 and 0.2 to 0.7	Hard, tough, high tensile strength.
	7–10 and 18	Stainless, strong.
Chromium	1.5–5	Hard, strong, tough.
	10–15	Stainless.
Vanadium	0.1	Tough.
Manganese	10–14	Hard, resistant, strong, tough.
Tungsten	4–18	Hard, holds temper when heated.
Carbon	0.1–1.5	Hard.
Molybdenum	6–7	Holds temper when heated.
Lead	1 pt. in 500	Easily machined.
Titanium	0.1	Very hard.

to these there is a third form, delta iron, which is stable above 1400°.

Chemically, iron is a relatively active metal. The displacement of hydrogen from steam by hot iron, the burning of finely divided iron in air and in oxygen, its direct combination with sulfur and with moist chlorine, and its displacement of hydrogen from hydrochloric and sulfuric acids will be recalled as examples of its activity. Like some of the metals (page 522) iron is made passive when it is dipped in fuming nitric acid. It becomes active again when it is scratched or struck. Its oxides and hydroxides are basic; and hence, its most important compounds are those that form positive ferrous or ferric ions, if they dissolve.

14. Oxides and Hydroxides of Iron

Ferrous oxide, FeO, is a black powder. It can be made by reducing ferric oxide. with hydrogen at a temperature of 300° or lower, or by the decomposition of ferrous oxalate, FeC_2O_4. It burns in air to produce ferric oxide. The corresponding hydroxide, $Fe(OH)_2$, is a white solid, which may be precipitated by adding a soluble hydroxide to a solution of a ferrous salt. It tends to become a colloidal gel, resembling aluminum hydroxide in this respect. When allowed to stand in contact with the air, it turns green and then brown as it is oxidized to hydrous ferric oxide, $Fe_2O_3.x\,H_2O$. *Ferric oxide*, Fe_2O_3, is produced by roasting pyrite, FeS_2, in the air, or from ferrous sulfate, which is first oxidized and then converted into ferric hydroxide by adding lime to the solution. The precipitated ferric hydroxide is then ignited to remove water and to form the oxide. It is an insoluble red powder. It occurs in nature as the important mineral hematite, which varies in color from brownish-red to black. Iron rust and the iron ore, limonite, contain hydrated forms of the oxide, of which $Fe_2O_3.H_2O$ and $(Fe_2O_3)_2.3\,H_2O$ are typical. Very pure, gritless ferric oxide is used commercially as jeweler's *rouge* and as *Venetian red*. As the latter it is used as a pigment in paints for barns, bridges, railway cars, etc., and as a pigment for pottery and rubber. Ferric hydroxide is precipitated as a reddish-brown gel when a soluble hydroxide is added to a solution of a ferric salt. This substance, although usually assigned the formula $Fe(OH)_3$, is probably a mixture of the hydrated forms of ferric oxide. It dissolves readily in acids but only slightly in solutions of alkali hydroxides.

The two oxides of iron are found together in nature as the mineral *magnetite*, Fe_3O_4. This substance is a compound whose composition is best represented by the formula $FeO.Fe_2O_3$. This compound is sometimes found on the surface of iron that is heated in the air. It forms a durable, tightly adhering, and non-porous film on the object and protects it against rusting. Such a film is found on gun barrels.

15. Ferrous Sulfate, $FeSO_4$

The most widely used ferrous salt is the *sulfate*, $FeSO_4$. It is prepared by dissolving iron in dilute sulfuric acid and evaporating the solution. Scrap iron may be used for this purpose, and a considerable quantity of commercial ferrous sulfate is recovered from the pickling baths in which sheet iron is dipped before it is galvanized or coated with enamel. Ferrous sulfate is also prepared by the oxidation of moistened pyrite in the air. The ferrous sulfate is later extracted from the mass with water. The salt crystallizes from solution as the green hydrate, $FeSO_4.7\,H_2O$, which is called *green* vitriol. The crystals lose the water of hydration when exposed to the air and become brown in color due to the oxidation of the ferrous sulfate. Solutions of the salts are not permanent, since the ferrous sulphate is readily oxidized to $Fe(OH)SO_4$, the basic ferric sulfate. To prevent this change, the solution is acidified with sulfuric acid and

kept in contact with metallic iron. Ferrous sulfate is used in the purification of water, where it acts in the same manner as aluminum sulfate (page 187). It is also used in medicine; as a disinfectant; as a weed killer and wood preservative; in the manufacture of black inks and dyes; and as a reducing agent in the laboratory and in commercial operations. When used in inks, tannin is also added. This reacts with ferrous sulfate to form the ferrous salt of tannic acid. This salt is oxidized to ferric tannate, which is black, but this change is prevented in the ink by the addition of sulfuric acid and a protective colloid, such as gum arabic. A blue dye is added to give the ink a color when it is first used in writing. After standing on the paper for some time, the ferrous tannate is oxidized to the black ferric salt.

Bluish green crystals of the double salt, *ferrous ammonium sulfate*, $FeSO_4.(NH_4)_2SO_4.6\,H_2O$ separate from a solution containing equimolecular amounts of ammonium and ferrous sulfates. This substance is stable in the air, and for this reason is preferable to ferrous sulfate in analytical chemistry.

16. Ferrous Chloride, $FeCl_2$

This salt crystallizes as the hydrate, $FeCl_2.4\,H_2O$, from solutions made by dissolving iron in hydrochloric acid. The crystals of the pure, hydrated salt are blue, but they turn green in the air as oxidation progresses. The anhydrous salt is prepared by the action of hydrogen chloride upon iron. The salt is used as a reducing agent and, in a limited way, as a mordant.

17. Ferric Chloride, $FeCl_3$

This is the most important ferric salt. It is made by the action of chlorine upon iron. This reaction gives the anhydrous salt as black crystals. The salt can be sublimed when heated. It is very soluble in water and forms several hydrates of which the most familiar is $FeCl_3.6\,H_2O$. When the hydrate is heated, hydrolysis occurs and HCl is liberated. When the material is heated to dryness, only the oxide remains. In solution, the salt is also strongly hydrolyzed. It is used as a mordant, as a reagent in chemical analyses, and in medicine.

18. Ferric Sulfate, $Fe_2(SO_4)_3$

This salt is produced by oxidizing ferrous sulfate. Since it does not crystallize satisfactorily from solutions, it is usually converted into alums, such as ferric ammonium alum, $(NH_4)_2SO_4.Fe(SO_4)_3.24\,H_2O$ or iron alum, $K_2SO_4.Fe_2(SO_4)_3.24\,H_2O$. These are readily separated from solutions as well-formed crystals.

19. Complex Iron Cyanides

Ferrocyanide ion reacts with ferric ion to form a dark blue precipitate called *Prussian blue*, which is used as a pigment in paints and in blueing for use in the laundry. This substance is *ferric ferrocyanide*:

$$3\,(4K^+ + Fe(CN)_6^{-4}) + 4\,(Fe^{+++} + 3\,Cl^-) \longrightarrow Fe_4(Fe(CN)_6)_3\downarrow + 12\,(K^+ + Cl^-).$$

Ferricyanide reacts with ferrous ion to form the dark blue, insoluble compound called *Turnbull's blue*. This substance is *ferrous ferricyanide*.

$$2(3\,K^+ + Fe(CN)_6^{\equiv}) + 3\,(Fe^{++} + SO_4^{=}) \longrightarrow Fe_3(Fe(CN)_6)_2\downarrow + 3\,(2K^+ + SO_4^{=}).$$

Ferrous ferrocyanide, if pure, is white and ferric ferricyanide is a soluble green compound. Since ferrous ion does not form a blue precipitate with ferrocyanide, the two valence-states of iron can be detected by means of these reactions. Ferric iron is also detected by means of potassium thiocyanate, KCNS, with which it forms the blood-red, soluble compound, $K_3Fe(CNS)_6$.

20. Blue-Prints

The paper used in making blue-prints is made sensitive to light by dipping it in a

solution containing ferric ammonium citrate and potassium ferricyanide. The paper is then dried in the dark. It is covered with a mixture of the two salts and ferric ferricyanide, which gives it a green color. A sheet of this paper is covered with tracing cloth, upon which the design to be blue-printed has been drawn, and exposed to the light. The ferric compound is reduced to the ferrous state, wherever light passes through the tracing cloth and strikes the paper. There is no change beneath the lines in the drawing. The paper is developed by dipping it in water. This brings about a reaction between ferrous and ferricyanide ions, forming insoluble Turnbull's blue wherever the ferrous salt has been made. At other points where there has been no reduction, the unchanged soluble substances are completely removed by the water.

COBALT

21. History and Occurrence

The name of this element is derived from the German word *kobold*, which means "a goblin." For a long time, the minerals from which cobalt was finally prepared resisted all efforts to decompose them because, as it was thought, goblins and devils carefully guarded the minerals and thwarted man's attempts to liberate the metal. Brandt succeeded in preparing the element in 1735. Cobalt occurs in nature in many minerals that contain compounds of iron, nickel, silver, arsenic, and copper. The common cobalt minerals are compounds of the element with sulfur or arsenic: *cobaltite*, CoAsS; *smaltite*, $CoAs_2$; and *linnalite*, Co_3S_4. The richest deposits of these minerals are in Ontario, Canada. The ores of this region contain large amounts of silver, and cobalt is produced as a by-product of the silver smelters. Cobalt is also produced from ores mined in Africa.

22. Metallurgy

The cobalt ores of Ontario are smelted in a small blast furnace, from which the silver is recovered as bullion, and the other metals are collected as a complex mixture of arsenides and sulfides. The mixture is roasted with suitable fluxes to remove arsenic and iron. Heating it with sodium chloride converts the cobalt and nickel into chlorides, which are extracted with water. The nickel and cobalt are then precipitated as $Co(OH)_2$ and $Ni(OH)_2$. The separation of these two metals is extremely difficult. In the Mond process the oxides are reduced with water gas, and nickel is removed by forming the volatile carbonyl, $Ni(CO)_4$ in an atmosphere of carbon monoxide. Metallic cobalt is made by the reduction of the oxide with carbon.

23. Properties and Uses

Pure cobalt is silvery gray, malleable, ductile, and magnetic at ordinary temperatures. It melts at 1480°. Like iron, it displays the phenomenon of passivity. It is less readily oxidized than iron. It reacts with oxygen to form Co_3O_4, which is analogous to Fe_3O_4. It displaces hydrogen from steam slowly when it is heated to redness and reacts slowly at ordinary temperatures with non-oxidizing acids. It also combines directly, at different temperatures, with the halogens, carbon, and sulfur.

Cobalt is not widely used. Its use in making *carbaloy* will be mentioned in the discussion of tungsten (page 548). Its most important use is in the manufacture of *stellite*, an alloy containing iron, cobalt, and varying percentages of metals such as chromium, nickel, tungsten, and molybdenum. Stellite is used in making high-speed cutting tools, surgical instruments, etc. Cobalt is sometimes electroplated on steel from the same bath as nickel, thus adding to the brightness of the nickel plating.

24. Compounds of Cobalt

The oxides of cobalt are CoO, Co_2O_3, CoO_2, and Co_3O_4. The last of these is a compound, $CoO.Co_2O_3$, or $2\ CoO.CoO_2$. The monoxide is used to produce a blue color in glass, enamels, and glazes, and in painting blue designs on china. The blue color is produced by the formation of a cobaltous silicate. Powdered blue cobalt glass, called *smalt*, is sometimes used in place of the oxide. The trioxide, Co_2O_3, is made by heating $Co(NO_3)_2$. The dioxide is made by the action of vigorous oxidizing agents upon cobaltous compounds in alkaline solutions. Although cobalt forms cobaltites, in which it acts as a non-metal, the principal compounds of the element are salts in which cobalt acts as a metal. The cobaltic salts are unstable, are not easily prepared, and are not well known. The cobaltous salts, such as $CoSO_4$ and $CoCl_2$ are easily prepared and are the most important compounds of the element. The anhydrous salts are blue, and the hydrates are red. Cobalt forms many complex salts such as: $Na_4CO(CN)_6$; $Co(NH_3)_6Cl_3$; and $K_3Co(NO_2)_6$. Potassium cobalti-nitrite, $K_3Co(NO_2)_6$, dissolves only slightly.

