

Chemistry and You

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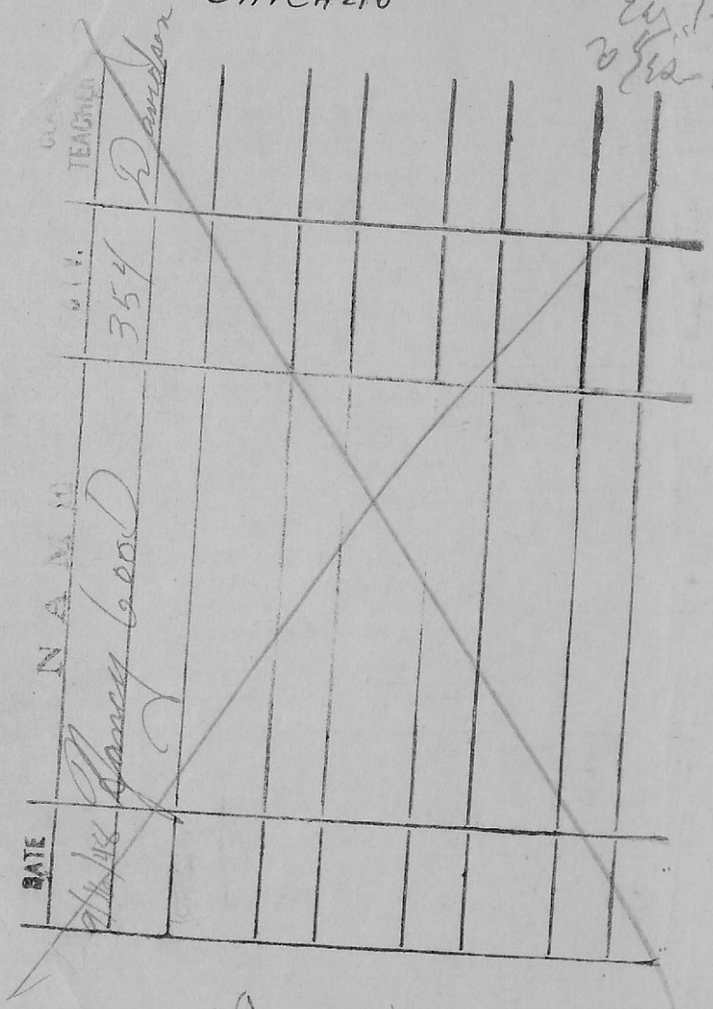

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Periods	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII		
Type Formulas →		E_2O ECl	EO ECl_2	E_2O_3 ECl_3	EO_2 ECl_4	E_2O_5 EH_3	EO_3 H_2E	E_2O_7 HE	Transition Elements		
Families →		A B	A B	A B	A B	A B	A B	A B			
0	The Inert Gases	1 Hydrogen H=1.008									
1	2 Helium He=4	3 Lithium Li=6.94	4 Beryllium Be=9.02	5 Boron B=10.82	6 Carbon C=12.01	7 Nitrogen N=14.01	8 Oxygen O=16	9 Fluorine F=19			
2	10 Neon Ne=20.18	11 Sodium Na=23	12 Magnesium Mg=24.32	13 Aluminum Al=26.97	14 Silicon Si=28.06	15 Phosphorus P=31.02	16 Sulfur S=32.066	17 Chlorine Cl=35.46			
3	18 Argon A=39.94	19 Potassium K=39.10	20 Calcium Ca=40.08	21 Scandium Sc=45.10	22 Titanium Ti=47.90	23 Vanadium V=50.95	24 Chromium Cr=52.01	25 Manganese Mn=54.93	26 Iron Fe=55.84	27 Cobalt Co=58.94	28 Nickel Ni=58.69
		29 Copper Cu 63.54	30 Zinc Zn 65.38	31 Gallium Ga 69.72	32 Germanium Ge 72.60	33 Arsenic As 74.91	34 Selenium Se 78.96	35 Bromine Br 79.92			
4	36 Krypton Kr=83.7	37 Rubidium Rb=85.48	38 Strontium Sr=87.63	39 Yttrium Y=88.92	40 Zirconium Zr=91.22	41 Columbium Cb=92.91	42 Molybdenum Mo=95.95	43 **Technetium** Tc 99	44 Ruthenium Ru=101.70	45 Rhodium. Rh=102.91	46 Palladium Pd=106.7
		47 Silver Ag=107.88	48 Cadmium Cd=112.41	49 Indium In=114.76	50 Tin Sn=118.70	51 Antimony Sb=121.76	52 Tellurium Te=127.61	53 Iodine I=126.92			
5	54 Xenon Xe=131.3	55 Cesium Cs=132.91	56 Barium Ba=137.36	57 to 71 Rare Earths	72 Hafnium Hf=178.6	73 Tantalum Ta=180.88	74 Tungsten W=183.92	75 Rhenium Re=186.31	76 Osmium Os=190.2	77 Iridium Ir=193.1	78 Platinum Pt=195.23
		79 Gold Au=197.2	80 Mercury Hg=200.61	81 Thallium Tl=204.39	82 Lead Pb=207.21	83 Bismuth Bi=209.00	84 Polonium Po=210 (?)	85 At 211 **Astatine**			
6	86 Radon Rn=222	87 **Francium** Fr 223	88 Radium Ra=226.05	89 Actinium Ac=227 (?)	90 Thorium Th=232.12	91 Protoactinium Pa=231	92 Uranium U=238.07				

5	57 Lanthanum La 138.92	58 Cerium Ce 140.13	59 Prasseodymium Pr 140.92	60 Neodymium Nd 144.27	61 Illinium Il 146 (?)	62 Samarium Sm 150.43	63 Europium Eu 152.0	64 Gadolinium Gd 156.9	65 Terbium Tb 159.2	66 Dysprosium Dy 162.46	67 Holmium Ho 164.94	68 Erbium Er 167.2	69 Thulium Tm 169.4	70 Ytterbium Yb 173.04	71 Lutecium Lu 174.99
6	89 Actinium Ac 227.05	90 Thorium Th 232.12	91 **Protactinium** Pa 231	92 Uranium U 238.07	93 **Neptunium** Np 237	94 **Plutonium** Pu 239	95 **Americium** Am 241	96 **Curium** Cm 242							

THE PERIODIC TABLE. Synthetic elements are shown in **bold-faced type.**

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Chemistry and You

A TEXTBOOK *for* HIGH SCHOOLS



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Preface

The first edition of *Chemistry and You* was prepared in order to present a practical and intimate picture of the science of chemistry and its numerous applications in our daily lives. In the earlier edition emphasis was placed upon the chemical principles on which the science of chemistry has been built, upon the broad generalizations which are useful in extending mental horizons, and upon the interesting applications which enrich modern life in its maze of intricate relationships. The success of this plan indicates that chemistry instructors and educators have confidence in its educational value. In keeping with the spirit of the book we offer this revised edition.

The size of this revision has been kept approximately the same as that of the first edition. It is obvious that more material is included than is usually taught during the school year. The majority of chemistry instructors, we believe, will use the first nine units with adequate drill. The remaining units in this book meet the varying needs of individual localities, individual schools, and individual pupils; consequently, the instructor will make selections as needed.

Chemistry and You continues to be a personal study of science in its applications to the life of each pupil regardless of his ultimate life's work. At the same time this text presents the fundamental theories and concepts which are so necessary for those who elect a career that is based on science.

We appreciate deeply the many suggestions which have been received from our fellow teachers of chemistry throughout the national field and wish to express again our thanks to the manufacturing firms, engineering concerns, and other agencies who have generously supplied materials for the illustrations.

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Worth-while Chemistry References

Books used as references in this text have been selected on the basis of interest and readability. Descriptions for books marked * are taken from the *Report of the Committee on Chemistry Libraries* of the Division of Chemical Education, and reported in the Journal of Chemical Education.

*BEERY, PAULINE G. *Stuff.* Appleton-Century Co., New York. 504 pp. Weaves man's discoveries of useful materials into a somewhat chronological story. Begins with a prehistoric royal family in Egypt and comes down to the present time, discussing the more important kinds of materials used by man and telling their history briefly.

BORTH, CHRISTY. *Pioneers of Plenty.* Bobbs-Merrill Co., Indianapolis. 1942. 391 pp. An account of what chemistry is doing to convert surplus farm products into other useful substances. This book portrays the role of "chemurgy."

*CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Harper and Brothers, New York. 374 pp. Intended for the intelligent layman. Presents in readable and systematic form the salient items of fact and theory that constitute the science of chemistry. Emphasis throughout is on the modern chemical viewpoint.

COITH, HERBERT. *So You Want to Be a Chemist?* McGraw-Hill, Chicago. 1943. 138 pp. A brief discussion of what is expected of a chemist by industry and what attitudes the young chemist should take. The book closes with a description of the life of a chemist and the problems that he meets.

*DARROW, F. L. *The Story of Chemistry.* Blue Ribbon Books, Inc., New York. 496 pp. Employs the historical approach in presenting theories and applications of chemistry more extensively than is possible in a secondary school text. Recent developments in many fields and numerous applications have been particularly stressed. The value of research is specifically illustrated and emphasized. American progress in chemistry is outlined.

DAVIS, WATSON. *The Advance of Science.* Doubleday, Doran and Co., New York. An excellent effort to bring the public abreast of the times in what all fields of science are doing today. Material is presented in such a manner as to be understood by general public.

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FOSTER, WM. *The Romance of Chemistry.* Appleton-Century Co., New York. 1936. 468 pp. The interest of a beginning student in high school or college chemistry will be heightened by this vivid picture of the part played by principles, reactions, and elements he is encountering for the first time in the processes of modern chemistry.

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Appleton-Century Co., New York. 1937. 226 pp. Thirty-three articles are selected from various chemical journals and appear in the general order in which they are presented by most high school textbooks in chemistry. Information is given in these articles about many important chemists, past and present. Most of the articles are nontechnical and can be understood by an interested chemistry student in high school.

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry, Second Series.* 1942. 1981 pp. Thirty-six articles.

HAYNES, WILLIAM. *This Chemical Age.* A. A. Knopf, New York. 1942. 385 pp. A narrative of how the chemist converts ordinary materials into most useful substances.

HOLMES, H. N. *Have You Had Your Vitamins?* Farrar and Rinehart, New York. 1938. Dr. Holmes is one of the authorities on vitamins. In this small book he presents in his interesting way what we should know about vitamins. It is written for the layman as well as the student of chemistry.

HOLMES, H. N. *Out of the Test Tube.* Emerson Books, New York. 373 pp. Written for the general public. This very interesting and readable book presents the possibilities of chemistry and explains many of the methods used by chemistry in waging "desperate battles on many fronts."

*HOWE, H. E. (Editor) *Chemistry in Industry.* The Chemical Foundation, Inc., New York. 2 vols. 802 pp. Forty-three authorities tell in nontechnical style how chemistry is applied in their industries. Not intended as texts.

*JAFFE, BERNARD. *Crucibles.* Tudor Publishing Co., New York. Humanizes the story of the development of chemistry. Built on the lives of great chemists from Bernard Trevisan, the alchemist, to Irving Langmuir.

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*KENDALL, JAMES. *At Home among the Atoms.* Appleton-Century Co., New York. 318 pp. A remarkably successful attempt to make chemistry enjoyable, understandable, and vital. Apt analogies are both informative and entertaining. Makes clear many chemical processes and their practical applications; also tells of the heroes of chemistry.

MORRISON, A. CRESSY. *Man in a Chemical World.* Scribner's, New York. 1937. 292 pp. A book telling the service that chemical industry renders.

REED, W. MAXWELL. *America's Treasure.* Harcourt, Brace & Co., New York. 1939. 395 pp. A scholarly description of our raw materials of the earth and how they are used to build our civilization.

*ROGERS, ALLEN. *Manual of Industrial Chemistry.* D. Van Nostrand Co., New York. 1942. 2 vols. Many details of plant construction and plant operation. Many drawings of apparatus. Comprehensive, and covers sources, preparation, properties, and uses of the chemicals of commerce. Also published in one volume, which is more concise treatment of the above two volume manual. Title of one volume edition is *Elements of Industrial Chemistry.*

*SLOSSON, EDWIN E. *Creative Chemistry.* Appleton-Century Co., New York. 311 pp. (Original edition, The Chemical Foundation, Inc., New York.) The triumphs of the past three decades of chemistry; political, economic, and social effects of these achievements and the international rivalry for raw materials that has stirred the chemist to practical achievement.

*STEIGLITZ, JULIUS (Editor) *Chemistry in Medicine.* The Chemical Foundation, Inc., New York. 780 pp. 45 leaders in chemical and medical research have collaborated to tell the advances, the victories, and the problems of the campaign against disease.

STOKLEY, JAMES. *Science Remakes Our World.* Ives Washburn, Publisher. New York. 1942. 298 pp. A good account of the newer materials which are being produced for better living through chemistry.

*TILDEN, W. A. *Chemical Invention and Discovery in the Twentieth Century.* E. P. Dutton and Co., New York. 1936. Three chapters describing several of the largest laboratories in the world and apparatus used in chemistry; ten chapters on modern discoveries and inventions; fourteen chapters on modern applications of

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chemistry; and five chapters on modern progress in organic chemistry. Many illustrations.

WEEKS, MARY ELVIRA. *The Discovery of the Elements.* Journal of Chemical Education, Easton, Pa. 355 pp. The author has gathered from old chemical journals, biographical dictionaries, old letters, and obsolete textbooks interesting stories about the discovery of the elements and the life stories of the discoverers. Ten pages of important dates in chemistry are given, starting with January 25, 1627, the date of birth of Robert Boyle.

The following magazines are recommended for the library:

**Journal of Chemical Education,* Norris W. Rakestraw, editor, Brown University. Publication and business offices, 20th and Northampton Sts., Easton, Pa. This magazine, the official organ of the Division of Chemical Education of the American Chemical Society, publishes the advances in thought and practice in chemical education. It is the only publication of its kind. It contains many original papers with an abundance of illustrations, abstracts of articles of interest in other publications, and chemical book reviews.

School Science and Mathematics, Glen W. Warner, editor. Central Association of Science and Mathematics Teachers, publication office, 450 Ahnaip St., Menasha, Wis. Problems of the teachers of science and mathematics are discussed in this magazine, as well as recent advances in science, and the experiences of teachers.