NICKEL

Nickel ores, like those of cobalt, are difficult to reduce and consequently early efforts to produce the metal were unsuccessful. It was thought that these minerals contained copper, and so they were called *kupfernickel*, a German word from which the element nickel derives its name. *Kupfer* refers to copper, and *nickel* to the devil which was thought to prevent the preparation of copper from the mineral. The element was first prepared in 1857 by Cronstedt.

25. Occurrence

Nickel occurs in meteorites as an alloy with iron; in *pyrrhotite* (sulfides of nickel, iron, and copper); in *garnierite*, a silicate containing magnesium; and in other minerals containing cobalt, copper, iron, and silver as complex sulfides and arsenides. The largest part of the world's supply of nickel is obtained at present from pyrrhotite deposits in Ontario, Canada. Some nickel is recovered in the electrolytic refining of copper.

26. Metallurgy

The Canadian ores are roasted and smelted in a blast furnace. This yields a matte of the sulfides, which is then mixed with silica and treated in a Bessemer converter. Iron is oxidized and converted into slag, and the enriched nickel matte is then further heated to oxidize nickel sulfide to the oxide. In another process the matte is heated with sodium sulfide, which dissolves the sulfide of copper and leaves the sulfide of nickel. The residue containing the nickel is then thoroughly roasted to form the oxide, which is reduced by means of carbon. Still another method is the Mond process, which has been described in the section dealing with cobalt. The nickel carbonyl, which is formed in this process, is decomposed, when it is heated, into pure nickel.

27. Properties and Uses

Nickel is a silvery, hard metal, which takes a high polish. It is malleable and can be welded with iron. Like iron and cobalt, it is highly magnetic. It melts at 1452°. It is not attacked by air under ordinary conditions, but very finely divided nickel ignites spontaneously. It resembles cobalt very closely in its action upon steam and dilute acids, although it is less reactive toward all of these. It dissolves readily in dilute nitric, but it is made passive by the concentrated acid. It is not attacked by fused alkali, and for this reason crucibles made of nickel are used in the laboratory when such fusions have to be made.

Nickel is used in making several varieties

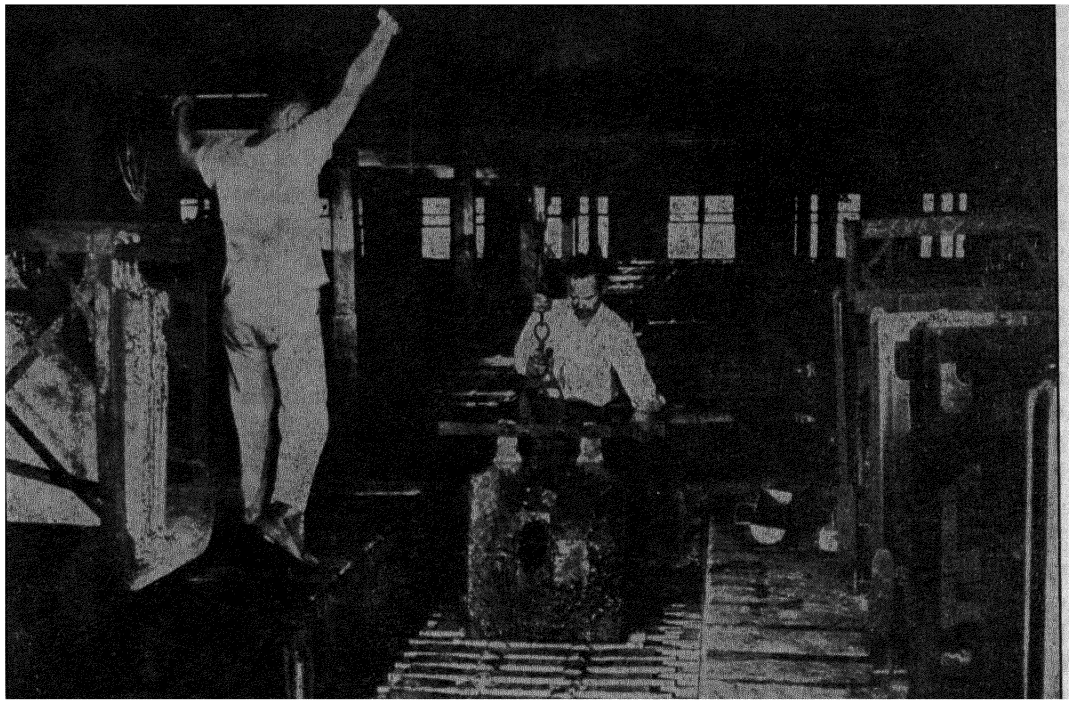


Figure 285. Refining Nickel

Anodes are being transferred from the electrolytic tank to a rack.

(Courtesy of International Nickel Company)

of alloy steels and many other alloys. *Monel* metal, which contains nickel, copper, and a small percentage of iron, is one of the most important nickel alloys with nonferrous metals. It is familiar as a covering for kitchen sinks and soda fountains. *German silver* is an alloy of copper, nickel, and zinc. The alloy used for nickel coinage (U.S.) contains 25 per cent of nickel and 75 per cent of copper. *Manganin* (Ni 4, Cu 84, Mn 12) is used as electrical resistance in heating units of small furnaces and electric heaters. *Invar* is a high-nickel steel (Ni 35). There are several hundred alloys of nickel, each specifically adapted for certain uses.

Nickel is also used extensively to electroplate iron, copper, and other metals. The nickel coating is attractive because it can be highly polished, and it is resistant to corrosion. An active, finely divided nickel powder is produced by reducing the oxide with hydrogen below 300°. This material is used as a catalyst in the hydrogenation of fats (page 74) and in the separation of hydrogen from the carbon monoxide in water gas (page 70).

28. Compounds of Nickel

Nickel forms the monoxide, NiO, when it is heated in air. This oxide and the hydroxide, $Ni(OH)_2$, are basic. The dioxide, NiO_2, is produced by the action of strong oxidizing agents upon nickel salts in an alkaline solution. There is some question concerning the existence of nickelic oxide, Ni_2O_3, and the corresponding nickelic salts are unknown. The nickelous salts are usually green or blue in color. The most familiar of these are: $NiCl_2.6\,H_2O$; $Ni(NO_3)_2.6\,H_2O$; $NiSO_4.7\,H_2O$; and nickel ammonium sulfate, $NiSO_4.(NH_4)_2.SO_4.6\,H_2O$. The last of these is used in the solution from

which nickel is plated. Nickel combines with carbon monoxide at 50° or lower to form nickel carbonyl, $Ni(CO)_4$. Like iron and cobalt, it forms many complex ions, such as $Ni(NH_3)_6^{++}$ and $Ni(CN)_4^{=}$.

THE PLATINUM FAMILY

Ruthenium, rhodium, palladium, osmium, iridium, and platinum are known as the *platinum metals*, since they have very similar properties. Platinum, or its alloys, was known several hundred years B.C. and the other members of the family were discovered during the first decade of the nineteenth century.

29. Occurrence and Metallurgy

These metals occur usually in the free state. Platinum is found as nuggets or small grains in alluvial sands. This metal is not pure; it is alloyed with gold and other metals, especially those of its own family. Platinum is found in the combined state in one mineral, the arsenide, *sperrylite*, $PtAs_2$. The most important deposits of platinum are in the Ural Mountains of Russia, in Canada, and in South Africa. Minor deposits occur in some of the western parts of the United States. Canada produces platinum as a by-product of the smelting of the nickel ores of Ontario, and some is produced during the electrolytic refining of copper, nickel, and gold. The source of the other members of the family is crude, native platinum.

To separate platinum from the others, the native ore is first washed in running water in sluices, or it is panned to remove the sand and other materials in which the platinum particles are found. The metal is then treated with aqua regia which dissolves the platinum, forming chloroplatinic acid, H_2PtCl_6. Some of the other metals also dissolve, but osmium and iridium, which are usually present in larger amounts than the others, are left as an undissolved alloy. The platinum is then precipitated as ammonium chloroplatinate, $(NH_4)_2PtCl_6$, by adding ammonium chloride. When this precipitate is heated, it decomposes, and the platinum is set free. When made in this way the metal is spongy and lacks its usual brilliant luster. The massive, compact metal is made by melting the spongy material in an electric furnace.

30. Platinum Properties and Uses

Platinum is a white metal. Its density is very high (21.45), and its melting point is 1755°. It is somewhat harder than gold, but it can be drawn readily into wire or hammered into sheets. In its finely divided state it absorbs gases readily. Its catalytic effect upon reactions, such as the combination of hydrogen and oxygen, is undoubtedly due to this property. Its use as a catalyst in the production of sulfuric acid by the contact process and in the oxidation of ammonia by the Ostwald process will be recalled from earlier chapters. The red-hot metal is not attacked by oxygen, and it does not dissolve in the simple acids, not even in hot nitric acid. Free chlorine reacts with it to form platinous chloride, $PtCl_4$. It dissolves in aqua regia, forming chloroplatinic acid, H_2PtCl_6. When heated with fused alkali hydroxides or nitrates, it is converted into platinates, such as Na_2PtO_3. Because of its resistance to the effects of air and most reagents, and because of its high melting point, platinum is used in the manufacture of crucibles, wire, and foil for many laboratory purposes.

Platinum is used in dentistry and in the manufacture of jewelry, X-ray tubes, and electrical apparatus. Since the metal has the same coefficient of expansion as glass, it is frequently used wherever metal must be sealed in glass as, for example, in making the electrodes in electric lamps, X-ray tubes, neon signs, and electrical discharge tubes of all kinds. A less expensive alloy has now replaced platinum for such purposes to a very great extent. A small sheet

of platinum covered with finely divided *platinum black* and saturated with hydrogen is used as the hydrogen electrode in electrical cells. The use of finely divided platinum or fine wire in gas lighters depends upon the ability of the metal to absorb oxygen and hydrogen or other combustible gases.

31. Compounds of Platinum

The oxidation number of platinum may be + 1, + 2, + 3, + 4 or + 6. The only important compounds of the metal are those in which its oxidation number is + 2 or + 4. It forms an extremely large number of complex compounds. The tendency to form platinates when heated with a mixture of an alkali hydroxide and the nitrates of an alkali metal, or with other strong oxidizing agents, indicates a slight acid-forming property. It forms two chlorides, $PtCl_2$ and $PtCl_4$. Both of these react with an excess of HCl to form complex acids, $PtCl_2$ forming *chloroplatinous* acid and $PtCl_4$ forming *chloroplatinic* acid. Each of these acids forms a series of salts, e.g., K_2PtCl_4 and K_2PtCl_6. The chloroplatinates are the most important compounds of the metal.

32. Other Members of the Platinum Family

Ruthenium is a gray, hard, brittle metal. The oxidation number of the metal in its compounds may be positive 2, 3, 4, 6, 7, or 8. In its higher oxidation states the element resembles hexavalent and heptavalent manganese, forming ruthenates, Na_2RuO_4, and perruthenates, $NaRuO_4$. In its lower valences (2 and 3) ruthenium forms metallic salts, such as $RuCl_2$ and $RuCl_3$. The dioxide, RuO_2 is amphoteric.

Osmium is the heaviest of the metals (density 22.48), and is hard enough to scratch glass. It forms *osmates* (K_2OsO_4); chlorides and fluorides ($OsCl_2$, $OsCl_4$, OsF_8, and $OsCl_3$); oxides OsO, Os_2O_3; OsO_2, and OsO_4; and many complex compounds. The tetroxide, OsO_4, in which osmium apparently has a number of + 8, is volatile. It is sometimes called *osmic* acid, although it does not act as an acid. It is a very active oxidizing agent, and is used to harden and stain biological materials.

Rhodium is softer than osmium or ruthenium and melts at a lower temperature. It looks like aluminum but, of course, is much more noble. In its principal compounds the element has an oxidation number of + 2 or + 4. Chlorine attacks the metal more readily than it does platinum, forming the trichloride $RhCl_3$. Like the other metals of the family, rhodium forms many complex compounds.

Iridium is silvery white and is somewhat softer than osmium. It is used sometimes in the form of an alloy with platinum or gold, to make crucibles and other laboratory articles, which are usually made of pure platinum. Pen points are tipped with a very hard alloy of iridium and osmium, called *iridosmine*. Iridium is the most expensive of the platinum metals. In its compounds iridium has an oxidation number of + 3 or + 4. It forms the following representative compounds: $IrCl_3$; Ir_2O_3; K_3IrCl_6; IrO_2; K_2IrCl_6; and Na_2IrO_3.