**The Science Leaflet,* Pauline Beery Mack, editor, State College, Pa. Business offices, Lancaster, Pa. This publication is devoted exclusively to the interests of the beginning science student. It is published each school week. It follows the order of the subject matter as presented in the average elementary textbook. Not only the young student but also the teacher and layman will find it very interesting and instructive.

**Science News Letter,* Watson Davis, editor, Science Service, 21st and Constitution Ave., Washington, D. C. Each week the current progress of science is summarized in the fully illustrated pages of this concise, easily read, and authoritative magazine. Articles in the magazine are reliable scientifically. It supplements regular textbooks by keeping the students thoroughly up-to-date on happenings in the world of science.

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Looking Ahead into

Unit One

Your mother's iron kettle *rusts* unless it receives special care, the milk you like for breakfast *sours,* and that big sweet apple in your locker was once a green, sour thing and may soon lose its sweetness as it *decays.* If you live in a wooden house, it may, by a little carelessness, burn to the ground.

Do changes of this kind always make materials less useful? Can you control these changes?

The causes of the changes mentioned above are hidden from the average person who has not made a study of chemical processes. These changes, which transform substances into different substances, offer wonderful possibilities to you. If you can obtain control over Nature's changes through a knowledge of how they operate, you can construct many substances that people need and want; best of all, you can understand some of Nature's interesting secrets.

In this unit—*A Bird's-eye View of Chemistry*—you will see the significance of the *properties of substances;* you will see what kinds of materials make up the entire world; and you will see how these materials can be changed.

In short, in this unit you are beginning the study of a branch of science that can add much to your welfare and happiness. Chemistry is the story of material things from a viewpoint which is different perhaps from your ordinary viewpoint. It is a way of looking at certain events which occur. It is an attempt to understand how materials act as they do. Chemistry is a method of obtaining certain desired results, based on a knowledge of cause and effect. And always the underlying idea is that materials change.

Note the following problems in this unit.

Problem 1. *Why Are You in This Chemistry Class?*

Problem 2. *What Is the World Made Of?*

Problem 3. *How Can Matter Be Changed?*

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A Bird's-eye View: What Is It All About?—A Bird's-eye View of Chemistry

Problem 1

WHY ARE YOU IN THIS CHEMISTRY CLASS?

Out of the test tube of the chemist has come a wealth of beautiful, useful, merciful products that would have dazzled Aladdin. Scientific medicines help fight our diseases; modern fertilizers give us crops from lands that, except for the chemist, would be valueless; fast automobiles in bright colors flash along smooth, well-built roads; giant buildings with metal ribs reach dizzily into the sky; airships braced with metals stronger than steel and lighter than wood glide through the air. Everywhere there is a richness and a beauty to the world made possible largely by the chemist who uncovers nature's secrets and takes advantage of her laws.[1] Such is the work of the chemist in times of peace.

In times of war the continued existence of our nation and the lives of hundreds of thousands of fighting men depend largely on the chemist and his fellow scientists.

The science of chemistry has added much to your comforts and your conveniences. What can your study in this chemistry class do for you?

Chemistry can help you to "keep your eyes open" and to observe. Although industry through chemistry gives you many wonderful and useful products, it may also provide products that are useless or even harmful, products that may be used for the destruction of life as well as for the saving and the enjoyment of life. The fault is not with chemistry but with men—for society, no doubt, always has

[1] Adapted by permission from Holmes, *Out of the Test Tube*, published by Emerson Books, Inc., 333 Sixth Ave., New York, 1934.

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had some unscrupulous men and perhaps will continue to have such men. The products of chemistry that are offered you are not always desirable.

You must know something about chemistry if you would know the truth about the substances you buy and use. The study of chemistry should help you to "keep your eyes open" and to observe. It should help you to observe not only the things you buy and use, but it should also help you form the habit of accurate observation and appreciation of the many things with which you come in contact each day.

Chemistry can help you to think straight. If you have an iron pan in your kitchen at home, you, no doubt, have noted that it does not rust when kept perfectly dry. But if by mistake a little moisture is left on it overnight, it becomes considerably rusted. What causes the rust? You might be tempted to say that water causes the iron pan to rust. You might even go so far as to say that water *alone* causes iron to rust or that water *always* causes iron to rust. Such statements would not show clear thinking for things are not always "what they seem." The way of science study is to ask nature a question by means of an experiment. Here is an interesting one: Cover some powdered iron with boiled water and let it stand for a considerable time. You will find that the iron rusts very little, if any. This simple experiment shows that water alone does *not* cause iron to rust. Something else is necessary. Another experiment will show you where that "something else" comes from.

After wetting the inside of a test tube with water, you can make a thimbleful of powdered iron stick to the inside surface by shaking the powdered iron in the tube. If you now invert the tube with the open end standing in water as in Fig. 1a and leave it overnight, the next morning it will appear as in Fig. 1b. The powdered iron has rusted, and the volume of air in the tube has decreased. Water has taken the place of the air that is gone. This shows that a part of the air was removed as the rust was formed. By proper tests you can

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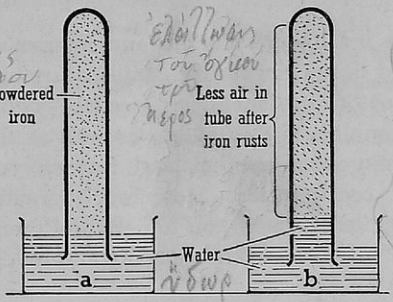
prove that the part of the air that was removed was oxygen. The iron rust contains both iron and oxygen. The water hastened the union of these two substances.



As iron rusts, part of the air disappears by combining with the iron to form rust. This experiment, which seems so simple to us today, was a research problem in 1770. From the study of experiments of this kind the science of modern chemistry has developed.

1. Moist Iron Rusts in Air

You see therefore that the rust on your mother's iron pan is not what it may have seemed at first.

The study of chemistry should help you to think straight not only in your chemistry class but also in your everyday business and social activities.

Chemistry can teach you that nature is governed by law. Nature is never haphazard. Under identical conditions, identical changes occur. Iron powder left in a wet tube, in the presence of ordinary air under the conditions described for Fig. 1, *always* yields rust. However, with this same air and this same powder you can get a product entirely different from rust *if the temperature is raised* sufficiently.

In other words, you can control nature's changes but you must control her with her own laws. These laws never vary.

Chemistry can show you that you owe your modern comforts and conveniences to many great men—past and present—who have labored long hours to learn nature's secrets. Nature is governed by law—but these laws are not always evident. Many of our great scientists have devoted their entire lives to uncovering one or more of nature's secrets. The problems that some of these men solved are intensely interesting in

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themselves. The study of chemistry should teach you to appreciate more our great men of science. Largely through their discoveries this modern age of machines has been made possible.

Chemistry can give you a wealth of valuable and interesting information. Iron rusts and is no longer iron; milk sours and is no longer sweet milk; doctors use chemicals to cure "incurable" diseases. The commonplace things of life as well as the "unusual" things can give you enjoyment and furnish you with interesting topics of conversation. How much greater the appreciation of these things can be if you understand them. Learning the "hows" and "whys" of science affords an endless source of enjoyment.

The importance of chemistry in modern society will continue to become greater and greater. For the enterprising chemistry student who understands the big chemical principles under which nature works and who is interested in uncovering nature's secrets, there will always be worth-while opportunities.

Readings for Pleasure and Profit

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 1, pp. 1-8, "The Human Side of Chemistry."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. I, pp. 1-19, "The Upward Sweep."

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. I, pp. 1-12, "Nature Points the Way."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. I, pp. 1-13, "Three Periods of Progress."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. I, pp. 1-11, "New Frontiers."

Applying in Life What You Have Learned in Chemistry

A study hint: Do you have clearly in mind exactly what you are trying to learn?

One of the differences between a successful man or woman and an unsuccessful one is that the successful person knows where he is going and what he is doing. He does not trust to luck.

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If you had but two days to visit a strange city, you would not ride from one end to the other all day to see as much as you could. This would result in a confused blur of buildings, people, and noise. Instead you perhaps would get a visitor's guide and plan your short visit so as to see the main points of interest.

The problems in this book have been planned carefully to aid you in finding the big points in chemistry. They are designed to keep you from getting lost in a mass of details. Note now how each unit in the book is divided into interesting and practical problems; and how the problem questions are answered by the sideheads in bold-faced type.

This arrangement is designed to help you develop planned study habits which will be invaluable to you in your other studies and in life.

Putting Chemistry to Work

A

(1) Is it childish to be curious? Explain your answer. (2) What attitude should everyone take regarding new things? (3) What can you say to justify the statement, "The common man today lives better than kings did one hundred years ago"? (4) Give an instance in which the chemist has changed waste materials into useful substances.

B

(5) Why is laboratory work so important in chemistry? (6) How do we ask questions of Nature? How does she answer us? (7) Mention five ways in which your study of chemistry can be valuable to you. (Hint: Study again the five sideheads in bold-faced type which answer the problem question, "Why are you in this chemistry class?") (8) What are the chief natural resources of your state? How are they converted into wealth? (9) What chemical industries are located in your city? in your state?

Research and Activities That You Will Enjoy

A forum: By means of a small discussion group develop the theme, "The savage discovers. The barbarian improves. The civilized man invents."

An enlightening discussion: Ask other members of your class to give the steps of the scientific method. Then invite several to join you, each choosing one step and giving a one-minute talk on it.

A report: Skin Deep, by Phillips, tells how many toilet preparations are misrepresented in their advertisements.

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Problem 2

WHAT IS THE WORLD MADE OF?

You learn to recognize your classmates by their "looks" and their behavior. In much the same way, you can learn the nature of matter by its properties and its behavior. The material things about you affect your sense of color, smell, taste, touch, and hearing. Many materials change from solid to liquid and to the vapor state at different temperatures. Some disappear in water, while others do not. Some may be flattened into thin sheets or drawn into flexible wires, while others are so brittle that they may be broken into pieces. Heat and electricity travel rapidly through some materials, while they hardly pass through others at all. In this way materials exhibit properties. *Properties* are the marks or signs by which one kind of matter may be distinguished from another.

When a chemist examines carefully a piece of matter and finds that it has the same properties throughout every part of it, he knows that the whole piece of matter is *one* kind of matter. It is called a *pure substance.* Under constant conditions, a pure substance always has a definite and characteristic set of properties by which it can be described. This invariable behavior in nature is known as the *law of properties.* It may be called the first fundamental chemical law.

If some portion of a specimen of matter is found to differ in properties from some other part of it, then it is known as a *mixture* of two or more substances and not a single substance. If the quantity of one substance in a mixture is small and naturally or accidentally present, it may be referred to as an *impurity.*

Some of the common physical properties of substances are:

color
odor
taste
density (heaviness)
solubility
freezing point
boiling point
ductility (can be drawn into wires)
malleability (can be flattened)
conductivity of heat and electricity

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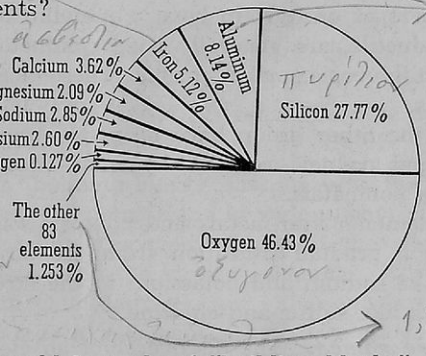
In addition to their physical properties, all substances may be described by their *chemical properties* which are found by answering such questions as these: Is the substance chemically active or inactive? Does it burn in air? Does it help other substances to burn? Does it react with water or other reagents?



2. Relative Quantity of Elements in the Earth's Crust.

The world is made of "building blocks" called elements. As an electric current passes through water, the water decomposes into two gases, hydrogen and oxygen. No one ever has been able to separate either of these gases into simpler substances by ordinary chemical methods. These gases are examples of elements—the primary building materials of nature.

There are said to be 92 elements found in nature, but man has been able to supplement nature by producing some additional elements through the use of special devices such as the uranium pile (p. 793). For the present you will be concerned mostly with the elements that are found in nature. These elements differ greatly in their relative abundance. Some are so common as to be ever present, while others are so scarce as to be merely chemical curiosities. The relative abundance of the commonest elements is shown in Fig. 2.

Nine elements make up more than 98 per cent of the earth's crust. The other eighty-three make up less than 2 per cent. Some of the scarce elements have come into rather common use because they have certain properties which man has adapted to his use. Among them are tungsten in electric

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light filaments, chromium for plating, neon for electric signs, helium for airships, vanadium and tantalum in alloy steels, and thorium and cerium in gas mantles.

The 92 elements that make up the world are grouped into metals and nonmetals. Elements may be divided into two great groups. The members of one group have a metallic luster, are malleable and ductile, are generally good conductors of electricity, and form the basic portion of salts. These elements are known as metals.

The members of the other group have properties that are quite the opposite and are acid-forming elements. These elements are known as nonmetals.

The division of elements into metals and nonmetals is not sharp, for there is a gradual transition from the strongly metallic elements like sodium and potassium to the strongly nonmetallic elements like sulfur and chlorine.

How elements are named. The discoverer of an element usually proposes a name for it. The names of the early elements were selected without plan. The metallic elements which were discovered since 1800 have been given names ending in *-ium*. The nonmetallic elements have been given names ending in *-on* or *-ine*. The name of an element may be derived from some locality (such as germanium, polonium, or illinium) or from some property which it may possess (such as chlorine from the Greek word for green, or hydrogen which means water-former).

For each element there is a symbol. The symbol is either the first letter of the name or the first letter followed by some significant letter. For example, the symbol for carbon is C; for calcium, Ca; for chromium, Cr; and for cobalt, Co. Some elements derive their symbols from other languages. These include the following:

Antimony	Sb	Stibium
Copper	Cu	Cuprum
Gold	Au	Aurum
Iron	Fe	Ferrum
Lead	Pb	Plumbum

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Mercury	Hg	Hydrargyrum
Potassium	K	Kalium
Silver	Ag	Argentum
Sodium	Na	Natrium
Tin	Sn	Stannum
Tungsten	W	Wolfram

The preceding symbols are all derived from the old Latin names for the elements, except the last which is from the German. The symbol for each element should be written with but *one capital letter*. A complete table of the elements and their symbols is given on pages 772-773.