Palladium closely resembles platinum. It is soft and malleable and melts at a lower temperature than any other member of the family. It has a pronounced tendency to absorb many gases, especially hydrogen (page 73). It is the most abundant and least expensive of the six metals of the family. It is used in dentistry, in the manufacture of scientific instruments and jewelry, and as a catalyst. In its compounds palladium has an oxidation number of + 2 or + 4. It is more strongly basic than the others; it dissolves in boiling nitric acid to form $Pd(NO_3)_2$, while the others are insoluble. Other typical compounds are: K_2PdCl_4; K_2PdCl_6; PdO; and PdO_2.

REVIEW EXERCISES

1. What are the principal ores of iron? In what other forms does the element occur in nature?
2. Write the equations for the reactions that occur in the blast furnace and indicate the portion of the furnace where each reaction occurs.
3. What is the advantage of height in the blast furnace? Why should the furnace be operated as nearly continuously as possible?
4. What are the products of the blast furnace?

5. Compare the properties and composition of pig iron, wrought iron, and steel.
6. Describe the furnaces used and the reactions involved in the two principal processes for making steel. What are the relative advantages and disadvantages of each of these?
7. What changes occur in the heat treatment of steels? What is case-hardened steel?
8. Identify: Venetian red; duriron; green vitriol; crucible steel; malleable cast iron; stellite; Prussian blue; cementite; invar.
9. Why is aluminum sometimes used in the manufacture of steel? What other substances are used for the same purpose?
10. How would you determine whether or not there was any ferrous sulfate in a sample of ferric sulfate?
11. Summarize the properties of nickel and cobalt, comparing them with those of iron. Which of these elements resembles iron more closely? State one or two facts to support your answer.
12. What are the sources of nickel and cobalt? How are they used?
13. What are the sources of the metals of the platinum family? How do these elements differ from iron, cobalt, and nickel?
14. Name three chemical properties of platinum. Name two or three of its most important compounds.

REFERENCES FOR FURTHER READING

Hudson, R. P., *The Blast Furnace.* New York: Chemical Publishing Company, Inc., 1942.

Stoughton, B., *Metallurgy of Iron and Steel.* New York: McGraw-Hill Book Company, 1923.

Walker, J. B., *Story of Steel.* New York: Harper and Brothers, 1926.

Cobalt: *Chem. and Met. Eng.*, **24,** 439 (1921); **29,** 1135 (1923).

Iron Ores: *J. Chem. Ed.*, **10,** 195, 288 (1933).

Nickel: *J. Chem. Ed.*, **8,** 1749, 1954, 2325 (1931); **26,** 600 (1949).

Pig Iron: *J. Chem. Ed.*, **8,** 143 (1931).

Platinum Metals: *Chem. Reviews*, **32,** 277 (1943); *Ind. and Eng. Chem.*, **28,** 1412 (1936); *J. Chem. Ed.*, **5,** 1371 (1928).

Steel Alloys: *J. Chem. Ed.*, **4,** 583 (1927); **20,** 94 (1943); **23,** 142, 170 (1946); *Chem. and Met. Eng.*, **30,** 186, 316, 391 (1924).

44

OTHER ELEMENTS

THE most important metals have been discussed in previous chapters. There are, however, several other metals that have important, but somewhat limited, applications.

METALS OF GROUP THREE

1. Gallium

This element was named *gallium* after France (Gallia). The metal is white and soft. It melts at about 30° and, consequently, is in the liquid state in warm weather. It corrodes easily in the air. It forms compounds in which it has a valence of two and other compounds in which it has a valence of three. In its trivalent state it greatly resembles aluminum. Gallium hydroxide is amphoteric, forming gallates when it dissolves in bases and gallic salts when it reacts with acids. Examples of these are sodium gallate, $NaGaO_2$, and gallium chloride, $GaCl_3$. The metal is produced by electrolyzing a salt of gallium in an alkaline solution. Its compounds occur in small amounts in the ores of iron, zinc, aluminum, and chromium.

2. Indium

Zinc blende yielded another new element to which the name of *indium* was given. This name refers to the two blue lines of its spectrum. It occurs in small amounts in some of the ores of zinc, lead, manganese, iron, tungsten, and tin. Most of the indium which is recovered is obtained in the purification of zinc spelter. The pure element resembles gallium and aluminum. Like these metals, its usual valence is three, but it also acts as a bivalent and as a univalent metal. Indic hydroxide, $In(OH)_3$, is amphoteric, but it is not as soluble as aluminum hydroxide in bases. It reacts slightly, forming the indate ion, InO_2^-. The metal is used to a limited extent in articles of jewelry, in alloys employed in dentistry, and as an alloying metal with silver to decrease tarnishing.

3. Thallium

The name of this element comes from a Greek word which means "green budding twig." It refers to a characteristic green line in the spectrum of the element. It is found in zinc ores in which it occurs in larger amounts than gallium and indium. It is also found in iron pyrites and in minerals containing lead, tellurium, and the alkali metals. It is recovered from the dust that collects in the flues of sulfuric acid plants in which sulfur dioxide is obtained by roasting pyrites. The metal has a bluish-white color, is soft and malleable and melts at about 303°. Thallous hydroxide, TlOH, is moderately soluble and is strongly basic. Thallous chloride, bro-

mide, and iodide are slightly soluble. Thallic hydroxide, $Tl(OH)_3$, is not amphoteric; it does not react with bases. With acids it forms salts such as $TlCl_3$ and $Tl(NO_3)_3$. These salts are highly hydrolyzed, partly because the hydroxide is a weak base, and also because it is very slightly soluble. Metallic thallium is used to some extent in making alloys. Thallium compounds are sometimes used in the manufacture of optical glass to increase the index of refraction.

4. The Rare Earths

The A Division of group three contains scandium, yttrium, lanthanum and 14 elements whose atomic numbers lie between 58 and 71. All of these elements are generally included in the group which is called the lanthanide *rare-earths*, although in the periodic classification this term refers only to the 14 elements immediately preceding hafnium.

The rare-earths are metallic in character. They are obtained from *monazite sand*, which is found along the coast of Brazil and in India. The metals are produced by the electrolysis of their oxides dissolved in a bath of melted rare-earth fluorides. In the combined state they are separated from the compounds of other metals by precipitating them as oxalates in the presence of nitric acid. *Misch metal* is an alloy of the rare-earth metals; it is made by the electrolysis of a mixture of the chlorides. It is used as a pyrophoric alloy in cigarette and gas lighters, because of the ease with which it may be ignited by scratching. It may also be used to remove oxygen from cast iron and in the tracer bullets of machine guns and in luminescent shells, which show the positions of the "hits" by the light emitted when the alloy is ignited. Cerium dioxide, CeO_2, is used in making Welsbach gas mantles (page 410). For this purpose a mixture containing 1 per cent of CeO_2 and 99 per cent of thorium oxide, ThO_2, is used. Thorium occurs with the rare-earth metals in monazite sand.

A valence of 3 is common for all the rare earths, and some of them (cerium, terbium, and praseodymium) also form compounds in which they have a valence of 4, while samarium, europium, and ytterbium are divalent.

Element 61 has been reported as existing in nature, and the name illinium has been suggested for it. It is now believed, however, that this element has no natural existence. Radioactive isotopes of it have been produced, and the name *promethium* has been proposed.

The discovery of isotopes of elements having atomic numbers greater than 92 has recently raised interesting qustions regarding their positions in the Periodic Table. All evidence points to the beginning of another series of rare earths with actinium, corresponding to the series in the sixth period that begins with lanthanum. This series includes elements 89 to 98, actinium to californium. Actinium displays in its compounds an oxidation number of +3. It is one of the rarest of the elements. Neptunium and plutonium form compounds in which their oxidation numbers are +3, +4, +5, and +6. Americium forms similar compounds, but it appears that only those in which its oxidation number is +3 are of any importance. Very little about the chemical behavior of numbers 96, 97, and 98 is known.

Protoactinium is an element from which actinium is produced during radioactive decay by the loss of an alpha particle. It is extremely rare.

OTHER ELEMENTS OF GROUP FOUR

5. Germanium

This element is a grayish-white, brittle, durable, metallic substance. It melts at 958° and has a density of 5.36. It occurs in small amounts in the sulfide ores of several of the metals, but it is usually produced as a by-product of the refining of zinc. Like tin and lead, it forms two oxides, GeO and GeO_2; both of these are amphoteric. The metal is produced by reducing the oxide with carbon. In many of its compounds germanium resembles carbon and silicon; but it differs from these elements in forming some compounds in which a more definitely metallic character is revealed. Thus, its tetrachloride, $GeCl_4$, is volatile like CCl_4, and it also forms a compound $GeHCl_3$, which is analogous to chloroform. Sodium germanate, Na_2GeO_3, is analogous to sodium carbonate or sodium silicate. On the other hand, GeO dissolves in acids to form divalent germanium compounds of a salt-

like character. It also dissolves in alkalies and therefore is amphoteric. In this respect the element is unlike carbon.

6. Thorium

This element is the only member of the A division of group four that is strictly metallic. It occurs in the mineral *thorite*, $ThSiO_4$, and in monazite sand. The latter is the commercial source of the compounds of thorium. The sand contains amounts of thorium oxide that vary from 1 up to 15 or 20 per cent. This oxide is extracted for the preparation of Welsbach gas mantles (page 410). The metal can be prepared by the reduction of the oxide with an alloy of the rare-earth metals called misch metal (Section 4). It is heavy and melts at 1850°. In many respects it resembles platinum. In its compounds thorium acts as a metal and displays a valence of four. The hydroxide, $Th(OH)_4$, dissolves in acids to form salts, such as $ThCl_4$, $Th(NO_3)_4$, and $Th_3(PO_4)_4$. It also forms basic salts such as $ThOCO_3$; double salts such as $KNO_3.Th(NO_3)_4.9\ H_2O$; and complexes, of which K_2ThF_6 is an example. The radioactivity of thorium has been mentioned in connection with the general treatment of radioactivity in Chapter 11.

METALS OF GROUP FIVE

7. Vanadium

This element was discovered in 1830. It occurs as *vanadinite*, $3\ Pb_3(VO_4)_2.PbCl_2$; *carnotite*, $2\ K_2O.2\ UO_3.V_2O\ .3\ H_2O$; *roscollite*, a vanadium bearing mica; *patronite*, a complex sulfide; and *pucherite*, $BiVO_4$. The principal producing localities are in Peru, Africa, Mexico, and in Arizona, Colorado and Utah.

The metal is difficult to prepare because of its tendency to combine with carbon, nitrogen, and other elements. It can be prepared by reducing the oxide with misch metal, or by reducing VCl_2 with hydrogen. Commercially, the alloy with iron, which is called *ferrovanadium*, is produced instead of the pure metal. This alloy is used in the steel industry to produce vanadium steel. It is made by reducing the oxides of iron and vanadium with carbon. Vanadium steel has a high tensile strength and resistance to shock and vibration. It is used as a high-speed tool steel, in many automobile parts, in car wheels, and in locomotives.

Vanadium is silver-white, hard, brittle, and crystalline. It forms the oxides, VO_2 and V_2O_5; the chloride, VCl_4; the carbide, VC; the nitride, VN; and the sulfides, VS_2 and V_2S_5. It forms, also, vanadous salts such as VSO_4 and VCl_2; vanadic salts, such as VCl_3; vanadites, produced by dissolving VO_2 in solutions of alkali hydroxides, which are salts of vanadous acid, $H_2V_4O_9$; and vanadates, such as $NaVO_3$, $Na_4V_2O_7$, and Na_3VO_4.

8. Columbium

The principal source of this element is *columbite*, which contains $Fe(CbO_3)_2$ and other minerals containing tantalum, titanium, and the rare earths. The pure metal has few applications at this time. It is used in a few alloys that are of value in making jewelry and stainless steel. Its best known compounds are the columbates which are salts of *columbic acid*, $HCbO_3$; chlorides, $CbCl_3$ and $CbCl_5$; and oxy-salts, such as $CbOCl_3$.

9. Tantalum

This metal occurs in *tantalite*, which is essentially $Fe(TaO_3)_2$, and in minerals that also contain columbium. It is hard, ductile, has a density of 16.6, and melts at about 1800°. It is extremely resistant to all reagents, except strong alkalies and hydrofluoric acid, at ordinary temperatures. It readily adsorbs gases, and for this reason is used to remove traces of gases in radio tubes. It is also used in making electrodes for current rectifiers, in the manufacture of surgical instruments, and as a substitute for platinum in making articles and utensils used in the laboratory.

At a red heat the metal burns in the air to form the pentoxide, Ta_2O_5. This oxide reacts when

fused with alkali hydroxides to form *tantalates*, of which $Na_8Ta_6O_{19}$ is an example.

The metal also forms the pentachloride, $TaCl_5$; the sulfide, TaS_2; and the nitride, Ta_3N_4.

METALS OF GROUP SIX

10. Molybdenum

The principal ore of this metal is *molybdenite*, MoS_2. The element also occurs in molybdates, of which lead molybdate, $PbMoO_4$, is most important. This is the mineral called *wulfenite*. Most of the molybdenum produced comes from Norway or from Colorado and New Mexico.

To produce the metal from molybdenite, the ore is roasted and then treated with ammonium hydroxide which dissolves the oxide of molybdenum, forming ammonium molybdate. This substance is recovered by evaporation, and the solid salt is ignited to drive off the ammonia. The final product is molybdenum trioxide, MoO_3. This oxide is then reduced with carbon or hydrogen in the electric furnace. This process gives the metal in the form of a finely divided powder. Ferromolybdenum is produced in the same way as ferrochromium; it is used to make alloy steels. These steels are resistant to chemical action, hard, strong, and tough. Pure molybdenum has a silvery white color. The powdered metal produced by the reduction of the oxide can be made into wire by first pressing the powder into a rod and passing an electrical current through it. The resistance of the rod produces enough heat to partially fuse the particles of the metal and cement them together. This material may then be rolled into sheets or drawn into wire. The metal melts at about 2620°.

In addition to its use in the manufacture of steels, molybdenum is used to make the supports for the filaments in electric lamps; to make certain portions of the interior structures of radio tubes; to make the terminals, or points, of spark plugs and automobile distributors; and as electrical resistance in small electrical furnaces.

In its compounds, the element has positive valences of 2, 3, 4, 5, and 6. In the laboratory the most familiar compound of molybdenum is ammonium molybdate, which is used in the detection and quantitative determination of phosphate ion. When a solution containing a phosphate is made strongly acid with nitric acid and a solution of ammonium molybdate is added, a yellow, powdery precipitate is produced when the mixture is heated. The yellow compound is called *ammonium phospho-molybdate* and has the approximate formula $(NH_4)_3PO_4.12\ MoO_3$, but the composition may vary slightly as to the amount of MoO_3 that the compound contains.

In its lower valence states molybdenum is basic and in its higher valence state it is acidic. Many of the compounds of the metal are deeply tinted and are used as coloring for cloth and leather and in making the painted designs and glazes of chinaware. One such compound, which is called molybdenum blue, is made by the reduction of molybdic acid.

11. Tungsten

The principal ore of this metal is *wolframite*, essentially ferrous tungstate, $FeWO_4$. Tungsten ore is produced in China, Burma, and the United States (Colorado and California).

The ore is fused with sodium carbonate, and the mass is leached with water. The solution thus obtained contains sodium tungstate, Na_2WO_4. When this is acidified with HCl, tungstic acid, H_2WO_4, is precipitated. The metal is prepared in the same way as molybdenum. As first prepared, the metal is hard and brittle but it is made malleable and ductile by pressing the powdered metal into rods and passing a current of electricity through them to fuse the particles. This treatment is followed by heat treatments and mechanical working of the metal, such as hammering and rolling, to give it the desired malleability and ductility required for different uses.

Tungsten is used to make the wires or filaments used in electric lamps. To make the small wires required for this purpose

the tungsten is drawn through many diamond dies, each of which is smaller than the preceding one. Its high melting point (3370°) makes the metal extremely useful for this purpose, but since the metal is a good conductor, a very fine wire must be used so that the resistance will be sufficient to liberate enough heat to make the wire white-hot. Ferrotungsten is made by reducing wolframite with carbon and is used to make tungsten steels. These steels are strong and do not lose their temper when heated to redness. This property is useful in making cutting tools that are operated at very high speed, and which become very hot during this operation. It is also used to make steel rails and many parts of automobiles, such as axles and steering apparatus. Tungsten is a constituent of many other alloys and is also used in making the targets or anti-cathodes of X-ray tubes, the filaments for radio tubes, phonograph needles, contact points, etc.

In general, tungsten and its compounds closely resemble molybdenum and its compounds. In its compounds the metal has a positive valence of 2, 3, 4, 5, or 6. The divalent compounds are represented by such substances as WCl_2 and WBr_2. The most important compounds of the element are those in which tungsten is hexavalent. The trioxide, WO_3, is the anhydride of tungstic acid, H_2WO_4, and several condensed acids. The sodium salt of one of these is $Na_{10}W_{12}O_{41}$, which is the substance usually called sodium tungstate. The oxide also forms acids similar to phospho-molybdic acid. Phospho-tungstic acid, $H_3PO_4.12\ WO_3$ is used to precipitate proteins and alkaloids in the analytical chemistry of such substances.

The carbide of tungsten, W_2C, is almost as hard as diamond. When crystals of this substance are embedded in cobalt, a material is produced that may be used to make extremely hard cutting tools. These tools can be used to machine practically all metals, alloys, and other materials, such as glass, stone, and hard rubber. This material is best known under its trade name, *Carbaloy*.

12. Uranium

This metal has been known as an element since 1789, when it was discovered in *pitchblende*, which contains the oxide U_3O_8 and the oxides and sulfides of several other elements. This mineral is found in Austria and in the Belgian Congo. Another uranium mineral called *carnotite* is found in Colorado and Utah. This is a potassium uranium vanadate, $K_2O.2\ UO_3.V_2O_5.3\ H_2O$. The chief interest in these minerals lies in their radium content and in their use as a source of uranium to be used in the liberation of atomic energy by fission. For many years the chief source of radium and uranium was the pitchblende deposits of Austria. Later the carnotite deposits of Colorado superseded the Austrian source and, in turn, were overshadowed by the production from the Belgian Congo and Canada.

The element, uranium, is prepared by the reduction of the oxide by carbon and of the chloride by calcium or by the electrolysis of UF_4 in a bath consisting of the melted chlorides of sodium and calcium. It is a white metal, which melts at about 1850°, and has a density of 18.7. It is slowly oxidized in the air. It dissolves in the common acids, forming salts. The valence which it displays in its compounds is almost always 4 or 6. The oxide, UO_3, is amphoteric, forming uranates, which have the formula M_2UO_4 or $M_2U_2O_7$, or uranyl salts. The latter correspond to the base, $UO_2(OH)_2$, which is uranyl hydroxide. The uranyl ion is divalent and its salts are such compounds as uranyl nitrate, $UO_2(NO_3)_2$, uranyl arsenate, $(UO_2)_3\ (AsO_4)_2$, and uranyl acetate, $UO_2(C_2H_3O_2)_2$. The "oxide," U_3O_8, is a compound, uranous uranate, $UO_2.2\ UO_3$. Uranium compounds are used in coloring glass and glazes or in painting designs upon chinaware.

REFERENCES FOR FURTHER READING

Columbium and Tantalum: *Ind. and Eng. Chem.*, **28,** 1166 (1936).

Indium: *J. Chem. Ed.*, **11,** 270 (1934); *Ind. and Eng. Chem.*, **30,** 611 (1938).

Molybdenum: *Fortune*, **14,** No. 4, 105.

Smithells, C. J., *Tungsten*. New York: D. Van Nostrand Company, 1936.

Tungsten: Li, K. C., and Chung yu Wang, *Tungsten*. New York: Reinhold Publishing Corporation, 1943.

Vanadium: *Ind. and Eng. Chem.*, **19,** 786 (1926).

APPENDIX

TABLE 1. VAPOR PRESSURE OF WATER AT DIFFERENT TEMPERATURES

Temperature (degrees C.)	Vapor Pressure (mm. of mercury)	Temperature (degrees C.)	Vapor Pressure (mm. of mercury)	Temperature (degrees C.)	Vapor Pressure (mm. of mercury)
0	4.57	22	19.63	40	54.87
5	6.51	23	20.86	45	71.36
10	9.14	24	22.15	50	91.98
11	9.77	25	23.52	55	117.52
12	10.43	26	24.96	60	148.88
13	11.14	27	26.47	65	187.10
14	11.88	28	28.07	70	233.31
15	12.67	29	29.74	75	288.76
16	13.51	30	31.51	80	354.88
17	14.40	31	33.37	85	433.20
18	15.33	32	35.32	90	525.47
19	16.32	33	37.37	95	633.67
20	17.37	34	39.52	100	760
21	18.47	35	41.78		

TABLE II. SOLUBILITY PRODUCTS

The principle of the solubility product can be applied only to the saturated solutions of slightly soluble substances. For such substances, the value of the solubility product can be calculated from the solubility expressed as gram-molecular weights per liter. Since the saturated solutions of slightly soluble substances are very dilute, we may assume that they are completely ionized; the Debye-Hückel theory, of course, regards them as actually 100 per cent ionized. The solubility products in the table below have been calculated for temperatures of 18°–25°.

Compound	Solubility (Product)	Compound	Solubility (Product)
Aluminum hydroxide, $Al(OH)_3$	1×10^{-15}	Ferrous sulfide, FeS	4×10^{-19}
Arsenic trisulfide, As_2S_3	4×10^{-29}	Lead chloride, $PbCl_2$	1×10^{-4}
Antimony trisulfide, Sb_2S_3	3×10^{-27}	Lead chromate, $PbCrO_4$	2×10^{-14}
Barium carbonate, $BaCO_3$	8×10^{-9}	Lead sulfate, $PbSO_4$	1×10^{-8}
Barium chromate, $BaCrO_4$	2×10^{-10}	Lead sulfide, PbS	3×10^{-28}
Barium oxalate, BaC_2O_4	2×10^{-7}	Magnesium hydroxide, $Mg(OH)_2$	1×10^{-11}
Barium sulfate, $BaSO_4$	1×10^{-10}	Manganese sulfide, MnS	2×10^{-15}
Bismuth sulfide, Bi_2S_3	5×10^{-31}	Mercuric sulfide, HgS	4×10^{-53}
Cadmium sulfide, CdS	4×10^{-29}	Nickel sulfide, NiS	2×10^{-24}
Calcium carbonate, $CaCO_3$	1×10^{-8}	Silver chloride, AgCl	1×10^{-10}
Calcium chromate, $CaCrO_4$	2×10^{-2}	Silver sulfide, Ag_2S	2×10^{-49}
Calcium oxalate, CaC_2O_4	2×10^{-9}	Strontium carbonate, $SrCO_3$	1×10^{-9}
Calcium sulfate, $CaSO_4$	2×10^{-4}	Strontium chromate, $SrCrO_4$	3×10^{-5}
Cobalt sulfide, CoS	3×10^{-26}	Strontium oxalate, SrC_2O_4	6×10^{-8}
Cupric sulfide, CuS	9×10^{-45}	Strontium sulfate, $SrSO_4$	3×10^{-7}
Ferric hydroxide, $Fe(OH)_3$	1×10^{-36}	Zinc sulfide, ZnS	1×10^{-23}

TABLE III. SOLUBILITIES OF COMPOUNDS

(Grams per 100 grams of water at 20° C.)