The 92 "building blocks" that make up the world are found in chemical compounds and in various physical mixtures. When you examine the many things in the world, you find very few of them in the form of elements. Most of the things you meet in your daily life are either mixtures of substances or compounds of elements. These two classes of material have definite characteristics.

How you may distinguish mixtures from compounds. If you mix some iron powder with sulfur, it is quite evident that you can mix them in any amount you wish. You can put a pound of iron into a barrel of sulfur, or a pound of sulfur into a barrel of iron powder. By stirring long enough you can get a uniform mixture in either case. Mixtures like these can be made in any proportions and when they are being made, there is no evidence of any energy change.

If you wish to separate a mixture into its component parts, you can make a physical separation. In the mixture none of the components has lost its identity. By making use of the difference in physical properties, you can separate the materials. Iron is attracted by a magnet; sulfur is not. By using a magnet, the iron may be taken out and the sulfur left. Sulfur is soluble in carbon disulfide; iron is not. By shaking the mixture with this solvent, the sulfur dissolves, leaving the iron.

If, however, you mix about five parts by weight of sulfur with seven parts by weight of iron powder and heat the mixture, at first you notice that the sulfur melts and some of

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it boils away. Finally when a definite temperature is reached, a glow appears in the mixture. Even if the material is removed from the flame, the glow continues to spread through the entire mass. It is evident that energy in the form of heat and light is liberated. This is visible evidence that a chemical change is taking place. The result of this change is a compound, a single substance. It is a nonmagnetic substance, no part of which is soluble in carbon disulfide—showing that *it is neither iron nor sulfur.* In fact it has a different set of properties from either of the substances which entered into its composition. By carefully weighing the iron used and the product obtained, chemists have found that iron combines with a definite proportion of sulfur by weight. In this case, 32 parts by weight of sulfur always combine with 56 parts by weight of iron. In simpler terms, sulfur combines with iron in the ratio of 4 to 7 (by weight). All chemical compounds show a similar definite composition. Common salt, for example, is always made up of 23 parts of sodium combined with 35.5 parts of chlorine (by weight). This fact concerning the composition of compounds is expressed by the *Law of Definite Proportions* (Definite Composition). *In any one chemical compound the elements always are combined in the same proportion by weight.* This is the second fundamental chemical law.

Since chemical compounds are the result of chemical action, they can be separated into their constituent parts only by chemical action.

CLASSIFICATION OF MATERIALS

A pure substance is matter that always has a definite and characteristic set of properties (under constant conditions).

1. An element is a primary form or "building block" of matter.
   (a) A metal is a base-forming element.
   (b) A nonmetal is an acid-forming element.
2. A compound is a substance composed of chemically united elements in definite proportions by weight.
3. A mixture is an association of substances not chemically united.

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A Comparison of Compounds and Mixtures

Point of Contrast	*Compounds*	*Mixtures*
1. How made and separated	By chemical change.	By physical change.
2. Energy of formation	Energy always given out or taken in.	No energy change.
3. General properties	Different from its constituents.	An average of the components.
4. Proportions	Alike in every part.	Variable at will.
5. Structure	Like molecules of different atoms.	Different molecules.

Readings for Pleasure and Profit

Goldblatt, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 5, pp. 23-31, "The Derivation of the Names of the Elements."

Holmes, Harry N. *Out of the Test Tube.* Chap. V, pp. 51-65, "Language and Tools."

Kendall, James. *At Home among the Atoms.* Chap. II, pp. 12-22, "Kinds of Things"; Chap. IV, pp. 48-62, "Getting Down to the Nature of Things."

Morrison, A. Cressy. *Man in a Chemical World.* Chap. II, pp. 13-33, "Chemistry in Overalls."

Stokley, James. *Science Remakes Our World.* Chap. XI, pp. 129-135, "Mining the Ocean."

Applying in Life What You Have Learned in Chemistry

Jack Stone had cut his finger rather badly. The cut had bled freely for several minutes and now Jack wished to stop the bleeding.

He had heard that cotton dipped into a solution of chloride of iron and applied to a cut would act as an astringent to stop the bleeding. He found a solution labeled "ferric chloride," but he was uncertain whether, or not, to use it. What would you have done? What elements are combined in this compound?

What can you say to justify the statement: "The value of things and of people is determined by the service they render"?

The ancients thought that water was an element. Why do we not think that it is an element?

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Putting Chemistry to Work

A

(1) What relation do you see between the word *plumber* and the name of an element? (2) What property does copper have which makes it valuable in the electrical industries? What property of glass makes it unsuitable for such uses? (3) Make a list of ten materials you use frequently and mark each as an element, a compound, or a mixture. Give a reason for your choice in each case. (4) Matter would be useless without properties. Explain. (5) Why is a knowledge of the properties of materials important in the professions and in the trades? Give examples. (6) How does the law of properties greatly simplify the study of chemistry?

B

(7) Sulfur burns in air to form sulfur dioxide gas. Is this behavior physical or chemical? Justify your answer. (8) We speak of the analysis of a compound into its constituent elements. Can we accurately speak of the analysis of an element? Why? (9) One sample of chloride of mercury contains 200 grams of mercury combined with 35.5 grams of chlorine. Another sample contains 200 grams of mercury combined with 71 grams of chlorine. Are they the same substance? Justify your answer. (10) Why can you not consider the chemical properties of an element without also considering other elements? (11) Explain the statement: "A chemical element is known by the company it keeps." (12) "Matter cannot be destroyed, but substances can." What does this statement mean to you?

Research and Activities That You Will Enjoy

A panel discussion: Organize a small group of students to give ideas on the topic: "Money spent in competitive advertising of different brands of a pure substance is economic waste."

A reported interview: Talk with persons of different occupations, such as a farmer, a garage man, a doctor, a painter, to see whether you can find what use they make of chemistry in their work. Report to the class any points of interest.

A chart: Prepare and display to the class a chart contrasting the symbols used by the alchemists with those used by modern chemists.

A historical report: Tell the class briefly about the elements which were known in different years, such as 1800, 1830, 1860. (A good reference is: Weeks, *Discovery of the Elements.*)

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Problem 3

HOW CAN MATTER BE CHANGED?

Matter can be changed either physically or chemically. Many things are undergoing continual change. Iron rusts, iron may be melted or it may be magnetized, water evaporates, fats turn rancid, and wood burns. In some of these changes new substances with new characteristics or properties are formed. In others there is only a change of state or form. For example, after iron rusts, it changes to a different substance with different properties. When iron is melted or is magnetized, it still is iron although it is easy to see that it has undergone a change. The changes which produce *new substances* are *chemical changes;* those that produce *no new substances* are *physical changes.*

If the bright silvery metal *platinum* is heated in a flame until it becomes white hot, there is no change in its properties when it is cooled. But if another silvery metal *magnesium* is similarly heated, it burns with a brilliant white light and becomes a white crumbly ash that in no way resembles the original metal. The change in the platinum was only a temporary physical change, but the change in the magnesium resulted in the formation of a new substance. This was a chemical change.

Physical changes do not alter the composition of the molecules—the physical units of matter. The physical units of matter are called *molecules.* Any change in matter which does not alter the composition of the molecule is a physical change. It has been estimated that the diameter of the oxygen molecule is about 1/250,000,000 of an inch. In a milliliter (see Appendix) of air under ordinary room conditions there are about 10^{19} molecules. This number is so large that it is difficult to comprehend. The oxygen molecule contains only one element, oxygen, but the molecules of substances other than elementary substances contain more than one element. Any change in the composition of the molecule is a chemical change.

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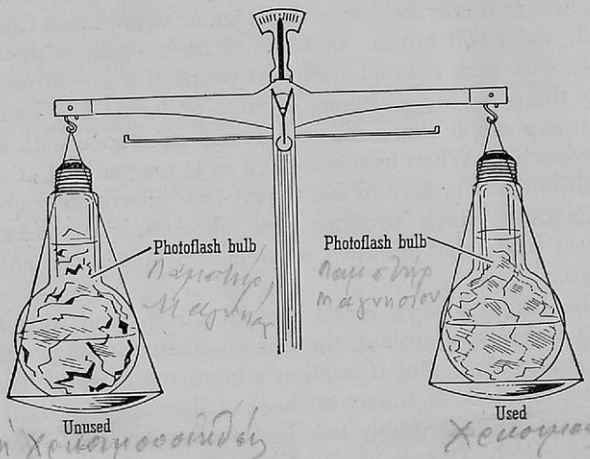
A Principle for You to Remember

Physical changes do not alter the composition of the molecules. Any change in the composition of the molecule is a chemical change.



3. THERE IS NO WEIGHT CHANGE DURING A CHEMICAL CHANGE. The burning of a flashlight bulb is a striking example of a chemical change. If you weigh the bulb before and after it has burned, you will find no change in weight.

Chemical changes involve the chemical units of matter—the atoms. The small particles of elements, which combine to form molecules, are called *atoms*. They are even smaller than molecules. The name atom is derived from a Greek word meaning undivided. Atoms are the chemical units of matter. They are transferred without division in chemical changes. Each different kind of atom has a definite atomic weight.

Atoms are complex particles. Originally the atom was thought of as a small particle of matter which was not capable of further subdivision. Recent discoveries have shown that the atom itself has a complex structure in which extremely

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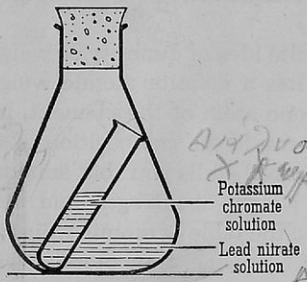
small particles are arranged in an orderly manner according to a systematic plan. A more extended study of atomic structure is given in a later unit.



There is no gain or loss in the weight of the flask after mixing the contents and after allowing a chemical change to take place. This shows that in the chemical change which occurs, matter has neither been created nor destroyed, but remains constant in amount.

4. Chemical Change Causes No Change in the Total Weight

Chemical changes do not destroy matter. In chemical changes in which the properties of substances are so completely altered, you may wonder whether any of the matter is lost in the process. You can find an answer to this question in a scientific manner. In a flask containing some lead nitrate solution place an upright tube containing some potassium chromate solution. Securely stopper the flask and balance it on a scalepan. Then invert the flask so the two solutions are mixed. The formation of a yellow solid, lead chromate, shows that a chemical change has taken place. Again place the flask on the scalepan—after the chemical change has taken place. The weight *is the same* as before. Many such experiments have been tried, and the result is *always* the same. These experiments show that *in any chemical change, matter is neither created nor destroyed, but remains constant in amount.* This general conclusion is known as the *Law of Conservation of Matter* (or *Mass*), our third fundamental law in chemistry. In science a law is the statement of a constant mode of behavior.

How chemical composition may be expressed: formulas. The molecule of hydrogen chloride is made up of one atom of hydrogen and one of chlorine. You can express the composition of hydrogen chloride by representing each atom by its

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symbol in this way: HCl. The molecule of ammonia is composed of one atom of nitrogen and three atoms of hydrogen. Its combination may be expressed as NH_3. Such a combination of symbols used to denote the composition of a molecule is called a *formula.*

A formula carries with it a definite idea of quantity or weight. Since each atom of an element has a definite atomic weight, and since the symbol stands for one atom of the element, it is possible to determine from the formula the composition of the compound by weight. The formula NH_3 tells you that ammonia is made up of fourteen parts by weight of nitrogen and three parts by weight of hydrogen. (See the table of atomic weights.) Keep in mind that the symbol of an element denotes not only *which* element, but also *how much.*

Energy may be used to change matter. In addition to the matter present in a definite quantity of a substance, there is also always a definite quantity of energy. The coal and other fuel that you use in your home is purchased for its *heat energy* content that is released when it is burned—and not for the matter that is formed by the combustion (gases and ashes). Your household electric bill each month states the units of *electrical energy* used by your various appliances which convert electric energy into other forms of energy. The lamp bulb changes electricity into *light energy;* the rotary fan forms *motion energy;* the toaster or grill forms *heat energy;* and the bell forms *sound energy.* In charging a storage battery, the electricity causes a chemical change inside the battery, forming substances of a much higher energy content. This energy absorbed in making the new substances is known as *chemical energy.*

In general chemical changes take place more readily between substances of high energy content. They react readily because of this energy. The substances formed have considerably less energy, and the difference usually appears in the form of heat. In every chemical change, energy is either given out or taken in. This effect is one of the indications of a chemical change. When heat is given out, the change is called an

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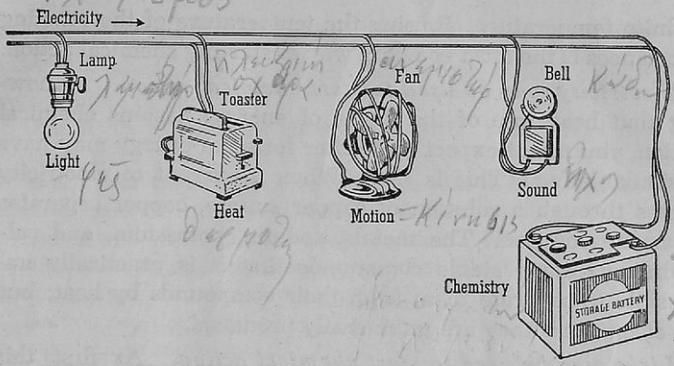

5. Electricity Can Be Changed Into Other Forms of Energy. Electricity can be changed into light energy, into motion energy, into heat energy, into sound energy, or into chemical energy.

exothermic one; when the heat is absorbed, the reaction is called endothermic (heat taken in). If the heat given out is intense, light also accompanies the heat. When the new substances are gases, violent motion or explosions may occur.

The electric cell is only a chemical engine furnishing electricity. But energy, like matter, is not created or destroyed. It may be changed into other forms, but the total quantity of it in the universe is constant. Beyond the field of ordinary chemistry in the building of atoms, it has been shown that matter may be transformed into energy. Matter then, may be only a form of energy, but the law of conservation of "energy-matter" is valid and unchanging.

Heat may be used to start chemical action. Some substances may react when they merely are brought together. For example, when iodine and phosphorus are brought together, they react at once. They are chemically active. Ordinary black gunpowder (a mixture of carbon, sulfur, and potassium nitrate) may be safely stored without any reaction at ordinary temperature. But if it is heated sufficiently, a violent reaction takes place. Many other mixtures behave similarly. Wood does not burn until it has been heated to a

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definite temperature. Raising the temperature of the reacting substances is the most common way of starting chemical action.