Antimony sulfide	Sb_2S_3	1×10^{-4} (18°)
Arsenic sulfide	As_2S_3	0.517×10^{-4} (18°)
Barium chromate	$BaCrO_4$	3.7×10^{-4}
Barium carbonate	$BaCO_3$	2.2×10^{-3}
Barium oxalate	BaC_2O_4	7.1×10^{-4}
Barium sulfate	$BaSO_4$	0.24×10^{-3}
Bismuth sulfide	Bi_2S_3	0.18×10^{-4}
Cadmium sulfide	CdS	9.0×10^{-7}
Calcium carbonate	$CaCO_3$	6.5×10^{-3}
Calcium chromate	$CaCrO_4$	0.17×10^{2}
Calcium oxalate	CaC_2O_4	5.6×10^{-4} (18°)
Calcium sulfate	$CaSO_4$	2.02×10^{-1} (18°)
Cobalt sulfide	CoS	3.8×10^{-4}
Copper (ic) sulfide	CuS	3.3×10^{-5}
Lead chromate	$PbCrO_4$	0.7×10^{-5}
Lead sulfate	$PbSO_4$	4.1×10^{-2}
Lead sulfide	PbS	8.6×10^{-5}
Magnesium carbonate	$MgCO_3$	9.7×10^{-2}
Magnesium oxalate	MgC_2O_4	0.15×10^{-3} (18°)
Manganese sulfide	MnS	6.23×10^{-4} (18°)
Mercurous chloride	HgCl	0.38×10^{-4}
Nickel sulfide	NiS	3.6×10^{-4}
Silver chloride	AgCl	0.16×10^{-3}
Strontium carbonate	$SrCO_3$	0.109×10^{-2}
Strontium chromate	$SrCrO_4$	1.2×10^{-1}
Strontium oxalate	SrC_2O_4	0.461×10^{-2}
Strontium sulfate	$SrSO_4$	1.43×10^{-2}

TABLE IV.

Conc. of H^+ (or H_3O^+)	No. of liters which must be taken to obtain 1 gram ion of H^+ or H_3O^+	pH	Conc. of OH^-
1 N or 1×10^0 N	1 or 1×10^0	0	1×10^{-14}
0.1 N or 1×10^{-1} N	10 or 1×10^1	1	1×10^{-13}
0.01 N or 1×10^{-2} N	100 or 1×10^2	2	1×10^{-12}
0.01 N or 1×10^{-3} N	1000 or 1×10^3	3	1×10^{-11}
0.0001 N or 1×10^{-4} N	10,000 or 1×10^4	4	1×10^{-10}
0.00001 N or 1×10^{-5} N	100,000 or 1×10^5	5	1×10^{-9}
0.000001 N or 1×10^{-6} N	1,000,000 or 1×10^6	6	1×10^{-8}
0.0000001 N or 1×10^{-7} N	10,000,000 or 1×10^7	7	1×10^{-7}
0.00000001 N or 1×10^{-8} N	100,000,000 or 1×10^8	8	1×10^{-6}
0.000000001 N or 1×10^{-9} N	1,000,000,000 or 1×10^9	9	1×10^{-5}
0.0000000001 N or 1×10^{-10} N	10,000,000,000 or 1×10^{10}	10	1×10^{-4}
0.00000000001 N or 1×10^{-11} N	100,000,000,000 or 1×10^{11}	11	1×10^{-3}

INDEX

Absolute zero, 81, 86
Acetaldehyde, 408, 420
Acetamide, 426
Acetic acid, 325, 408, 421
Acetone, 421
Acetylene, 408
Acheson process, 291
Acids, 53, 121, 321
  acetic, 325, 408, 421
  acetyl salicylic, 427
  alpha stannic, 514
  amino, 426
  aminoacetic, 426, 434
  anhydride, 126
  arsenic, 382
  arsenious, 382
  ascorbic, 436
  benzoic, 426
  beta stannic, 512
  bismuthic, 385
  boric, 395
  Bronsted concept of, 322
  bromic, 287
  butyric, 422
  caproic, 422
  carbolic, 426
  carbonic, 304
  chloric, 285
  chloroauric, 493
  chloroaurous, 493
  chloroplatinic, 542
  chloroplatinous, 542
  chlorous, 285
  chromic, 523
  citric, 422
  columbic, 546
  degree of ionization, 324
  dibasic, 304
  effect of ions upon, 332
  fatty, 421
  formic, 301, 421
  glacial acetic, 421
  hydriodic, 277
  hydrobromic, 277
  hydrochloric, 277
  hydrocyanic, 356
  hydrofluoric, 265, 277, 281
  hydrosulfuric, 363
  hydroxybenzoic, 427
  hypobromous, 287
  hypochlorous, 283
  hypoiodous, 287
  hypophosphoric, 379
  iodic, 287
  ionization constants, 325
  ionization of weak, 222
  lactic, 422
  metaphosphoric, 379
  metaphosphorous, 379
  molybdic, 547
  muriatic, 279
  names of, 122
  nicotinic, 436
Acids
  nitric, 350
  nitrosyl sulfuric, 367
  nitrous, 349
  oleic, 422
  orthophosphoric, 379
  osmic, 542
  oxalic, 301, 422
  palmitic, 422
  pantothenic, 436
  perchloric, 286
  periodic, 287
  permanganic, 525
  peroxysulfuric, 372
  phosphoric, 379
  phosphorous, 278, 378
  picric, 354
  polybasic, 323
  polyprotic, 323
  polysilicic, 391
  properties, 122
  proprionic, 422
  prussic, 356
  pyroligneous, 296
  pyrophosphoric, 379
  pyrophosphorous, 379
  pyrosulfuric, 365
  reactions with metals, 68
  salicylic, 427
  silicic, 391
  stearic, 422
  strengths, 322
  sulfuric, 365
  sulfurous, 364
  tartaric, 422
  tetraboric, 395
  thio, 383
  thiosulfuric, 372
  tungstic, 547
  uric, 434
  valeric, 422
Actinium series, 134
Activity, 325
Activity coefficient, 325
Activity series of metals, 68
Adrenalin, 444
Adsorption, 231, 296
Aerogel, 225
Aerosol, 225
Agate, 388
Air conditioning, 235
Air, liquid, 50, 236
Alabaster, 472
Albite, 241, 391
Albumen, 434
Alcohols, 416
  butyl, 416
  denatured, 419
  ethyl, 302, 416, 417
  isobutyl, 417
  isomers, 416
  isopropyl, 416
  methyl, 76, 301, 416, 417

Alcohols
  monohydric, dihydric, and trihydric, 417
  primary, secondary, and tertiary, 417
  propyl, 416
  secondary butyl, 417
  tertiary butyl, 417
Aldehol, 419
Aldehydes, 419
Alkali metals, 240–251
  properties, 240
Alkaline earth metals, 481
Alkaline solution, 53
Alkaloids, 442
Alkylation, 405
Alkyl radicals, 416
Alloys, 460–462
  low melting, 385
  steel, 535
Alpha particle, 33, 132
Alpha rays, 132
Alum, 509
Aluminum, 459, 503–510
  compounds, 507
  metallurgy, 503
  occurrence, 503
  properties, 504
  uses, 504
Alundum, 507
Amalgam, 498
Amalgamation, 489, 492
Americium, 147, 545
Amethyst, 388, 503
Amides, 426
Amines, 425
Amino radical, 426
Amitol, 355
Ammonal, 355
Ammonia, 340–346
  complex ions, 344
  from coal, 341
  liquid, 343
  nitric acid from, 352
  production, 340–342
  properties, 343
  reactions, 344
  solvent action, 345
  synthetic, 76, 341
  uses, 345
Ammoniates, 500
Ammonium compounds, 345
  cyanate, 399
  magnesium phosphate, 478
  phosphomolybdate, 547
  polysulfide, 363
  thioarsenate, 383
  thioarsenite, 383
  thiostannate, 515
Ammonolysis, 500
Ampere, 447
Amphoteric hydroxides, 166, 507
Amyl acetate, 422
Androsterone, 444
Aniline, 426
Anode, 50
Anode mud, 485, 487
Anthracene, 409
Anthracite coal, 293
Antibiotics, 444
Antichlor, 284, 371
Antifreeze, 417
Antiknock gasoline, 405
Antimony, 383–384
Antimony
  compounds, 384
Aqua ammonia, 345
Aqua regia, 354
Aragonite, 470
Argon, 237
Arrhenius' theory of ionization, 213
Arsenic, 380–383
  compounds, 382
  Marsh test, 381
Arsenopyrite, 380
Arsine, 381
Asbestos, 391, 383, 476
Asphalt, 402
Aspirin, 427
Atmosphere, 233–239
  composition, 233
  humidity, 235
  inert gases of, 236
  nitrogen in, 337
  precipitation of moisture, 235
  pressure, 79
Atomic numbers, 36, 158–165
  periodic system, relation to, 161
Atomic theory, 19–30
  history, 21
Atomic weight, 28
  determination, 29, 98
  gram, 29
  scale, 28
  value, 30
Atoms, 19–30
  Bohr theory, 150
  bonds, 164
  disintegration of nuclei, 143
  energy states, 150
  nucleus of, 35, 142
  radius of, 157
  reactions of, 39
  structures of, 33–39
Atropine, 444
Austenite, 534
Aureomycin, 445
Avogadro's number, 29, 137
Avogadro's principle, 93

Babbitt metal, 495
Baking powder, 246
Baking soda, 246
Bakelite, 420
Balance, chemical, 10
Barite, 358, 478
Barium, 478
  compounds, 479
  peroxide, 191
Barometer, 79
Baryta water, 479
Bases, 53, 122, 321
Bauxite, 503
Beehive coke oven, 294
Benzaldehyde, 426
Benzene, 409, 426
Bergius process, 76, 407
Berkelium, 147
Beryl, 391, 480
Beryllium, 480
Bessemer process, 531
Beta particles, 34
Beta rays, 132
Betatron, 143
Betts process, 516
Bismite, 384

Bismuth, 384–386
  compounds, 384
Bismuthine, 385
Bituminous coal, 293
Blast furnace, 528
Blast furnace gas, 300, 442
Bleaching, 56, 284, 364
Bleaching powder, 261, 284
Blister copper, 485
Blowpipe, 54
Blueprints, 537
Blue vitriol, 487
Bohr theory, 150
Boiling point, 179
  different liquids, 180
  elevation by solute, 208
  solutions, 206
Bomb, atomic, 9, 145–147
Bomb calorimeter, 109
Bonds
  coordinated covalent, 185, 345
  factors determining nature, 164
  hydrogen, 185, 190
  single, double, and triple, 399
Bone black, 296
Borax, 395
Bordeaux mixture, 486
Boron, 394–396
  carbide, 396
  compounds, 395
Bosch process, 70
Boyle's law, 79, 85
Brass, 486
Bredig arc process, 226
Brimstone, 358
Britannia metal, 486
Bronsted theory of acids and bases, 322
Bromine, 261–264
  occurrence, 262
  oxygen compounds, 281, 287
  production, 262
  properties, 263
  uses, 264
Bronze, 486
Brownian movement, 227
Bullion, 489, 575
Buna S, 413
Burette, 197
Butadiene, 413
Butane, 401
Butter, 423
Butylene, 407
Butyl rubber, 414
By-product coke oven, 294

Cadmium, 497–498
Caffeine, 442
Calciferol, 436
Calcite, 470
Calcium, 468–475
  arsenate, 382
  bicarbonate, 304, 471
  bisulfite, 365, 472
  carbide, 308, 343
  carbonate, 317, 470
  chloride, 471
  compounds, 469
  cyanamide, 308, 343
  cyanide, 356
  dihydrogen phosphate, 246
  hydroxide, 470
  nitrate, 473
Calcium
  phosphate, 380
  production, 468
  properties, 468
  sulfate, 472
  sulfite, 472
  uses, 468
Californium, 147
Calomel, 499
Calorie, 97
Calorific value of foods, 437
Calorimeter, 109
Caoutchouc, 413
Carat, gold, 493
Carbaloy, 538, 548
Carbohydrates, 429
Carbon, 290–298
  amorphous, 290, 293
  compounds, 300–308
  diamond, 290
  disulfide, 306
  occurrence, 290
  properties, 297
  radioactive isotopes, 144
  tetrachloride, 307
Carbon black, 296
Carbon dioxide, 302
  in atmosphere, 234
Carbon monoxide, 300
Carbonization, 293
Carbonyls, 538, 539
Carborundum, 308
Carboxyl radical, 421
Carnallite, 248, 478
Carnelian, 388
Carnotite, 481, 548
Carotene, 436
Carter process, 518
Casein, 434
Casing head gasoline, 405
Cassiterite, 511
Catalysis, 51, 64, 311
  contact, 312
  heterogeneous, 312
  homogeneous, 312
Catlayst, 51, 64
  effect upon speed of reaction, 311
Cathode, 50
Cathode rays, 135
Caves, 304, 471
Celestite, 480
Cell, electrochemical, 448
    types of, 452
  electrolytic, 216
  Nelson, 257
  photoelectric, 372
  voltaic, 448
Cellophane, 442
Celluloid, 433, 440
Cellulose, 432
  acetate, 475
  molecular structure, 432
  nitrate, 354, 433
Cement, hydraulic, 475
Cementite, 530, 534
Ceramics, 509
Cerium, 410
Cesium, 251
Chain reactions, 145
Chalcedony, 388
Chalcopyrite, 484
Chalk, 471