Electricity may be used to start chemical action. Knowing that heat, one of the forms of energy, hastens chemical action, you might expect that other forms of energy may have a similar effect. This is true. When a current of electricity passes through a solution of copper sulfate, copper separates from the solution. The metals, sodium, potassium, and calcium form such stable compounds that it is practically impossible to separate them from their compounds by heat; but by *electrolysis* they are quite easily produced.

Light may be used to start chemical action. At first this method of starting chemical action may seem unimportant. Remember, however, that the fourth largest industry is photography, including motion pictures. This industry depends upon the ability of light to record visual images by the decomposition of a silver compound. Without this chemical reaction, hand drawings would be the only means of illustrating books and periodicals.

Mechanical motion—percussion—may be used to start chemical action. Energy is needed to set objects in motion. When resistance is offered to the movement of an object, friction caused by the resistance transforms the energy of motion to heat. In this case the effect produced is that of heat. Rubbing a friction match against a rough surface makes enough heat from friction to cause the match to take fire.

Some reactions started by strictly mechanical processes are not due directly to heat. For example, when a mixture of sulfur and potassium chlorate is struck by a hammer (dangerous—don't try it), a chemical reaction occurs with explosive effect. Similarly, many unstable compounds (such as nitroglycerin) decompose explosively when jarred or struck.

Readings for Pleasure and Profit

BORTH, CHRISTY. *Pioneers of Plenty.* Chaps. I-II, pp. 13-46, "Chemurgy and Its Crowded Stage."

KENDALL, JAMES. *At Home among the Atoms.* Chap. III, pp. 28-47, "What Can Be Done with Things?"

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Applying in Life What You Have Learned in Chemistry

On the way home from a picnic in the woods, George picked up a small piece of pipe.

One of his companions observingly said, "You always pick up the most junk. What good is it?"

"Well," said George, "it's very heavy, and it bends easily so it must be lead. I can use part of it for 'sinkers' on my fishing lines."

James who was in high school remarked, "We learn in chemistry that there is no such thing as 'junk' to the chemist. He knows how to change it into something useful."

Do you see the value of properties? Would you like to be able to make things more useful?

Putting Chemistry to Work

A

(1) When water evaporates, we frequently say that it disappears. Is this contrary to the law of conservation of matter? Explain. (2) What forms of energy do you get from the electricity which enters your home? (3) Can you tell from the appearance of a compound anything of its composition? Explain your answer. (4) Justify the statement: "To save time in chemistry, we learn and use symbols and formulas." (5) Explain as fully as you can the statement: "Molecules are the physical units of matter, while atoms are the chemical units." (6) A rifleman applies mechanical energy (pull) to the trigger of his rifle. What energy changes take place before the bullet leaves the gun? What chemical changes?

B

(7) Make a list of questions to answer in deciding whether a change is physical or chemical. (8) What different information is given by these two formulas: CO, Co? (9) Match the following terms in two columns: formula, element, atomic weight, compound, molecule, symbol, molecular weight, atom. (10) What information does the formula for sulfuric acid (H_2SO_4) give to you? (11) What is meant by the statement: "All living things are transformers of energy"? (12) Point out and explain several examples illustrating the transformation of energy. (13) Think of what would be done in separating such mixtures as salt and water, sugar and sand, sawdust and gravel; then see if you can make a correct *general* statement of how all mixtures are separated.

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Research and Activities That You Will Enjoy

An appreciation: As a result of advances in chemical science, what opportunities for better health and enjoyment may you now have as compared with those of a hundred years ago? (If it is available, refer to: Harris and Butt, *Scientific Research and Human Welfare.*)

A demonstration: Arrange to show the class the demonstration suggested on page 15. State and explain the law involved and point out how your demonstration illustrates this law.

A forward-looking report: Ask several interested students to join you in preparing brief reports on what opportunities chemistry offers as a vocation, and how chemistry contributes efficiency to various vocations. Let each student choose the part of the topic in which he is most interested. These reports may be given any time during the next month.

Looking Back into Unit 1

Be sure you know the purpose of this unit. Read again the material on the page that faces page 1, "Looking Ahead into Unit 1." Then study the following Summary Test.

Summary Test

1. *Why are you in this chemistry class?*
   (a) In what ways can your study of chemistry be valuable to you?
   (b) From your own experience give an instance showing the importance of—
      (1) Careful observation.
      (2) Straight thinking.
2. *What is the world made of?*
   (a) What is the importance of properties?
      (1) Distinguish between physical properties and chemical properties.
      (2) Give examples of each.
   (b) Of what three types of materials is the world made?
      (1) Why are elements called "building blocks"?
      (2) Distinguish between elements and compounds.
      (3) Distinguish between compounds and mixtures.
         A. Name and state a law which applies to compounds but not to mixtures.

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3. *How can matter be changed?*
   (a) How do physical changes and chemical changes differ?
   (b) How are molecules and atoms involved in chemical changes?
      (1) How do symbols express quality and quantity?
      (2) How do formulas express composition?
   (c) What kind of substances react chemically very readily?
      (1) In what ways are chemical changes hastened?
      (2) Give examples of each.

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

This chemistry book, Chemistry and You, is bringing you face to face with many interesting and many practical situations. After taking a journey that thrills you, you enjoy living it over. Many of the high spots come back to you in later days to make your experience real and worth while. At the end of each unit in this book it will be worth your time to stop and view the panorama that *chemistry* presents—man's conquest of the nature of matter.

As you look back over each unit, try to contrast the pictures given there with your own impressions of the vital things you would like to carry on as permanent possessions. Make each important point a peg on which to "hang your memory."

In this unit you are presented with *92* "building blocks," called *elements.* You "discover" that these elements may be combined (if the elements really like each other well enough to combine) into *compounds* in which the elements unite in very *definite proportions* by *weight.* Once a compound does not mean always one, for a compound may be broken down or it may be converted into still other compounds. You distinguish also a compound from a *mixture.*

The world seems to be full of *changes—physical* and *chemical.* Although *matter* may undergo one change after another, it cannot be *created* or *destroyed. Energy* is just about as important in these changes as matter itself and the above "law" holds for energy as well as for matter.

These first steps in your study of chemistry will continue to lead you into interesting paths in the coming units.

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Looking Ahead into

Unit Two

In your study of chemistry this year you will deal with changes in which the *molecules* of substances are changed—"old" molecules may be broken down in your laboratory work and different ones formed. How do scientists know that there are such things as molecules? Perhaps the simplest proof of the existence of molecules lies in a study of the atmosphere which surrounds you at all times.

You know, of course, why this mixture of gases—the atmosphere—is so tremendously important to you: It contains the gaseous element oxygen—your "breath of life." You will also be interested to learn just how this same element, oxygen, enables materials to burn by chemically uniting with them. In fact it was only after the nature of burning was understood that chemistry could properly be called a modern science.

Note how the following problems portray the story of your world of gases.

Problem 4. *What Is Air?*

Problem 5. *How Are You Affected by the Gases of the Atmosphere?*

Problem 6. *How Does a Study of Air and Other Substances Indicate That Matter Is Composed of Tiny Moving Molecules?*

Problem 7. *How Is It Possible to Learn the Characteristics of the Colorless, Odorless, Tasteless Element—Oxygen?*

Problem 8. *Why Is Oxygen One of the Most Useful Elements in the World?*

Problem 9. *In What Ways Is It Necessary to Overcome the Action of Oxygen?*

Problem 10. *How Is It Possible to Learn the Qualities of Hydrogen?*

Problem 11. *How Does Hydrogen Serve Your Daily Needs?*

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The Atmosphere: Your World of Gases; the Atmospheric Gases and Hydrogen

Problem 4

WHAT IS AIR?

Air is not a simple substance; it is made up of more than eight different gases. In 1868 a new element was discovered in a striking manner. This element was helium now widely used in dirigibles and balloons. Helium was first discovered in the sun's atmosphere, not as you might expect in material found upon the earth! More than twenty-five years later this gas was discovered also in the earth's atmosphere. Every bit of air that you breathe is made up in part of helium.

The air you breathe is made up of more than eight different gases including nitrogen, oxygen, carbon dioxide, argon, neon, helium, krypton, xenon, and a varying amount of water vapor. Of these different gases, nitrogen and oxygen are by far the most plentiful in the atmosphere. More than 77 per cent by volume of the air you breathe is nitrogen and about 21 per cent is oxygen.

These facts are shown by the analyses of samples of air taken near the earth's surface. See the table on the next page. As an interesting comparison the second column of figures in this table shows the analysis of a sample of air brought down from a height of 13 miles by one of the latest stratosphere flights.

Air is not a compound; it is a mixture of gases of different weights. The gases in the atmosphere have different weights (densities). Nitrogen, oxygen, and xenon are heavy gases compared with the light gas helium. A volume of oxygen is eight times as heavy as an equal volume of helium (under

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the same conditions); xenon is more than thirty-two times as heavy. Helium is a very light gas; it weighs only 0.18 gram per liter.

AVERAGE COMPOSITION OF THE AIR

	Per cent by volume at the earth's surface	*Per cent by volume at 13 miles above the earth's surface*
Nitrogen	77.805	77.865
Oxygen	20.945	20.895
Carbon dioxide	0.03	0.029
Water vapor	varies	not determined
Argon	0.95	not determined
Neon	0.0018	not determined
Helium	0.0005	not determined
Krypton	0.0001	not determined
Xenon	0.000009	not determined

Although the gases in the atmosphere have different weights, a glance at the figures in this table will reveal to you that the percentage of any gas at a height of 13 miles does not differ materially from the percentage at the earth's surface. This shows that the gases in the air near the earth's surface do not form in layers as we might expect from their weights, but remain almost uniformly mixed. This means that although light helium can float a balloon, it can not "float" itself.

How you can prove that air is a mixture of different gases. Note the following facts.

1. The composition of a chemical compound does not vary. Although the composition of air is nearly uniform, analyses of air from different localities and from different altitudes do show a *slight* variation in the percentage composition of air.

2. When oxygen and nitrogen are mixed in the same proportion in which they are found in air, there is no evidence of any chemical action. The resulting mixture behaves in most respects as ordinary air.

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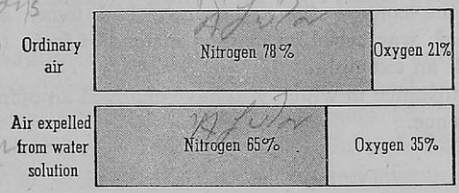
3. A compound has a definite boiling point. However, when liquid air boils, the nitrogen comes off first (boiling point, —195° C.), leaving the oxygen to boil off last (boiling point, —183° C.).

4. Dry air contains about 78 per cent nitrogen and about 21 per cent oxygen by volume. When the air dissolved in a sample of water is analyzed, the ratio is found to be approximately 65 per cent nitrogen and 35 per cent oxygen. If the air were a compound, the ratio of the gases dissolved in water would be the same as their ratio in air. Since the gases of the air dissolve in water independently of each other, air must be a mixture. (See the figure below.)



6. PERCENTAGE OF OXYGEN AND NITROGEN IN AIR. Note that there is a greater percentage of oxygen in the air that has been expelled from water solution than there is in ordinary air. This is evidence that air is not a compound.

Air is a mixture that has definite physical characteristics. Since air is a mixture of gases, its properties are the blended properties of the gases in it. It is colorless, odorless, and tasteless, unless these properties are somewhat changed by the presence of impurities which have color, odor, or taste. When you walk into a stiff wind you can easily realize that air has weight. Under standard conditions,[1] one liter of air weighs 1.29 grams, a weight which lies between that of oxygen, 1.43 grams, and nitrogen, 1.25 grams. Both nitrogen and oxygen are slightly soluble in water. When a sample of natural water is heated, it is this "air" that escapes as small bubbles before the actual boiling begins. You may have noticed these bubbles in a glass of water which was standing in a warm room.

[1] Standard conditions are 760 mm pressure and 0° C.

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Readings for Pleasure and Profit

DAVIS, WATSON. *The Advance of Science.* Chap. X., pp. 108-122, "Exploring Upwards."

Applying in Life What You Have Learned in Chemistry

A study hint: You cannot think well until you are able to distinguish facts and opinions. A good thinker considers the evidence carefully before he accepts an idea as being true. Yet he is willing to change his ideas on the basis of new and adequate evidence.

What is the difference between a fact and an opinion? Give an illustration of each. Do you find any opinions in this problem?

What opportunity have you had in this problem for considering adequate evidence before accepting an idea as being true? Think back over the conversations you have had today and recall a decision which was based on opinion instead of fact. (Was it difficult to recall an example?)

Give an instance in which you have changed an opinion because of new evidence.

Putting Chemistry to Work

(**1**) Why are mere opinions, which have no basis of fact, of little use in science study? (**2**) The relative weights of gases are often expressed by comparing them with air as a standard (air = 1). On this basis, carbon dioxide is 1.52. What is the weight in grams of a liter of carbon dioxide? (**3**) Upon what principle do chemists base the statement that since the composition of air is variable, it is not a compound? (**4**) Suggest why the atmosphere is most dense at the earth's surface. (**5**) Why is the composition of air by weight not the same as its composition by volume? (**6**) Why do two components of the air vary considerably?

Research and Activities That You Will Enjoy

A report: Look up references to various stratosphere flights and report to the class some of the interesting experiences and findings of the men who took part in these flights. It will also be interesting to find out why several of the flights failed.

An advanced topic: With proper preparation and care, you could present a most excellent and enlightening report on the use of the spectroscope in identifying elements.

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Problem 5

HOW ARE YOU AFFECTED BY THE GASES OF THE ATMOSPHERE?

Carbon dioxide feeds you. Without carbon dioxide the world of plants would soon die; there would be no grass, no trees, no vegetables—for all green plants absorb carbon dioxide and use it for food. Naturally, without plants there also could be no animal life and consequently no meat or food of any kind for you to eat. Can you explain why this is true? Consequently no animal or human life is possible without carbon dioxide.

Food is manufactured in green leaves. Here carbon dioxide absorbed from the air reacts with water and is made into sugar. Oxygen is given off as a "by-product." This process takes place only in the presence of sunlight and in the presence of the green chlorophyll in leaves. The sun supplies necessary energy; the chlorophyll helps to bring about the chemical reaction. This process is called photosynthesis (a putting together by light).

$$\text{carbon dioxide} + \text{water} \xrightarrow[(+\text{ catalyst})]{(+\text{ energy})} \text{sugar} + \text{oxygen}$$

Photosynthesis is one of the most important chemical processes in the world since by this process plants provide us with food to eat and also oxygen to breathe.

Plants use tremendous quantities of carbon dioxide, but the supply of carbon dioxide does not diminish. Why? Throughout the world, carbon dioxide is being formed in great quantities. It spouts from the chimneys of manufacturing plants and from the furnace of your own home; it is thrown off into the air by your breathing, by the respiration of all animal life, and by the decay of dead animals and dead plants. But the balance between the amount of carbon dioxide thrown into the air and the amount taken from the

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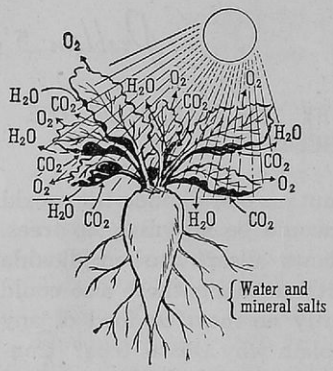

Carbon dioxide is taken from the air by green plants through their leaves. It is combined with water, taken in through the roots to form sugar. This reaction takes place only in the presence of sunlight and in the green parts of the plant. The sugar is converted into cellulose to make woody tissue, or into starch for storage. Much energy from the sun is absorbed in this process.

7. HOW PLANTS USE CARBON DIOXIDE

air by growing plants is surprisingly uniform. As a result the quantity of carbon dioxide in the air varies only slightly and there is always a plentiful supply of it for the food of plants. On the other hand, because plants throw off great quantities of oxygen in the process of photosynthesis, there is always a plentiful supply of oxygen for your breathing and for animal respiration in spite of the fact that great quantities of oxygen are used through burning, respiration, and decay.

The presence of carbon dioxide in the air can be readily demonstrated by letting some limewater (calcium hydroxide) stand in an open dish. A whitish scum of calcium carbonate forms on the surface of the limewater. This action between carbon dioxide and limewater is the test for carbon dioxide.

Water vapor in the air furnishes the rain that enables plants to grow. You have noticed, no doubt, that either in the sunshine of a hot day or in an over-heated room, an unwatered plant wilts. It wilts because it loses moisture to the air. Every hour tons of water vapor pass into the atmosphere from plant life, from bodies of water, and from moist soil.

Warm air can hold more moisture than cool air, as you can see from the graph in Fig. 8. Air containing all the moisture

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that it can hold at a given temperature, is said to be saturated with water vapor. If saturated air is cooled, it cannot hold all its moisture and consequently precipitation (rain) results. Drops form by the condensation of atmospheric water vapor.

Water vapor and temperature make you comfortable or uncomfortable. You are not comfortable when the air around you is either too warm or too cold. You may not realize that air at about 70° F. can be either comfortable or uncomfortable. In other words, the temperature of air can remain exactly the same and yet be comfortable for you at one time and uncomfortable for you at another time. Why is this?

Evidently your comfort depends upon some other factor or factors in addition to temperature. One other factor necessary for comfort is a suitable humidity or moisture content. Air that has a temperature of approximately 70° F. is comfortable for most people when it contains about 40 per cent of the water vapor that it is possible for it to hold; in other words, when the *relative humidity* is about 40 per cent.

Water vapor in the air and temperature have led to a new industry—"air conditioning." A new industry has rapidly come to the front—the air conditioning industry. Air conditioning attempts to control the following conditions.

Temperature. Air is heated in winter and cooled in summer.

Humidity. For homes, offices, and schools a relative humidity of about 40 per cent is comfortable for most people when the temperature is kept at approximately 70° to 72° F. When needed, moisture may be added to air by passing it through finely divided spray or by releasing water vapor into it. Any excess moisture may be removed by a chemical drying agent or by chilling the air.

Circulation. Air should be kept in gentle motion.

Cleanliness. Air may be washed by forcing it through water; or it may be filtered through glass wool or a similar substance. Odors are difficult to remove, but they may be effectively overcome by admitting a liberal amount of fresh air.

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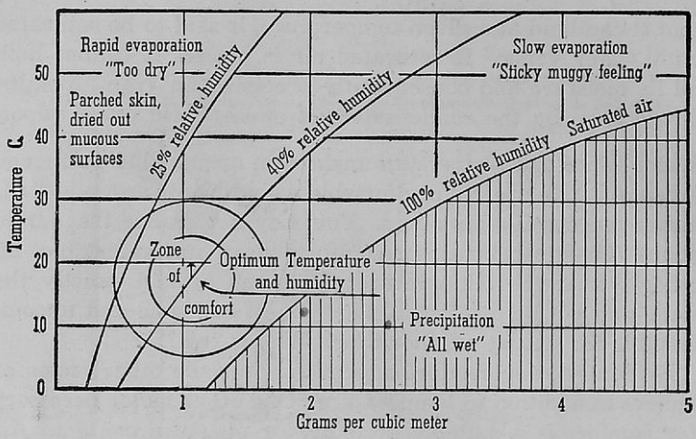

8. HUMIDITY CHART. Air must have the proper humidity and temperature for you to be comfortable. 20° C. is equivalent to 68° F.

The presence of water vapor in the air may be proved by allowing some calcium chloride to remain in an open dish for a few hours. The dry calcium chloride becomes moist and eventually dissolves in the water which collects about it from the air.

Argon from the air gives you high-grade electric lamps. The atmosphere contains small amounts of gases known as inert gases or noble gases because they do not form chemical compounds. These elements might be called lazy elements. The most abundant member of this group is *argon* which is less than one per cent of the atmosphere by volume. It may be separated from the other gases in the atmosphere in somewhat the same way that alcohol may be separated from water. When you use alcohol in the radiator of your car as an antifreeze, you frequently have to buy more alcohol because it boils at a lower temperature than water and evaporates into the air.

The boiling point of argon differs from the boiling point of other gases in the atmosphere and hence argon can be separated from liquid air.

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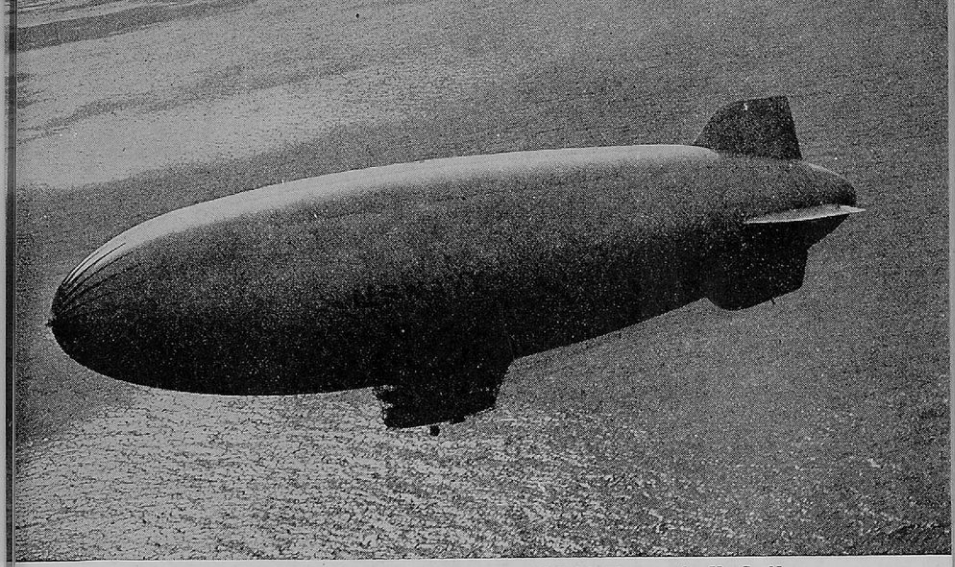

Official Photograph, U. S. Navy

9. Helium Is a Safe Gas. Helium has one important advantage over hydrogen as a buoyant gas for blimps and balloons; it does not burn.

Argon is used to fill high-grade electric bulbs. It reduces the blackening of the inside of the bulb which is caused by the evaporation of metal from the filament. It also enables the bulb to be operated at higher temperatures, and allows the filament to glow with greater brilliancy.

Helium enables man to go high in the "ocean of air" and deep in the ocean of water. Helium is another inert gas in the atmosphere. Small amounts (1 to 2 per cent) of it are present in some natural gas from Texas, Kansas, and Colorado. It is therefore obtained from this natural gas rather than from the atmosphere. Helium is separated from the natural gas in which it occurs by liquefying all the gases except helium.

Next to hydrogen, helium is the lightest gas known and, since it does not burn, is valuable for filling balloons and dirigibles. Although it is twice as heavy as hydrogen, it has a lifting force about 93 per cent of that of hydrogen.

Deep-sea divers have descended more than 400 feet below the surface. With the usual diving suit used at this depth,

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great pressure is needed to force air to the diver for breathing. Unfortunately, however, under such pressure considerable nitrogen from the air is dissolved in the blood. If the diver is pulled to the surface too quickly, the dissolved nitrogen in the blood expands suddenly and causes the "bends," a painful condition which may cause death. However, "synthetic air," composed of oxygen and *helium* rather than oxygen and nitrogen, is useful in decreasing the danger from the "bends," since helium is 40 per cent less soluble in the blood than is nitrogen.

Helium enables us to go high in the "ocean of air" and deep in the ocean of water.

Neon helps to light airport fields and advertising signs. Another rare element, obtained from liquid air, is now widely used for advertising signs and beacon lights. The red rays of a neon light penetrate fog very well.

Will it be you who discovers important uses for krypton and xenon? *Krypton* and *xenon* are rare components of the atmosphere for which we have few uses at present. However, it is interesting to note that the "useless" substances of today may be the useful substances of tomorrow often because of the work of scientists.

Nitrogen is a lazy, sluggish element but scientists have learned to make it one of the most important gases of the atmosphere. The element nitrogen is an inactive gas which dilutes quick-acting oxygen. However, you will find later that although it is lazy, scientists have learned how to convert it into compounds. These compounds of nitrogen are exceedingly important.

Oxygen is your breath of life. Oxygen is so important and so active chemically that it is given special consideration in later problems in this unit.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff*. Chap. II, pp. 11-15, "A Breath of Fresh Air"; Chap. II, pp. 39-46, "The Rare Gases."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry*. Art. 17, pp. 121-125, "Traces from Tons (The Rare Gases)."

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HOLMES, HARRY N. *Out of the Test Tube.* Chap. XIII, pp. 159-167, "Romance of the Lazy Elements."

WEEKS, MARY ELVIRA. *The Discovery of the Elements.* Chap. XVIII, pp. 278-289, "The Inert Gases."

Applying in Life What You Have Learned in Chemistry

Joe Penderly was a straight thinker; already he was trying to put into practice what he had learned. He had tackled the practical problem of determining the relative humidity of the air in his home.

He obtained a shiny metal can and filled it half-full of water. He then dropped a little crushed ice into the water and stirred it with a thermometer. By watching closely for the formation of "dew" on the outside of the can, he found the temperature at which the air surrounding the can became saturated with moisture—that is, the dew point.

He found the temperature of the air in the room. By using the table of vapor pressure of water (see Appendix), he found the vapor pressure at the dew point and the vapor pressure at room temperature. He then found the relative humidity of the air in the room by dividing the vapor pressure at the dew point by the vapor pressure at room temperature. He set down his data like this:

Dew point, 5° *C.;* vapor pressure, *6.5 mm Hg*

Room temp., *22° C.;* vapor pressure, *19.6 mm Hg*

Relative humidity = _____ ÷ _____ = _____ %

Can you finish Joe's problem? Why don't you determine the relative humidity in your home?

Putting Chemistry to Work

A

(1) How important to you is the chemical process of photosynthesis? (2) Is it a good sign for the windows in your home to "steam up" in the winter? Explain. (3) When air is passed over heated copper, nitrogen remains. What does this show you about the activity of nitrogen? (4) In hospitals, flowers and plants are removed from patients' rooms at night. Is there any foundation of fact for such practice? If so, what is it? (5) A candle flame is extinguished when placed either in nitrogen or argon, yet many electric-light bulbs are filled with a mixture of these gases. Explain. (6) A current of air from an electric fan causes one to feel cool in summer, even though a thermometer in the air current

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indicates the same temperature as in other parts of the room. How can this be?

B

(7) If carbon dioxide should suddenly disappear from the atmosphere, how would our lives be affected? (8) Can you suggest why Lavoisier called nitrogen *azote* which means "without life"? (9) Name two processes that occur naturally that tend to increase the quantity of carbon dioxide in the air; name two processes that tend to decrease it. (10) Nature evidently intended the inert gases to be very "unsociable." How has man taken advantage of this property? (11) Name four components of the air that are necessary for life. What is the use of each? (12) What do the terms *relative humidity* and *dew point* mean? What is the meaning of a relative humidity of 50 per cent? (13) How can you demonstrate that you exhale carbon dioxide? (Be sure to tell what to look for.) (14) What reason have you learned in this problem for calling calcium chloride a "drying agent"? (15) How could you use limewater to obtain air which is free from carbon dioxide?

How Good Are You at Solving Problems?

(1) How much weight can a liter of helium lift? (The lifting force of a gas is found by subtracting the weight of the gas from the weight of an equal volume of air. Helium weighs 0.18 gram per liter.)

(2) A person exhales about 800 grams of carbon dioxide each day. If the population of the earth is one and a half billion people, how many *tons* of carbon dioxide are exhaled in a year?

(3) What is the relative humidity of the air in a schoolroom in which the temperature is 20° C. and the dew point is found to be 5° C.? [Study "Applying in Life What You Have Learned in Chemistry" (for this problem) if you have not already done so.] What recommendations would you suggest to the school authorities?

(4) Determine the relative humidity and tell whether it is too high or too low in each of the following cases: (a) Room temperature, 20° C.; dew point, 6° C. (b) Room temperature, 25° C.; dew point, 14° C.

Research and Activities That You Will Enjoy

Ramsay and Rayleigh: Read about Sir William Ramsay and Lord Rayleigh. Perhaps two students can re-enact for the class the spirited rivalry of these two men in their search for rare gases.