Changes, chemical and physical, 13
Charcoal, 296
Charles's law, 81, 87
Cheddite, 286
Chemical change, 17
  laws of, 22–27
Chemical energy, 11
Chemical equations, 102
Chemical equilibrium, 310–318
  factors that disturb, 316
Chemist, methods of, 3
  research, 4
Chemistry, 1
  definition, 5
Chile saltpeter, 264, 337
Chinaware, 509
Chloramine, 188
Chlorine, 255–261
  dioxide, 283
  heptoxide, 283
  monoxide, 283
  occurrence, 255
  oxygen compounds, 282
  production, 255
  properties, 257
  reactions of, 259–261
  test, 261
  uses, 261
  water purification, 187
Chlorobenzene, 279, 426
Chloroprene, 414
Chrome alum, 523
Chrome green, 522
Chromite, 521
Chromium, 521–523
  compounds, 522
Cider, 421
Cinnebar, 358
Clay, 234, 509
Cleansing action of soaps, 424
Coal, 293
  ammonia from, 341
  gas, 411
  hydrogenation, 76
Coal tar, 426
Coal tar products, 294, 409, 426, 439
Cobalt, 538
Cocaine, 444
Coinage silver, 486
Coke, 293
  petroleum, 403
Colemanite, 394
Collodion, 433
Colloidal dispersions
  electric charges, 227
  precipitation, 228
  preparation, 226
  Tyndall effect, 226
Colloidal state. 224–232
Colloids, 224
  adsorption, 231
  Bredig arc process, 226
  Brownian movement, 227
  classes of, 225
  dialysis, 229
  emulsions, 230
  gels and jellies, 230
  hydrophilic and hydrophobic, 225
  lyophilic and lyophobic, 225
  peptization, 226
  protective, 229, 431
  reversible and irreversible, 225
Columbium, 546
Combining proportions, law of, 25
Combustion, 47, 48, 54, 59–65
  definition, 59
  heat of, 111
  spontaneous, 62
Common ion effect, 332
Compounds, 13
  addition, 364, 407
  anhydrous, 189
  classification of, 120–127
  covalent, 42, 210, 270
  definite composition, 16
  formulas, 43, 102
  hydrates, 189
  ionic, 41, 209
  inorganic and organic, 127
  molecular weight, 95
  polar and non-polar, 175
  stability of, 164
  table of solubilities, 550
Concentration, 195
  effect of changes in, upon equilibrium, 316
  effect on speed of reaction, 63, 313
Condensed acids, 391
Conservation of energy, 11
  of mass, 22
Constant boiling solutions, 205
Contact sulfuric acid process, 368
Coordinated covalent bonds, 345
Coordination numbers, 344
Copper, 484–487
  compounds, 486
  metallurgy, 484
  ores, 484
  properties, 485
  refining, 485
  uses, 485
Coral, 471
Corn sugar, 429
Corrosion, 464
Corrosive sublimate, 499
Corundum, 503, 507
Cosmic rays, 138
Cottrell precipitator, 228
Coulomb, 136, 215, 447
Couples, metallic, 454
Covalent compounds
  oxidation numbers in, 270
  solubility, 210
Cracking, 72, 404
Cream of tartar, 246, 422
Critical temperature, 89
Cryolite, 265, 503
Crystals, 170
  atomic, 175
  classes of, 170
  ionic, 173
  isomorphous, 170
  lattices, 172
  metallic, 175
  polar compounds, 175
  non-polar compounds, 175
  slippage of planes, 175
  structure of, 170
Cupellation, 487
Cupola furnace, 530
Cuprite, 484
Curium, 147
Cyanides, 356
Cyanogen, 356
Cycloparaffins, 402

Cyclotron, 143

Dakin's solution, 26
Dalton's atomic theory, 21, 35
Dalton's law of partial pressures, 83, 88
Daniell cell, 452
DDT, 427, 445
Deacon process, 255
Debye-Hückel theory, 219
Decantation, 286
Definite proportions, law of, 23
Deliquescence, 202
Density, 168
  absolute, of gases, 6
Detergents, 425
Deuterium, 34, 75, 184
Developing, photographic, 491
Dewar flask, 236
Dextrin, 431, 432
Dextrose, 429
Diabetes mellitus, 430
Dialysis, 229
Diamines, 442
Diamond, 290
  artificial, 291
  crystal structure, 292
  uses, 291
Diastase, 431
Diatomaceous earth, 389
Diatoms, 389
Dielectric constant, 209
Diethyl ether, 419
Diffraction, 158
  X-rays, 171
Diffusion of gases, 84, 88
  of liquids and solids, 170
Dilution, infinite, 218
Diolefins, 408
Dipoles, 176
Disaccharides, 429
Dispersions, colloidal, 224
Distillation, 186
  destructive, 296
Dolomite, 468, 476
Double decomposition, 17
Down's cell, 241
Dreft, 425
Dry cell, 453
Dry ice, 303
Dulong and Petit, principle of, 97
Duplex process, 534
Duralumin, 504
Duriron, 389
Dust, effect upon precipitation of moisture, 235
  precipitation of, 228
Dyes, 439
  developed, 440
  direct, 440
  mordant, 440
  vat, 440

Ebonite, 413
Efflorescence, 190
Electrical conductivity, 217
Electrical units, 447
Electric lamps, 239, 297
Electrochemical series, 451
Electrode, 50
  hydrogen, 327
  normal hydrogen, 450
  potentials, 450
Electrolysis, 215
Electrolysis
  Faraday's law of, 215
  reactions during, 216
  sodium chloride brine, 256
  water, 50, 70
Electrolytes, 120, 121
  Debye-Hückel theory of, 219
  freezing and boiling points of solutions, 215
  percentage of ionization, 214, 218
  reactions of, 121, 219
  solutions of, 213–222
  weak, ionization of, 221
Electromagnetic unit, 136
Electromotive force, 447
Electrons, 34, 35, 134, 135
  charge, 137
  distribution in atoms, 150
  mass and charge, 136
  shells of atoms, 154–156
  valence, 43
Electroplating, 454
Electroscope, 131
Elements, 14
  abundance, 14
  atomic numbers, 36
  atomic weights, 28–30, 98
  combining proportions, 24
  equivalent weights, 98
  families of, 119, 162
  ionization potentials, 156
  isotopes, 37
  mass numbers, 36
  Mendeleeff's classification, 114
  metals and non-metals, 14, 40
  oxidation numbers, 61, 162, 269
  periodic table, 114–116, inside back cover
  properties of elements of a family, 162
  radioactive, 130, 134
    series, 134
  shared, 42
  shells of, in atoms, 28–39
  symbols, 43, 102
  tracer, 144
  transitional, 118, 163
  transmutation, 143
  transuranium, 147
  valence numbers, 43, 99, 104, 158–165
Emerald, 480
Emery, 503
Emulsion, 230
Endothermic and exothermic reactions, 109
Energy, 10
  atomic, 145–147
  changes of, in reactions, 109
  conservation of, 11
  kinds of, 11
Enzymes, 419
Epinephrine, 444
Epsom salts, 478
Equations, chemical, 43, 107
  balanced, 44
  ion-electron method of balancing, 274
  meaning of, 108
  oxidation-reduction, 269–275
  thermochemical, 111
Equilibria of ions, 321–335
  of ions in saturated solutions, 332
  of liquid and vapor, 178
  solutions, 197
Equilibrium constant, 314
Equivalent weight, 98
Ergosterol, 436

Esters, 422
Estriol, 444
Estrone, 444
Ethane, 450
Ethanol, 417
Ethers, 419
Ethyl acetate, 422
Ethylene, 407, 408
  dichloride and dibromide, 406
Ethylene glycol, 417
Ethyl gasoline, 519
Eutectic mixture, 206, 461
Exchange reaction, 17
Extraction of solute, 209
Evaporation, 177
  heat of, 181

Faraday's law of electrolysis, 215
Fats, 422
  hydrogenation, 74, 423
Fehling's solution, 430, 486
Feldspars, 234
Fermentation, 417
  acid, 421
Ferrite, 534
Ferrochrome, 521
Ferrosilicon, 388
Ferrotitanium, 396
Ferrovanadium, 546
Ferrozirconium, 397
Fertilizers, 339, 370, 380
Filtering, 17
Filtrate, 17
Fire brick, 507
Fire clay, 509
Fire damp, 402
Fire extinguisher, 305
Firefoam, 305
Fischer-Tropsch process, 407
Fission of atom, 145
Fixing, photographic, 491
Flames, 62, 410
  oxidizing, 410
  reducing, 410
  structure, 410
Flint, 388
Flotation process of concentrating ores, 231
Fluorine, 265
Fluorspar, 265, 277, 468
Flux, 459
Fog tracks, 131
Food, 435
  functions, 436
Formaldehyde, 301, 420
Formulas, 102, 106
  calculation of molecular weights from, 95
  determination, 103
  structural, 107, 400
Fractional crystallization, 200
Fractional distillation, 479
Fraunhofer lines, 153
Freezing point, 177
  lowering by solute, 208
  solutions, 205
Freezing mixtures, 206
Frequency of radiation, 151
Fructose, 429, 430
Fuel gas, 410
Fuller's earth, 408
Fusion, heat of, 177
  of salts, 462

Galena, 358, 515
Gallium, 544
Galvanized iron, 495
Gamma rays, 132, 151
Gangue, 459
Garnet, 503
Gases,
  combining volumes of, 92–93
  combustion of, 62
  compared with liquids and solids, 78
  diffusion, 84, 88
  elasticity of molecules, 87
  gram-molecular volume, 94
  inert, 236
  kinetic energy of molecules, 86
  kinetic molecular theory, 78–90
  liquefaction, 89
  molecular weights, 94
  mole volume, 95
  partial pressure, 83
  perfect, 88
  poisonous, 261
  pressure, 78, 85
  solubility, 198
  standard conditions, 82
  Van der Waals forces, 89
  volume, 80
Gas carbon, 296
Gas laws, 80–89
  deviations from, 88
Gas mantle, 410
Gas masks, 296
Gas oil, 403
Gasoline, 403, 404–407
  alkylation, 405
  anti-knock, 405
  casing head, 405
  octane number, 406
  polymerized, 404
Gay-Lussac's law of combining volumes, 92
Geiger counter, 133
Gel, 225, 230
Gelatin dynamite, 334
Germanium, 545
German silver, 486, 540
Giant molecules, 174
Glass, 392
  composition, 393
  Pyrex brand, 392
Glucose, 417, 429
Gluten, 434
Glycerine, 417, 354, 423
Glycine, 434
Glycogen, 432
Glycols, 417
Gold, 492–493
Graham's law of diffusion, 84
Gram, 6
Gram-atomic weight, 29
Gram-molecular weight, 29, 94
Graphite, 291, 530
  crystal structure, 292
Gravity cell, 452
Green vitriol, 536
Gun cotton, 354, 433
Gun metal, 486
Gunpowder, 250
Gypsum, 358, 468, 472