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Problem 6

HOW DOES A STUDY OF AIR AND OTHER SUBSTANCES INDICATE THAT MATTER IS COMPOSED OF TINY MOVING MOLECULES?

No one has ever seen a molecule. Perhaps no one ever will see one; they are exceedingly small. Langmuir, one of our most noted scientists, has estimated that if the molecules in a cubic inch of air were by some method changed to grains of sand, these grains of sand would fill a trench a mile wide and 3 feet deep, stretching from New York City to San Francisco!

How was it ever possible to discover molecules? The answer to this question is suggested by the following facts.

Light helium and the heavier gases do not separate in distinct layers; like all gases they diffuse—this suggests that matter is composed of moving particles. You already have learned that the air is a mixture—not a chemical compound—and that the different gases in the air do not form in layers as we might expect from their different weights, but remain almost uniformly mixed. This tendency of gases to mix of their own accord is called *diffusion.*

You can easily observe the tendency of gases to diffuse by releasing an odorous substance in one corner of a closed room when the air is quiet. The odor is soon noticed in all parts of the room.

Another example of diffusion can be noticed by releasing some liquid bromine at the bottom of a tall jar, Fig. 10. This liquid readily turns to a gas and the reddish gas can be seen rising in the air in the jar. Bromine gas is over five times heavier than air. In spite of this fact, the gas is able to move upward against the pull of gravity and against the resistance of the air above it. The odor of bromine is very irritating, so *do not smell it.* If the bromine is inclosed in a thin glass bulb and the air mostly removed from the jar by an air pump, then the bulb can be broken by a glass rod with spectacular results. What do you think occurs?

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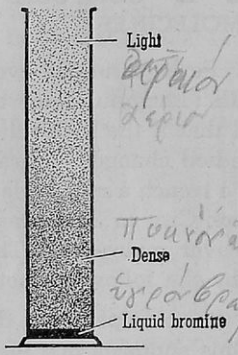
Why do gases diffuse? You can answer this question if you imagine that gases are composed of tiny moving particles with considerable space between them and that these particles are continuously bumping and jostling each other.



Although gaseous bromine is heavier than air, molecules of bromine rise in the jar of air against the force of gravity. After a short time the bromine vapor will be uniformly distributed throughout the jar of air. All gases show this ability to diffuse until a uniform mixture is obtained. Light gases diffuse more rapidly than heavier gases.

10. AN EXAMPLE OF DIFFUSION

The diffusion in gases suggests that gases are composed of tiny moving particles. Are liquids and solids also composed of small moving particles? Let us see if there is any diffusion in liquids and solids.

Why does not the volume of a cup of coffee increase noticeably when you add sugar? When a small amount of sugar is placed in a cup of coffee, it disappears from sight and every drop of the coffee acquires a sweet taste, yet the volume of coffee does not increase noticeably. You do not have to stir the sugar; give it time and it will diffuse through the coffee of its own accord. Here is an example of a solid diffusing in a liquid. This would be impossible if there were no "open spaces" in the liquid.

How is it possible to mix a quart of water and a quart of alcohol and have less than two quarts of the resulting mixture? At the beginning of winter do you put a mixture of alcohol and water in the radiator of your car as an antifreeze? If your car's radiator holds 9 quarts, perhaps you have noticed that you can get more than 9 quarts of alcohol

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and water in the radiator. In other words, you can prove to yourself that it is really possible to mix a quart of alcohol and a quart of water and have less than 2 quarts of the resulting mixture even though no chemical combination occurs.

You can demonstrate this fact in your laboratory by carefully pouring equal volumes of water and alcohol in a long glass tube. If you hold your finger tightly over the end of the tube and shake it, you will note (after the alcohol and water are thoroughly mixed) a decrease in volume of the mixed liquids and a slight vacuum in the tube. This suggests that each liquid is composed of tiny particles with spaces between the particles and that when mixed, the particles "fit together."

Clamp a smooth piece of gold on a smooth piece of lead and they will diffuse. If you clamp tightly a smooth piece of lead to a smooth piece of gold, after a considerable period of time you can find traces of gold *in the lead* and traces of lead *in the gold.* Apparently even solids are composed of moving particles. The fact that solids diffuse slowly indicates that the molecular motion in solids is comparatively slight.

You can put more air in a tire even when it already is "full" of air—this suggests that matter is made of separate particles with space between the particles. A cotton picker may have a bag apparently full of cotton and yet be able to put much more into it by pressing the cotton down. You know that the cotton does not actually fill all the space within the bag; it only seems to do so. Perhaps the same is true when you force into an auto tire several times its volume of ordinary air. Would not this fact indicate that air may not completely fill the space that it seems to occupy and that particles of a gas may be pushed much closer together? Does it not appear that space is never completely filled?

You are gradually piling up evidence that all matter whether gaseous, liquid, or solid, is made up of tiny moving particles. You will gather more evidence, but in the meantime you are justified in calling these moving particles—molecules.

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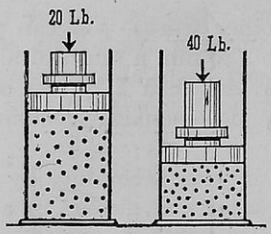

When the pressure on a gas is doubled, the volume is reduced one-half. The volume of a gas varies inversely with its pressure. This is known as Boyle's law. Helpful information concerning gas laws is given in the appendix.

11. BOYLE'S LAW

The air in your auto tires expands on a hot day and contracts on a cool day—this suggests that heat increases the motion of molecules thus spreading them farther apart. You perhaps have noticed that after driving some distance on a hot day, the air in your auto tires expands noticeably. Heat expands the air in the tires. Does this fact not suggest that heat increases the motion of the gas molecules, thus spreading them farther apart?

Air can be changed to a liquid form; in fact, all gases can be changed to a liquid form and to a solid form, and conversely liquids and solids can be changed to a gaseous form by the application of sufficient heat. These facts suggest that whether or not a substance is a gas, a liquid, or a solid depends not only upon the "binding force" among its molecules, which we call *cohesion,* but also upon the degree of molecular motion.

A very familiar example of this is water in gaseous form. When you cool steam sufficiently, it condenses to water; when you cool water sufficiently, it freezes to ice. This *change of state* can be explained if you imagine that the cooling of a substance slows down its molecules, thus allowing the molecules to come closer together; and conversely, the heating of substances increases their molecular motion.

The motion of molecules causes them to fly away from the surface of a liquid. This process is called *evaporation.* The pressure exerted by the molecules as they try to leave the liquid is known as the vapor pressure of the liquid. Since

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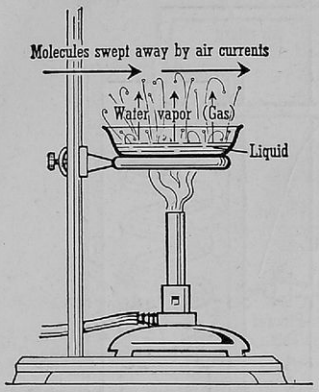
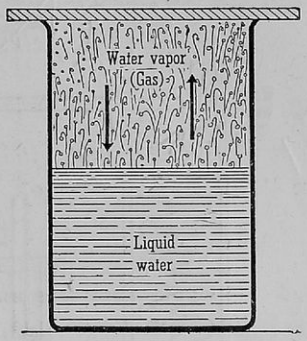


12. EVAPORATION IN AN OPEN VESSEL. A rise of temperature hastens the evaporation of a liquid. Lessening the atmospheric pressure and removing the air over the liquid (vacuum) also hastens evaporation.



13. EVAPORATION IN A CLOSED VESSEL. In a closed vessel, molecules evaporate from a liquid until the air space above can hold no more (saturation). Then some of the molecules return to liquid form as fast as others evaporate. Molecular motion is not lessened, but a balanced condition is established.

the molecular motion increases with a rise in temperature (see Figure 12), the vapor pressure is greater at higher temperatures. When the vapor pressure of a liquid becomes equal to the pressure of the air (the atmospheric pressure), the liquid boils. The corresponding temperature is the *boiling point* of the liquid. Figure 13 shows what happens to the molecules that evaporate from a liquid in a closed vessel.

It is thought that the molecules in a gas are bouncing far apart. A gas is like a few fast moving basketball players on a large open floor. In a liquid the molecules are rolling close together. A liquid resembles the vast crowds of people coming in through the gymnasium doors. The particles of crystalline solids like sugar or common salt are vibrating in rows and layers around fixed points, held in place by strong cohesive forces. A crystalline solid resembles somewhat the people seated in orderly rows in the bleachers. The molecules in amorphous (noncrystalline) solids like glass are not

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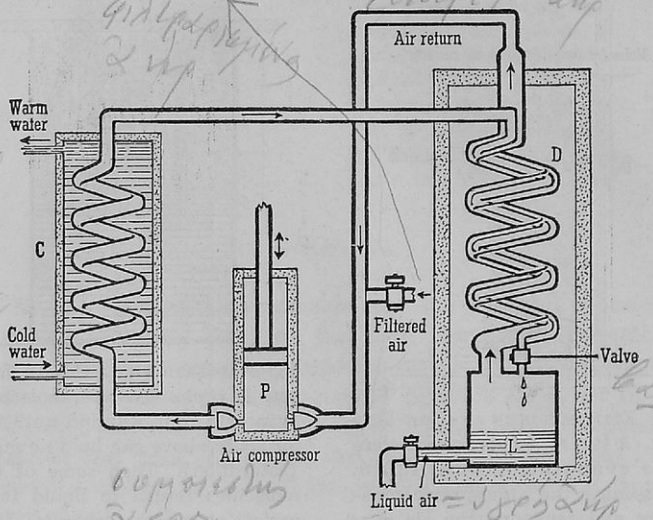

14. LIQUID AIR APPARATUS. Filtered air is compressed in the pump P. The compression causes the air to become heated. Part of this heat is removed from the compressed air in coil C by the surrounding cold running water. The main cooling effect takes place in coil D. Liquid air L evaporates and expands in the outer coil, thus cooling the entering air in the inner coil to a liquid state. The vaporized air returns to the compressor. Carbon dioxide and moisture must be removed from the air before it is used. Why?

arranged in so orderly a fashion. An amorphous solid may be said to be like a large crowd of people massed along the streets to view a parade.

What is the theory of moving molecules? The theory of moving molecules is called the *kinetic molecular theory.* Briefly this theory may be stated as follows:

1. Matter in all its forms (that is: gases, liquids, and solids) is composed of extremely small particles. Some of these small particles are called molecules.

2. Molecules of the same kind of matter are alike; molecules of different kinds of matter differ in composition and weight.

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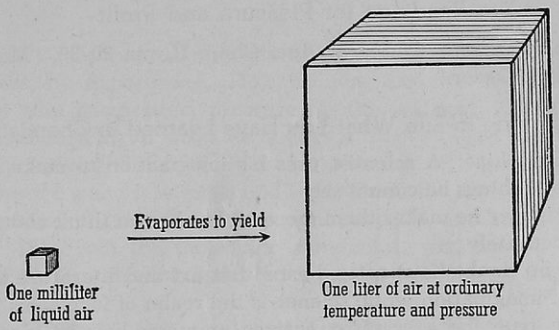

15. EXPANSION OF LIQUID AIR. Liquid air expands about a thousand times its volume in becoming ordinary air. This illustration shows that molecules of air need far more room in the gaseous state than they do in the liquid state.

3. Molecules do not fit together closely like the tile in a mosaic, but they are separated by spaces as though they were moving spheres. In solids the spaces are small and the motion is limited and resembles somewhat the swing of a pendulum; in liquids the motion is more free, so the molecules can move over each other, but they generally tend to cling together; in gases the spaces are large, the motion is much more extensive, and the molecules tend to fly away from each other.

4. When a gas is moderately compressed, the size of the molecules remains the same but the spaces between the molecules are decreased. This may result in forming a liquid or a solid.

5. Molecular motion is increased by a rise of temperature and decreased by cooling.

6. Gas pressures are produced by the fact that moving molecules strike the walls of the container. When the motion of the molecules is increased, the pressure becomes greater.

7. When a molecule of a liquid strikes the surface squarely, it may escape from the attraction of the other molecules and become a gaseous molecule. This is evaporation. Condensation takes place when a gaseous molecule strikes the surface of the liquid and is held by the attraction of the molecules in the liquid.

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Readings for Pleasure and Profit

HAYNES, WM. *This Chemical Age.* Chap. II, pp. 20-39, "Molecules Made to Order."

Applying in Life What You Have Learned in Chemistry

A study hint: A scientist uses his imagination to make mental pictures of things he cannot see.

In this way he makes them more real so he can think about them more accurately.

You no doubt have often heard that art and literature are the realm of imagination while science is the realm of fact. This is only partially true for a scientist arrives at many helpful ideas only through the use of his imagination.

In this problem you have a good opportunity to use your imagination to make mental pictures of molecules and how they act in gases, liquids, and solids. This will aid you greatly in understanding many of their physical properties and physical changes.

Learn to use your imagination to make mental pictures of things which you cannot see.

Putting Chemistry to Work

A

(1) Why is it not advisable to inflate high pressure auto tires as much in summer as in winter? (2) How can you tell the direction of the wind by a moistened finger? (3) Give two ways in which the molecules of the gases in air may be made to come closer together. What happens when these processes are continued? (4) Why would you not tightly stopper a vessel containing liquid air? (5) Gases may be collected over water by filling jars with water and inverting them in a pan of water—leaving the neck of the bottle under water. What holds the water up in the jar?

(6) Account for the fact that the volumes of gases are affected much more by changes in temperature and in pressure than are solids and liquids. (7) If you put a half liter (500 ml) of oxygen into a closed empty liter flask, why does the volume of oxygen become one liter? (8) To express accurately the volume of a given weight of gas, why is it necessary to state also the temperature and the pressure under which the gas was measured? (9) Why is it necessary to compare the volumes of gases when they are under the same conditions? (10) Refer to the Appendix and then explain what is meant by *standard conditions* of temperature and pressure.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

B

(11) The fact that a heavy gas will leave an open container may be shown by experiment. How do you explain this fact? (12) Explain why gases exert pressure on the walls of vessels which contain them. (13) In what ways does a *theory* differ from a *law?* (14) What is the effect upon the temperature of a gas when it is compressed? when it is expanded? (15) From the molecular standpoint, what is a gas, a liquid, a crystalline solid, and an amorphous solid? (16) From the molecular standpoint, why may a balloon tend to rise in the daytime, but tend to fall during the night?

Research and Activities That You Will Enjoy

A demonstration: Show the class how to make a simple mercury barometer to measure atmospheric pressure. Be sure to explain the meanings of such terms as *760 mm of Hg, 14.7 pounds per square inch,* and *one atmosphere.*

A report: How is liquid air stored? Make a drawing of a Dewar flask (thermos bottle) and point out how heat is kept in or out. (Do not fail to explain and use such terms as *conduction, convection,* and *radiation.)*

Problem 7

HOW IS IT POSSIBLE TO LEARN THE CHARACTERISTICS OF THE COLORLESS, ODORLESS, TASTELESS ELEMENT—OXYGEN?

Your problem of finding the characteristics of oxygen differs considerably from the problem that faced early investigators before oxygen had ever been discovered. Let us see some of the difficulties that faced them.

How was oxygen discovered? Have you ever held a piece of rubber in a flame? The resulting odor was unpleasant. The odor that came from the heated rubber indicated that a gas was being produced—a gas that reached the nerves of smell in your nose. If this gas had been odorless, colorless, tasteless, how difficult it might have been for you to know

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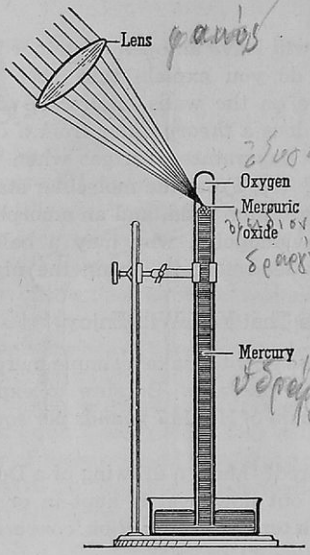

When the sun's rays were concentrated on mercuric oxide in the tube, a gas was formed. As the gas formed, it pushed down the column of mercury. What was the gas? If you have ever tried to use the sun's rays as a source of heat you may have some idea of the patience that Priestley must have had to obtain by this method enough of the gas to experiment with. Why didn't Priestley use a Bunsen burner? Recall your laboratory experiment of heating mercuric oxide. Did the mercuric oxide yield a gas easily?

16. PRIESTLEY'S EXPERIMENT

that it existed! It is not surprising then to note that although oxygen is the most plentiful element in nature, it was not discovered until shortly before the Revolutionary War.

In 1774 an English clergyman by the name of Priestley was interested in heating various substances and noting the results. He placed some mercuric oxide (a red powder) on a column of mercury in a glass container and heated the mercuric oxide by directing the sun's rays through a large lens (or burning glass). The mercury column was pushed down, indicating that a gas was forming above the mercury. "Airs" or gases had been produced from solids before so Priestley, no doubt, was not particularly surprised about this any more than you are surprised at the odor of burning rubber. But he collected some of the gas. It was colorless, odorless, invisible, tasteless. He thrust a glowing splinter into it and found that the splinter burst into flames. He also placed a mouse in it and found that the mouse suffered no ill effects.

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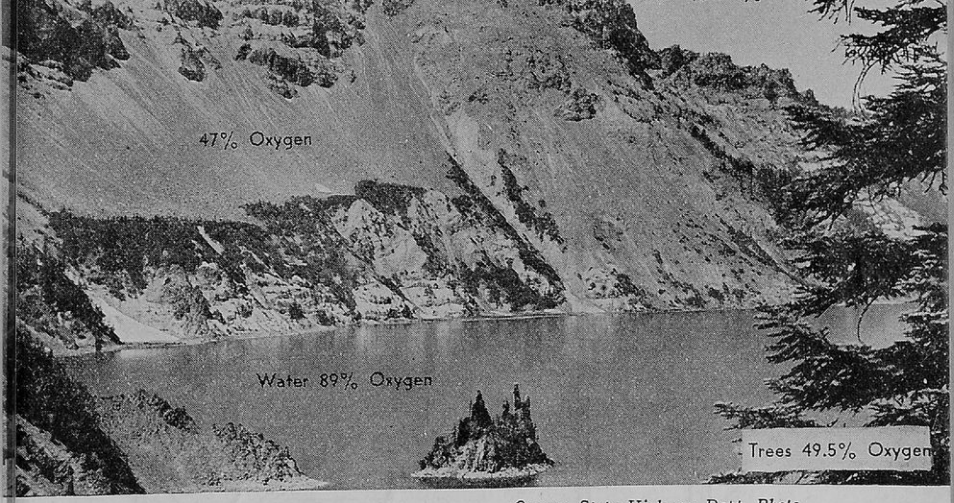

Oregon State Highway Dept. Photo

17. Crater Lake, Showing Distribution of Oxygen in Nature.

He himself breathed some of the gas and felt exhilarated. A new gas had been discovered! The French scientist Lavoisier named it *oxygen.*

We now know that oxygen is not only a constituent of mercuric oxide as Priestley discovered, but it also is a constituent of many other compounds and exists in uncombined form in the air.

Where can you find oxygen? It might be easier to ask where you cannot find oxygen. It is our most plentiful element. Twenty-one per cent by volume of the air you breathe is free or uncombined oxygen.

Oxygen also is found united with many other elements in compounds. The wood in your furniture, the bricks in your homes, the glass in your windows all contain oxygen combined with other elements. The water you drink is nearly 89 per cent oxygen by weight; the trees and shrubs on your school grounds are approximately 50 per cent oxygen; your own body is about 65 per cent oxygen; and even the sand at the seashore is composed of approximately 52.5 per cent oxygen. The total oxygen in the earth's crust weighs nearly

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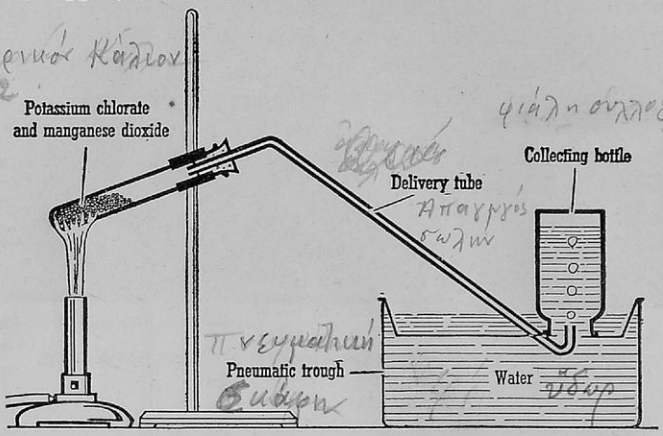
as much as all of the other 91 elements put together—including iron, copper, and all the metallic elements.



18. LABORATORY PREPARATION OF OXYGEN. You can obtain oxygen in the laboratory by decomposing potassium chlorate by means of heat, using manganese dioxide as a catalyst.

Now that you know where oxygen is, how can you obtain some of it in your own laboratory? Priestley obtained oxygen by heating mercuric oxide (HgO). Perhaps you can use this compound also. However, you must keep in mind that although mercuric oxide readily releases its 7.4 per cent oxygen, with moderate heating, its cost is comparatively high.

Perhaps you can find a better source. Why not use sand (silicon dioxide, SiO_2) since it is very plentiful and it is composed of more than 50 per cent oxygen? Here again you run into difficulties for although rich in oxygen, sand is miserly and no amount of heating will break it up into its two elements, silicon and oxygen.

You will have to consider other sources.

Water (H_2O) with its 89 per cent of oxygen was formerly used to provide the commercial supply of this element. The main cost was the electricity used to separate it from hydrogen through the process of electrolysis. This process will be described later.

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Potassium chlorate or sodium chlorate. For the small quantity of oxygen required for laboratory use it is more economical to use the more expensive compounds such as potassium chlorate ($KClO_3$) containing 39 per cent oxygen or sodium chlorate ($NaClO_3$) containing 45 per cent oxygen. These compounds yield all their oxygen with moderate heating (Figure 18). If a small quantity of manganese dioxide (MnO_2) or iron oxide (Fe_2O_3) is mixed with the potassium chlorate or sodium chlorate, the oxygen is released rapidly at a much lower temperature than if the potassium chlorate or sodium chlorate is heated alone.

Sodium peroxide. If a still smaller quantity of oxygen is sufficient, it may be prepared quickly by the action of water on sodium peroxide (Na_2O_2) which contains 41 per cent oxygen. Only half of the oxygen is given off.

Oxygen also may be obtained from numerous other substances but with less advantage than those just mentioned.

Summary of methods. Methods of preparing oxygen may be summarized as shown in the following table.

Substance Used	*Products Formed*	*Effectiveness*
1. Silicon dioxide (heated)	→ None	Impossible
2. Mercuric oxide (heated)	→ OXYGEN + mercury	Expensive
3. Water (electrolysis)	→ OXYGEN + hydrogen	Requires cheap electrical energy
4. Air mixture (liquefied)	→ OXYGEN, nitrogen, and argon	Commercial, cheapest
5. Potassium chlorate (heated—with catalyst)	→ OXYGEN + potassium chloride	Laboratory, simplest
6. Sodium peroxide + water	→ OXYGEN + sodium hydroxide	Quickest

What is a catalyst? A substance which changes the speed of chemical reaction is called a *catalyst* or a catalytic agent.

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In the reaction the catalyst may undergo some temporary change but it is in the same state and its quantity is the same at the end of the reaction as at the beginning. You have learned that manganese dioxide speeds up the decomposition of potassium chlorate or sodium chlorate to liberate oxygen. In this reaction the manganese dioxide is unchanged.

How do industrial concerns obtain oxygen in quantity? Air is mainly a mixture of oxygen and nitrogen, with small quantities of other gases and impurities. Industrial concerns first change air to a liquid form by compressing it and at the same time cooling it. Since the boiling point of nitrogen is lower than the boiling point of oxygen, the nitrogen can be evaporated from the liquid air, leaving the oxygen. If you use alcohol in the radiator of your car as an antifreeze, you can readily understand this process; the alcohol boils at a lower temperature than water and consequently boils off first. Oxygen obtained from liquid air may be 99.5 per cent pure.

Pure oxygen is obtained by the electrolysis of water.

Taking oxygen's "fingerprints": how does this gas differ from other substances? Substances are distinguished from each other by certain characteristic properties which they possess. Usually a few unique properties are sufficient for identification just as individuals may be identified by their fingerprints. For example, oxygen is the only common gas without odor which supports the ordinary burning of wood. The identification test for undiluted oxygen, then, is *an odorless gas which causes a glowing spark to become a flame.*

Physical properties.

1. Colorless, odorless, tasteless (when pure).
2. Solubility: slightly soluble in water; three volumes of it dissolve in 100 volumes of water at 20° C.
3. Density: a little heavier than air. One liter weighs 1.43 g under standard conditions. This is 1.1 times the weight of a liter of air.
4. Liquefiable: it may be changed to a liquid which boils at —183° C.

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Chemical properties.

1. It supports combustion.
2. An active element: oxygen combines readily with many substances. This combination of oxygen with other substances is called *oxidation.* This can be shown by a laboratory experiment in which you burn sulfur, carbon, phosphorus, iron, and magnesium. The resulting compounds can be shown in this manner.

Sulfur	+	oxygen	→	sulfur dioxide (SO_2)
Carbon	+	oxygen	→	carbon dioxide (CO_2)
Phosphorus	+	oxygen	→	phosphorus pentoxide (P_2O_5)
Iron	+	oxygen	→	iron oxide (Fe_3O_4)
Magnesium	+	oxygen	→	magnesium oxide (MgO)

Whenever oxygen combines with another element, the product is an oxide. In any compound of two elements the name of the compound is formed by using the name of the one element in full and adding *ide* in place of the last syllable of the other element — thus, magnesium oxide (MgO), iron sulfide (FeS), potassium chloride (KCl).

"Super-oxygen," ozone. Have you ever noticed a peculiar odor near high-voltage electrical machinery? Sometimes this same odor is noticeable during an electric storm. It is the odor of ozone.

When oxygen is subjected to a high voltage electric discharge, it is greatly changed. The product has a strong, irritating, distinctive odor, and in quantity is light blue in color. It is 50 per cent heavier than oxygen and is more soluble in water, more easily liquefied, and is much more active chemically. Ozone combines with silver and mercury at ordinary temperatures, which ordinary oxygen does not do. It is so vigorous in its oxidizing action that it makes rubber as inelastic as wet cardboard and bleaches indigo and other dyes very rapidly. Ozone was named from a Greek word signifying "having an odor."

The odor of ozone is also generally noticed near X-ray machines when they are in operation. The lightning flash also

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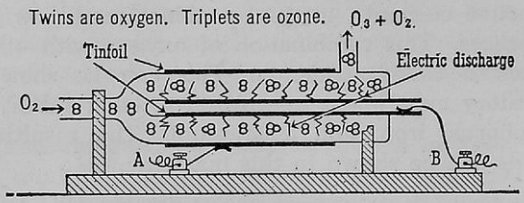
forms it from the oxygen of the air. It is found in the air at higher altitudes where it is formed by ultraviolet light. It is



19. OZONE GENERATOR. Oxygen $\xrightarrow{+\text{ energy}}$ OZONE (super-oxygen)

too powerful an oxidizer to be breathed in quantity. Ozone may be used where a strong, rapid, oxidizing agent is wanted. It has been used to sterilize air and water supplies and to remove odor and colors.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. II, pp. 21-39, "Oxygen."

DARROW, F. L. *The Story of Chemistry.* Chap. II, pp. 14-22, "Dawn of a New Day."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. V, pp. 58-63, "Atmosphere and Oxygen."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. III, pp. 29-34, "With Fire Man Arose above the Beasts."

JAFFE, BERNARD. *Crucibles.* Chap. IV, pp. 51-72, "Joseph Priestley"; Chap. VI, pp. 93-113, "Lavoisier."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. XX, pp. 267-284, "New Sources of Power."

WEEKS, MARY ELVIRA. *The Discovery of the Elements.* Chap. IV, pp. 35-48, "Oxygen."