Haber process, 341
Hafnium, 397
Half-life of radioactive elements, 134

Hall's process, 503
Halogens, 254–266
  compounds, 277–287
  oxides, 282
  oxygen compounds, 282
  phosphorus halides, 278
  properties, 254
  tests for ions, 282
Hardness of water, 186, 473, 474
Heat of combustion, 111
  of formation, 111
  of reaction, 109
  of vaporization, 181
Heat unit, 97
Heavy water, 184
Helium, 75, 237
Hematite, 527
Hemoglobin, 65, 302, 434
Henry's law, 199
Homologous series, 399
Hormones, 444
Humidity, relative, 235
Hydrates, 189–191
  efflorescence, 190
  hydrolysis, 331
  structure, 190
Hydrides, 73
Hydrocarbons, 298, 399–410
  acetylene series, 408
  aliphatic, 399
  aromatic, 399, 409
  cracking, 404
  derivatives, 416–427
  diolefins, 408
  homologous series, 399
  hydrogenation, 74
  isomers, 401
  olefin series, 407
  paraffin, 400
  reactions with chlorine, 260
  saturated, 400
  series of, 400
  unsaturated, 407
Hydrogel, 225
Hydrogen, 67–76
  atomic, 74
  history, 76
  isotopes, 75
  mass and charge of atom, 136
  occurrence, 67
  production, 68–71
  properties, 73
  reaction with chlorine, 259
  spectrum, 153
  uses, 75
Hydrogenation, coal, 76, 407
  fats, 74, 423
Hydrogen bonds, 185, 190
Hydrogen chloride, 277–280
Hydrogen electrode, 327
Hydrogen fluoride, 277, 281
Hydrogen ion, concentration, 327
Hydrogen peroxide, 191
Hydrogen sulfide, 334, 361–364
  precipitation of metallic sulfides, 363
  production, 361
  properties, 362
Hydrolysis, 188, 247
  hydrates, 331
  phosphates, 380
  salts, 331
Hydronium ion, 121
Hydrosol, 225
Hydroxides, 53, 123, 462
  amphoteric, 166, 496
  chemical behavior, 165
Hypo, 371

Ice, 177
  heat of fusion, 177
  manufacture, 343
  structure, 185
  vapor pressure, 181
Iceland spar, 471
Illuminating gas, 410
Indicator, 53, 328
Indigo, 439
Indium, 542, 544
Inert gases of atmosphere, 236
  atomic structure, 154
Inhibitor, 64
Inositol, 436
Insulin, 444
Intermetallic compounds, 462
Inulin, 430
Invar, 540
Invertase, 419, 431
Invert sugar, 431
Iodine, 264
  oxygen compounds, 282, 287
  tincture, 264
Ion-electron method of balancing equations, 274
Ionic compounds, 41
  solubility, 210
Ionization, 120, 213
  apparent degree of, 220
  Arrhenius's theory, 213
  Debye-Huckel theory, 219
  percentage, 215, 218, 324
  weak acids, 222, 325
Ionization constant, 325
  water, 326
Ionization potentials, 156
Ions, 41, 120, 124, 139
  activity, 326
  adsorption, 231
  common, 332
  complex ammonia, 344
  effect upon colloids, 228
  equilibria in reactions, 321–335
  equilibria in saturated solutions, 332
  influence upon precipitation, 334
  migration, 217
  production by action of solvent, 209, 222
  radii, 157
  reactions, 330
  valence numbers, 125
  water, 326
Iron, 527–538
  cast, 530
  compounds, 536
  forms, 534
  malleable cast, 531
  metallurgy, 528
  ores, 527
  pig, 530
  properties, 535
  tests for ions, 271
  white cast, 531
  wrought, 531
Iron pyrite, 358
Isobutane, 401
Isomers, 401, 416
Isomorphous substances, 170

Iso-octane, 406
Isoprene, 413
Isotopes, 37, 139–142, 162
  determination and identification, 141
  radioactive, 134, 144
  table, 142

Jasper, 388
Jelly, 225, 230
Joule, 447

Kaolin, 509
Kerosene, 403
Ketones, 420
Kieselguhr, 389
Kilogram, 6
Kilowatt-hour, 447
Kinetic energy, 11
  gas molecules, 86
Kinetic molecular theory, 78–90
Krypton, 237

Lactose, 431
Lampblack, 296
Lard, 422
Latex, 413
Lattices of crystals, 172
Laughing gas, 348
Law, 2
Lead, 515–519
  arsenate, 382
  compounds, 517
  metallurgy, 515
  ores, 515
  properties, 516
  refining, 515
  tetraethyl, 406
Lead chamber process, 366
Lead storage battery, 453
Lead tetraethyl, 519
Leather, artificial, 433
Le Chatelier's principle, 317
Legumes, 340
Length, units of, 6
Leucite, 247
Levulose, 430
Light, 151
  frequency, 151
  photons and quanta, 151
  spectra, 151
  ultra violet and infra red, 151
  wave length, 151
Lignin, 364, 433
Lignite, 293
Lignocellulose, 433
Lime, 469
  slaked, 470
Lime kiln, 469
Lime nitrogen, 343
Limestone, 468, 469, 470
Lime-sulfur spray, 361
Limonite, 527
Liquefaction, 50, 89, 236
Liquids, boiling, 179
  boiling points, 179, 180
  densities, 169
  evaporation, 177
  fractional distillation, 204
  freezing points, 181
  properties, 168–181
  surface tension, 169
  transition to solid, 177
Liquids
    to vapor, 177
  undercooled, 177
  vapor pressures, 178, 180
  viscosity, 169
Liter, 6
Litharge, 517
Lithium, 251
Lithopone, 479
Litmus, 53
Lucite, 441
Lunar caustic, 488, 490
Lye, 246

Magnalium, 505
Magnesia alba, 477
Magnesia, milk of, 477
Magnesite, 476
Magnesium, 476–478
  compounds, 477
  nitride, 339
Magnetite, 527, 536
Malachite, 484
Malt, 431
Maltose, 431
Manganin, 540
Manganese, 524–525
  compounds, 524
Manganese bronze, 524
Marble, 468, 471
Marl, 471
Marsh gas, 401
Marsh test, 381
Mass, 10
  conservation, 22
Mass action, law of, 313
Mass number, 36
Mass spectrograph, 141
Matches, 377
Matte, 484, 515
Matter, 9
  atomic theory, 19–30
  colloidal state, 224–232
  energy, relation to, 9
  states of, 13, 168, 177
  structure, 130–148
Mauve, 439
Measurement, units of, 5–7
Meerschaum, 476
Meker burner, 411
Melting point, 181
Menadione, 436
Mendeleeff's classification of elements, 114
Mercerization, 433
Mercury, 498–501
  compounds, 498
Metallic couples, 454
Metallurgy, 458
  methods, 459
Metals, 53, 240–251, 457–465
  actinide series, 545
  action of nitric acid upon, 353
  activity series, 68
  alkali, 240
  alkaline earths, 467
  alloys, 460
  carbides, 297, 308
  carbonyls, 301, 538
  compounds, 462
  corrosion, 464
  crystals, 175
  electroplating, 454

Metals
  hydrides, 73
  intermetallic compounds, 462
  lanthanide series, 545
  metallurgy, 458
  nitrates, 355
  occurrence, 457
  ores, 458
  oxides, 126
  passive state, 522
  pickling, 370
  platinum family, 541–542
  precipitation of sulfides, 334
  rare earth, 545
  reactions with acids, 68
    with chlorine, 259
    with water, 69
  refining, 458
  salts, 462
  smelting, 458
  sulfides, 363
Meter, 6
Methane, 42, 176, 400, 401
Methanol, 417
Methylamine, 425
Methyl benzoate, 426
Methyl methacrylate, 441
Mica, 390, 393
Migration of ions, 217
Milk of sulfur, 363
Miners' safety lamp, 410
Minium, 517
Misch metal, 251, 545
Mixture, 12
  eutectic, 206
  freezing, 206
  homogeneous and non-homogeneous, 194
Molal solution, 196
Molar solution, 195
Molecular weight, 29, 92–95
  formulas, calculated from, 95
  from properties of solutions, 208
  gram, 29
  liquids and solids, 95
Molecules, 19–30
  diatomic, 97
  dipole, 176
  elasticity of, 87
  elements, 96
  giant, 20, 174
  kinetic energy, 85, 86
  momentum, 85
  monatomic, 96
  polar and non-polar, 176
Mole volume, 95
Molybdenum, 547
Monazite sand, 545
Mond process, 538
Monel metal, 540
Monosaccharides, 429
Mordants, 440
Morphine, 444
Mortar, 470
Multiple proportions, law of, 26
Muscarine, 442
Mustard gas, 261, 408

Naphthalene, 409
Natrolite, 391
Natural gas, 402
Nelson cell, 257
Neon, 237
Neoprene, 414
Neptunium, 146, 545
Nessler's reagent, 500
Neutron, 138, 145
Niacin, 436
Nichrome, 521
Nickel, 539–541
  compounds, 540
Nicotine, 444
Nitrate, test for ion, 356
Nitric acid, 350
  fuming, 352
  production, 350–352
  properties, 352
  uses, 354
Nitric oxide, 348
Nitrobenzene, 354, 426
Nitrogen, 234, 337–340
  compounds, 348–351
  fixation, 337
  organic compounds, 425
  oxides, 348–349
  production, 338
  properties, 338
  uses, 339
Nitrogen cycle, 340
Nitrogen pentoxide, 349
Nitrogen tetroxide, 349
Nitrogen trioxide, 349
Nitroglycerine, 354, 422
Nitrosyl chloride, 354
Nitrous oxide, 348
Non-electrolytes, 120
Non-metals, 40, 53
  oxides, 126
  reactions with chlorine, 259
Non-polar compounds, 175
Normal solution, 195
Novocaine, 444
Nucleus of atom, 35, 142
  disintegration, 143
  fission, 145
Nylon, 442

Octane, 298
Octane number, 406
Ohm, 217, 447
Oil shale, 407
Oils, vegetable, 422
Old Dutch process, 518
Olefins, 407
Olein, 422
Oleomargarine, 423
Oleum, 368
Onyx, 388
Opal, 388
Open hearth process, 531, 532
Ores, 458
  concentration by flotation, 231
Organic acids, 421
Organogel, 225
Organosol, 225
Orpiment, 380
Orthoclase, 234, 247, 391
Osmium, 542
Osmosis, 207
Osmotic pressure, 207
Ostwald's process, 352
Oxidation, 59–65, 269–275
  definition, 60–61
  in body, 65
Oxidation numbers, 61, 106, 162

Oxidation-reduction, equations, 269–275
  electrical energy produced by reactions of, 447
Oxides, 126
  acidic, 126
  basic, 126, 462
  hydrous, 126
  names, 127
  reactions with water, 188
Oxidizing agent, 60, 274
  table, 275
Oxygen, 47–54
  discovery, 48
  fluoride, 266
  history, 47
  molecular structure, 56
  occurrence, 47
  production, 49–52
  properties, 52
  reactions in body, 65
  uses, 52, 54
Oxyhemoglobin, 65
Ozone, 54–57

Paints, 479, 518
  hardening, 54
Palladium, 542
Palmitin, 422
Panning, gold, 492
Panochromatic photographic film, 492
Paper, 433
Paris green, 382
Parke's process, 488, 516
Partial pressures of gases, 83
Passive state of metals, 522
Pearl, 471
Peat, 293
Pencil lead, 292
Penicillin, 444
Pentane, 401
Pepsin, 434
Peptizing agent, 226
Peptones, 434
Periodic law, 119, 162
Periodic table, 114, inside back cover
  A and B series, 118
  groups of elements, 115
  periods, 115
  uses, 119
Permutite, 474
Peroxides, 191
Persulfates, 372
Petroleum, 402
  base, 402
  ether, 403
  products, 403
  refining, 402–406
Pewter, 512
pH, 327
Phenol, 354, 420, 426
Phosgene, 260
Phosphine, 377
Phosphonium iodide, 377
Phosphorescence, 376
Phosphorite, 468
Phosphorus, 375–380
  acids, 378
  black, 376
  compounds, 377
  halides, 278, 378
  occurrence, 375
  oxides, 378
  production, 376
Phosphorus
  red, 376
  uses, 377
  yellow, 376
Photoelectrons, 135
Photography, 371, 490
Photon, 151
Photosynthesis, 435
Pile, uranium, 146
Pipette, 197
Pitchblende, 548
Placer mining, 492
Plaster of Paris, 472
Plastics, 440, 470
  acrylic, 441
  glyptal, 441
  thermoplastic, 441
  thermosetting, 441
  vinyl, 441
Platinum, 541
Platinum family, 541–542
Plexiglas, 441
Plumbago, 291
Plutonium, 146, 545
Polar compounds, 175
Polymerization, 349, 404, 407, 413
Polysulfides, 363
Porcelain, 509
Portland cement, 475
Positive rays, 139
  analysis, 139
Positron, 138
Potash, 247
Potassium, 247–251
  carbonate, 250
  chlorate, 286
  cyanate, 356
  ferricyanide, 272, 356, 537
  ferrocyanide, 271, 356, 537
  halides, 249
  hydroxide, 250
  nitrate, 250
  perchlorate, 287
  production, 248
  properties, 248
  sources, 247
  thiocyanate, 536
Potential difference, 447
Potentials, electrode, 450
  table, 451
Potential energy, 11
Precipitation, 17, 330
  conditions determining extent, 333
  solubility product, 332
Pressure of gases, 78
  critical, 89
  effect upon solubility, 199
  effect upon equilibria, 317
Producer gas, 412
Promethium, 545
Propane, 401
Properties, chemical and physical, 11–12
Proteins, 433
Proteoses, 434
Protoactinium, 545
Protolysis, 322
Protons, 35, 121, 138, 321
Prussian blue, 357, 537
Puddling furnace, 531
Pyralin, 433
Pyrite, 527
Pyrolusite, 524

Pyroxylin, 354, 433
Pyrrhotite, 539

Quartz, 388
  fused, 389
Quicksilver, 498
Quinine, 439, 444

Radicals, 124
  alkyl, 416
  carboxyl, 421
  valence numbers, 125
Radii of atoms and ions, 157
Radioactivity, 33, 130
  half-life period, 134
  induced, 144
  radiations, 131
Radium, 33, 481
Radon, 33, 237
Rain, 235
Raoult's law, 203
Rare earth metals, 545
Rayon, 442
Rays, alpha, beta, and gamma, 132
Reaction, 17, 39
  chain, 145
  conditions affecting speed, 63, 310
  electrolytes and non-electrolytes, 214
  electrolytic cells, reactions in, 216
  endothermic and exothermic, 109
  energy changes, 109
  equations, 102
  heat of, 109
  ionic, 330
  kinds of, 17
  photochemical, 435
  protolytic, 322
  reversible, 72, 314
  speed of, 63, 310
  velocity constant, 313
Realgar, 380
Reciprocal ohm, 217
Rectifier, current, 498
Red lead, 517
Reducing agent, 60
Reduction, 60–65, 269–275
Refraction, 152
Replacement reactions, 17
Resins, synthetic, 440, 441
Resonance, 56
Retarder, 64
Reversible reactions, 72
Rhodium, 542
Riboflavin, 436
Rock wool, 393
Rocks, weathering, 234
Rose's metal, 385, 512
Rouge, jeweler's, 536
Rubber, 413
  synthetic, 413
  vulcanization, 413
Rubidium, 251
Ruby, 503
Ruthenium, 542
Rutile, 396

Sal soda, 245
Salt, iodized, 264
Salts, 123, 462
  acid, 124
  double, 508
Salts
  fractional crystallization, 200
  fusion, 462
  hydrolysis, 331
  ionization, 323
  names, 124
  normal, 124
  solubility, 199, 463
  solubility products, 332
Saponification, 423
Sapphire, 503
Satin spar, 472
Saturation, 197
Scheele's green, 382
Science, 1
Searles Lake, 248
Sea water, bromine from, 262
  magnesium from, 477
Selenium, 372
Sherardized iron, 495
Siderite, 527
Silica, 388, 390
Silica gel, 230, 391
Silicates, 390, 391
  uses, 393
Silicon, 388–394
  carbide, 307
  compounds, 389
  occurrence, 388
  properties, 388
  uses, 388
Silicones, 394
Silk, 434
  artificial, 442
Silver, 487–492
  compounds, 489
  metallurgy, 488
  ores, 487
  refining, 489
Slag, 459
Smalt, 538
Smelter, 459
Smelting, 458
Smokeless powder, 354
Smoke prevention, 229
Soaps, 423
  cleansing action, 424
Soapstone, 393, 478
Sodamide, 344
Soda water, 303
Sodium, 241–247
  aluminate, 70
  aluminum sulfate, 246
  bicarbonate, 244, 246, 304
  bisulfate, 371
  bisulfite, 371
  borate, 395
  carbonate, 244, 304
  chloride, 41, 243
  chlorite, 285
  cyanide, 356, 488, 492
  formate, 421
  hexametaphosphate, 380
  hydroxide, 246
  hypobromite, 287
  hypochlorite, 260, 284
  iodate, 287
  lauryl sulfate, 425
  metaphosphate, 380
  nitrate, 350
  nitrite, 350
  occurrence, 241

Sodium
oxides, 243
palmitate, 423
perborate, 395
periodate, 287
phosphates, 380
production, 241
properties, 242
pyrophosphate, 380
silicate, 392
stannate, 514
sulfate, 371
sulfide, 372
thiosulfate, 371, 491
uses, 241
zincate, 70, 496
Softening of water, 186, 474
Soil, nitrogen in, 339
Sol, 325
Solder, 512
Solids, 168–181
melting points, 181
transition to gas, 181
to liquid, 181
Solubility, 197
curves, 201
effect of pressure and temperature, 198, 199
factors influencing, 209–210
ionic compounds, 209
Solubility product, 332
table, 549
Solute, 194
extraction, 209
Solutions, 194–210
alkaline, 53
boiling point, 206, 214
classes, 195
concentration, 195
constant boiling, 205
effect of dilution upon conductance, 218
effect upon properties of solvent, 200–207
electrical conductivity, 217
electrolytes, 213
equivalent conductance, 217
formation, 209
freezing point, 205, 215
gases in liquids and solids, 198
hydrogen and hydroxyl ion concentrations, 326
ideal, 203
infinitely dilute, 218
limiting conductance, 218
molar, normal, and molal, 195
molecular weight determination, 208
osmotic pressure, 207
pH, 328
properties, 200
saturated, 197
solvent and solute, 194
specific conductance, 217
standard, 196
supersaturated, 198
titration, 196
vapor pressure, 202
Solvates, 225
Solvay process, 244
Solvent, 194
effect of solute upon, 200–208
Specific conductance, 217
Specific gravity, 168
Specific heat, 97
Spectra
absorption, 153
Spectra
emission, 152
X-ray, 159
Spectral lines, 152
Spectroscope, 152
Speed of reactions, 63, 310
Spelter, 494
Sphalerite, 494
Spiegeleisen, 524
Spontaneous combustion, 62
Stalactites, 471
Stalagmites, 471
Standard conditions of gases, 82
Standard solutions, 196
Starch, 354, 429, 431, 432
Stassfurt deposits, 248
Steam, reaction with iron, 71
Stearin, 422
Steel, 528, 531–535
alloy, 535
case hardened, 535
crucible, 534
hardening and tempering, 534
Stellite, 521, 538
Sterling silver, 486
Stibine, 384
Stibnite, 383
Stoneware, 509
Storage battery, 453
Streptomycin, 445
Strontium, 480
Structure of atoms, 33–39
of crystals, 170
Strychnine, 444
Stucco, 470, 472
Styrene, 413
Sublimation, 181, 265
Substance, 11
Sucrose, 429, 430
Sugar of lead, 518
Sugars, 429
digestion, 430
invert, 431
reducing, 430
Sulfadiazine, 444
Sulfa drugs, 444
Sulfanilamide, 444
Sulfapyridine, 444
Sulfathiazole, 444
Sulfonamides, 444
Sulfur, 358–371
molecular structure, 359
monoclinic, 359
occurrence, 358
plastic, 360
production, 358
properties, 359
rhombic, 359
uses, 361
Sulfur dioxide, 364
Sulfuric acid, 365–370
fuming, 365
oleum, 368
production, 366–368
properties, 365, 369
uses, 369
Sulfur trioxide, 365
Superphosphate, 380
Supersaturation, 198
Sylvanite, 492
Symbols, 43, 102

Talc, 391, 393, 476
Tantalum, 546
Tantiron, 359
Tellurium, 372
Temperature
  absolute, 81
  critical, 89
  eutectic, 461
  equilibrium, effect upon, 318
  kindling, 62
  reaction speed, effect upon, 63, 311
  scales, 5
  solubility, effect upon, 199
  vapor pressure, effect upon, 179
  volume and pressure of gases, effect upon, 80–81
  volume of liquids and solids, effect upon, 168
Thallium, 544
Theory, 2
Thermite, 459
Thermometer, 5
Thiamin, 436
Thiokol, 414
Thorium, 410, 546
  series, 134
Thyroxin, 444
Time, units, 6
Tin, 511–515
  alpha and beta, 512
  black, 511
  compounds, 512
  disease, 512
  gray and white, 512
  metallurgy, 511
  ores, 511
  recovery from scrap, 261
  stream, 511
  uses, 512
Titanium, 396
Titration, 196
Tocopherols, 436
Toluene, 409
Topaz, 503
Torch, atomic hydrogen, 74
  oxyhydrogen, 75
Trinitrobenzene, 354
Trinitrophenol, 354
Trinitrotoluene, 427
Tritium, 34
Trona, 241, 244
Trypsin, 434
Tungsten, 547
  carbide, 548
Turnbull's blue, 357, 537
Turquoise, 503
Tyndall effect, 226
Type metal, 312
Tyrothricin, 445

Uranium, 130, 548
  isotopes, 145
  pile, 146
  series of elements, 135
Urea, 399, 434

Valence, 104
  electrons, 43
  numbers, 43, 99, 104
Vanadium, 546
Van der Waals forces, 89
Vapor, transition to liquid, 177
Vaporization, 177
Vapor pressure, 178
Vapor pressure
  effect of temperature, 179
  solutions, 202
Vaseline, 403
Velocity constant, 313
Venetian red, 536
Ventilation, 235
Verdigris, 485
Vermillion, 500
Vinegar, 421
Viosterol, 436
Viscose process, 442
Viscosity, 169
Vitamins, 435
Voltaic cells, 448, 452
Volume, 6
  gram-molecular, 94
Vulcanization of rubber, 413

Washing soda, 245
Water, 183–192
  action on base and acid, 189
  dielectric constant, 209
  dipoles, 209
  distillation, 186
  electrolysis, 50, 70
  filtration, 186
  freezing point, 177
  hardness, 186, 425, 471, 473
  heat of fusion, 177
  heavy, 75, 184
  hydrolysis, 189
  impurities, 185
  ionization constant, 326
  ions, 256, 326
  occurrence, 184
  oxides, reactions with, 188
  oxidizing action, 189
  pH, 328
  properties, 184
  purification, 186, 187
  reaction with metals, 69
  softening, 186, 187
  solvent action, 184
  stability, 188
  structure, 176, 185
  vapor, 235
  vapor pressures, table of, 549
Water gas, 70, 300, 412
Water glass, 392
Wall board, 472
Watt, 447
Wave length, 151
Weathering of rocks, 234
Weight, 10
  unit, 6
Welding, 459
White lead, 518
White vitriol, 497
Whiting, 471
Witherite, 478
Wood, destructive distillation, 296
  petrified, 389
  paper manufacture, 365
Wood's metal, 385
Wool, 434
Wrought iron, 531

Xenon, 237
X-rays, 151, 158
  determination of crystal structure, 171
  diffraction, 158, 171

X-rays
  spectra, 159
  tube, 158
Xylene, 409

Zeolites, 393, 474
Zinc, 493–497
  compounds, 495
  ores, 494
Zinc
  metallurgy, 494
  properties, 495
Zinc blende, 358
Zinc white, 496
Zircon, 397
Zirconium, 397
Zymase, 419, 431

PERIODIC CLASSIFICATION

Group →	1a	2a	3b	4b	5b	6b	7b	8
Period 1	1 H 1.008							
2	3 Li 6.94	4 Be 9.02						
3	11 Na 22.997	12 Mg 24.32						
4	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
5	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 Tc 99 (?)	44 Ru 101.7
6	55 Cs 133.91	56 Ba 137.36	57 * La 138.92	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2
7	87 Fr 223 (?)	88 Ra 226.05	89 ** Ac 227.05					

Atomic numbers above elements; atomic

Rare Earths * Lanthanum Series (58-71)	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il 147	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2
Rare Earths ** Actinium Series (90-96)	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu 239	95 Am 241	96 Cm 242	97 Bk 243

OF THE ELEMENTS

8 (*continued*)	1b	2b	3a	4a	5a	6a	7a	0
								2 He 4.003
symbols of weights below.			5 B 10.82	6 C 12.01	7 N 14.008	8 O 16.00	9 F 19.00	10 Ne 20.183
			13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
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 Kr 83.7
45 Rh 102.91	46 Pd 106.7	47 Ag 107.88	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 Xe 131.3
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 At 211 (?)	86 Rn 222

66 Dy 162.46	67 Ho 164.94	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99
98 Cf 244					