Putting Chemistry to Work

A

(1) Give examples of how a knowledge of the properties of substances may be used. (2) What facts are needed before you can make an intelligent choice of the chemical method of preparing a substance? (3) Why is it usually preferable to collect gases in containers by displacement of water rather than by displacement of

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air? What property of some gases compels the use of the latter method? (4) What particular properties are selected as a test for a substance? (5) Why do thoughtful science firms put a label on every inside container as well as on the outside wrapper of every chemical package? (6) When oxygen is obtained from liquid air, what becomes of the water vapor, carbon dioxide, nitrogen?

B

(7) What is the nature of the decomposition type of chemical change? Name several ways of causing it to take place. (8) Compare or contrast the decomposition type of chemical action with the combination type. (9) Which statement about ozone is false? (a) Ozone is more active than oxygen. (b) Ozone contains more energy than oxygen. (c) Ozone is more stable than oxygen. (d) Ozone is an *allotrope* of oxygen. (e) Ozone is a better oxidizing agent than oxygen. (10) Give a complete yet concise definition of a catalyst. (11) Point out differences between the chemical processes of oxidation and photosynthesis. (12) Note the formulas to find the difference between potassium chloride and potassium chlorate. How would a sulfide differ from a sulfate? a nitride from a nitrate? (13) How can it be proved that water dissolves air?

How Good Are You at Solving Problems?

(1) Assuming that there is no loss of oxygen, how many grams of potassium chlorate must you decompose to prepare 5 grams of oxygen? to prepare 5 liters of oxygen?

(2) Three students prepared oxygen, one from 50 grams of water, another from 50 grams of mercuric oxide, and the third from 50 grams of potassium chlorate. What weight of oxygen did each obtain?

(3) Sodium chlorate is frequently cheaper per pound than potassium chlorate. How does the lower atomic weight of sodium also cause sodium chlorate to be the cheaper source of oxygen? (Hint: You may answer this question by determining the weight of oxygen that can be prepared from 50 grams of each.)

A Principle for You to Remember

PRACTICE SAFETY, first, last, and all the time in the laboratory by *knowing* what you are doing.

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Research and Activities That You Will Enjoy

A strip cartoon: After reviewing the summary of methods of preparing oxygen, make original comic drawings using characters to personify the actions of substances in giving up their oxygen. (Hint: SiO_2, a miser; HgO, poor but generous; H_2O, rich but thrifty—a chance for very clever ideas.)

Joseph Priestley: Summarize the work of Priestley in preparing oxygen. You may wish to do the same for the work of Scheele or Lavoisier.

Problem 8

WHY IS OXYGEN ONE OF THE MOST USEFUL ELEMENTS IN THE WORLD?

Oxygen unites chemically with many substances. The chemical union of oxygen with any substance is called *oxidation.* If this union takes place slowly, no light is given off; and although heat is given off, it is not noticeable. The rusting of metals is an example of *slow oxidation.*

If you are to appreciate the part that oxygen plays in your life, you must understand the significance of *oxidation.*

Oxygen is your "breath of life"; without it you could not live. You need oxygen more than any other element. Without it you would die in a short time. It is your "breath of life."

When you inhale air, oxygen enters the blood stream through the lungs. This oxygen is distributed by the blood to every cell of the body where oxidation of the digested food takes place. In this oxidation (as in the oxidation of all compounds containing carbon and hydrogen) water and carbon dioxide are formed. Heat is also given off, and it is this heat that maintains the normal body temperature at 98.6° F. The carbon dioxide formed in the cells enters the blood stream, is carried to the lungs, and is exhaled.

All animal life requires oxygen. All the higher forms of animal life require oxygen for respiration. Even animals living in water require oxygen. With very few exceptions the

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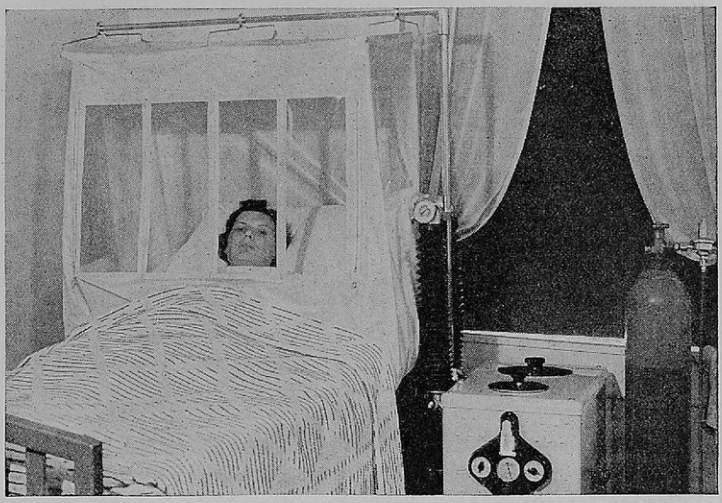

Courtesy, McKesson Appliance Co.

20. OXYGEN TENT. Equipment of this kind is frequently a "lifesaver" for persons with pulmonary afflictions.

multitude of creatures that live in water are cold-blooded. This means that in order to live it is not necessary for them to maintain any given body temperature as we do. The temperature of cold-blooded water creatures varies with the temperature of the water in which they live. They, therefore, require much less heat energy than the warm-blooded land animals and hence require much less oxygen.

Oxygen dissolves in water somewhat like salt dissolves in water. Although oxygen is only slightly soluble in water, enough is dissolved for the needs of sea creatures. Fish obtain the dissolved oxygen by passing water through their gills.

Oxygen helps destroy waste materials and bacteria. During the middle ages sewage was often dumped directly into the streets where it gave off unpleasant odors and endangered health. Our modern sanitary methods have enabled us to combat most contagious diseases and to be in general a healthy people. Oxygen has been a useful servant in this respect.

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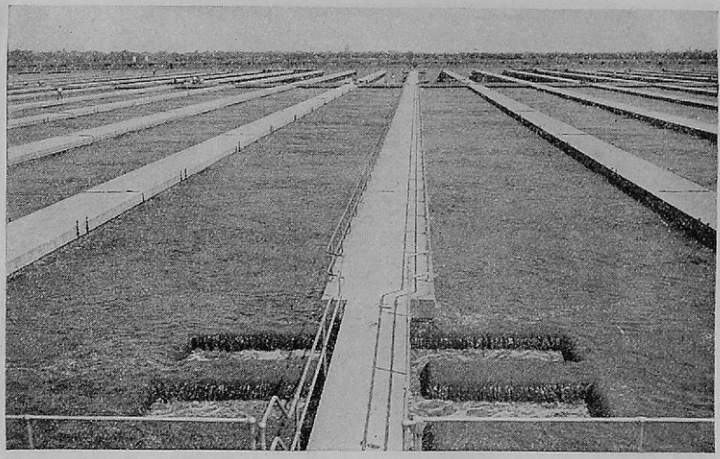

Courtesy, The Sanitary District of Chicago

21. SEWAGE TREATMENT. Air is bubbled up through the water to convert a menace into useful fertilizer. Note the outlets.

Many cities use the activated sludge method of treating sewage. By this method air is forced through sewage tanks for from ten to twelve hours. Bacteria and organic matter are oxidized and thus changed into harmless materials. If this method is carried out properly, the outflowing water is clear and has little odor.

Many cities purify their water supply by spraying the water into the air. In this way bacteria and undesirable wastes are oxidized and undesirable odors and tastes are removed.

Nature herself is continuously removing dead plants and dead animal matter from the earth through the process of decay which is oxidation aided by certain bacteria. Nature also is continuously oxidizing the impurities in the water of streams and lakes.

Man has found other valuable ways to use oxygen. Most of us have known of some instance in which a resuscitator was needed to revive a drowning person or one overcome by gas.

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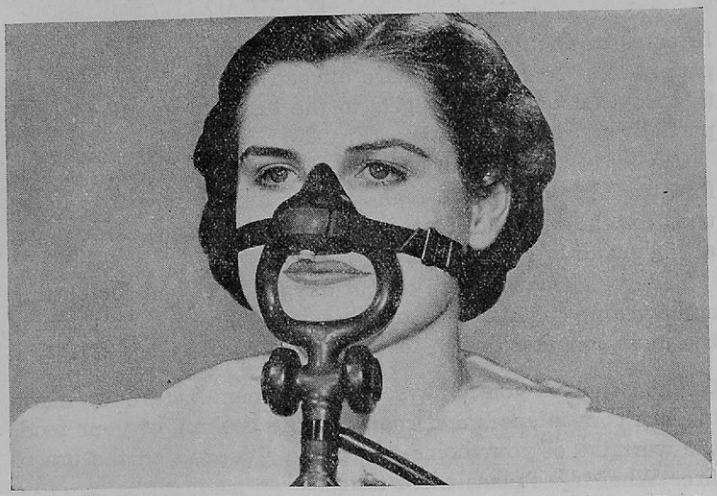
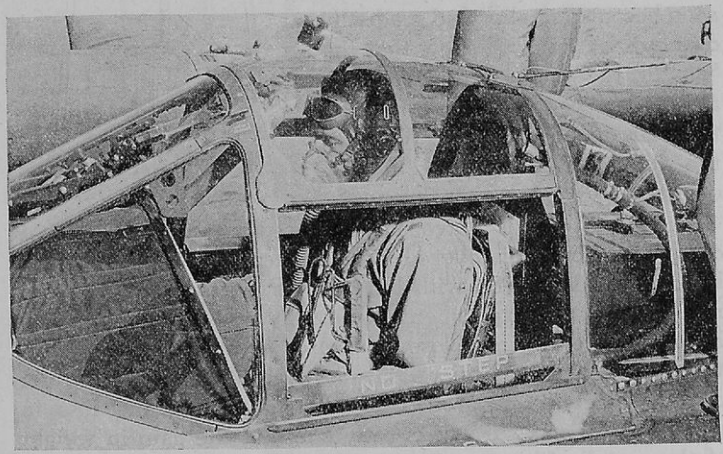


Courtesy, The Ohio Chemical & Mfg. Co.

22. Oxygen Therapy. Affected lung tissue can be treated by mixing healing vapors with oxygen.



U. S. Army Air Forces Photo

23. Aviators Use Oxygen Masks. Air at very high altitudes is so "thinned out" that high-flying aviators must carry a supply of oxygen with them.

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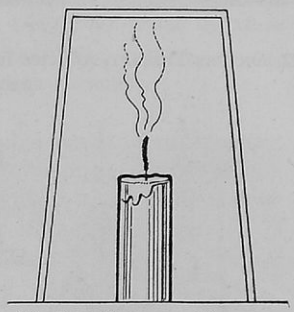
In cases of pneumonia, where breathing is very difficult, the patient may be furnished pure oxygen in an oxygen tent. In this way, enough oxygen gets to the lungs to permit at least partially normal respiration (Fig. 20).

Oxygen is finding an increasing use in aviation. It was first used by aviators in high-altitude flights; now it is being used for the comfort of passengers and to permit safer flying at higher altitudes (Fig. 22).

Today enormous quantities of oxygen are used for cutting and welding metals. The oxyacetylene blowpipe or torch is the most common device for doing this work (Fig. 23).

Oxygen enables you to have fire. The manufacture of many modern conveniences and comforts, the cooking of your food, the warming of your home, still largely depend on the use of fire. What takes place when things burn? Perhaps the following will help you answer this question.

If you invert a glass jar over a lighted candle (Fig. 24), the flame soon becomes smaller and gradually dies out. A test will show that the "air" in the glass jar now contains a smaller percentage of oxygen than air outside the jar. Why has the supply of oxygen in the jar decreased as the candle burned?



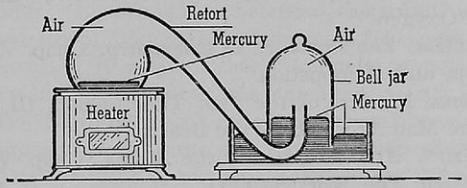
24. FIRE REQUIRES OXYGEN

The great scientist Lavoisier answered that question. After oxygen had been discovered, Lavoisier concluded that it must have something to do with burning since substances burn so readily in it. He experimented carefully and found that when he burned metals in a closed vessel containing oxygen or air, the metals increased in weight and part of the oxygen in the closed vessel disappeared. He also found that the loss in weight of the oxygen was exactly equal to the gain in weight of the metal. After experimenting in a similar manner with the burning of nonmetals, he concluded that *when any substance burns, it combines with oxygen. Ordinary burning* **or**

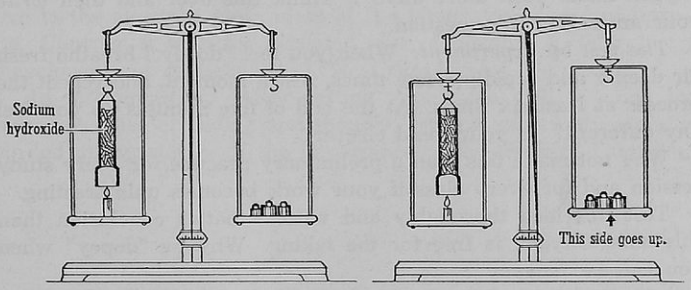
Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

combustion, therefore, is rapid oxidation during which both light and heat are liberated. Most of our fuels burn with a flame. This combustion of fuel is called fire.

Lavoisier's discovery is one of the greatest of all scientific discoveries because it is one of the foundation stones of modern chemistry.



25. LAVOISIER'S EXPERIMENT. When Lavoisier heated metals in air, he found a decrease in the volume of air and an increase in the weight of the metal. Lavoisier showed that when materials burn, they combine with oxygen, forming oxides.



26. A BURNING CANDLE GAINS WEIGHT. If the gaseous products of the combustion of a candle (water and carbon dioxide) are trapped and weighed, it can be proved that combustion increases weight.

A Principle for You to Remember

The chemical union of oxygen with any substance is called oxidation. Ordinary oxidation usually results in the liberation of heat and causes the substance oxidized to increase in weight.

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It is interesting to note that the heat given off by slow oxidation is exactly the same as the heat given off by rapid oxidation (combustion) provided equal weights of the same compound are formed.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. X, pp. 149-157, "Oxygen."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. V, pp. 66-76, "Oxidation and Combustion."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. III, pp. 34-40, "With Fire Man Arose above the Beasts."

KENDALL, JAMES. *At Home among the Atoms.* Chap. VII, pp. 91-111, "Oxygen, The Working Girl."

Applying in Life What You Have Learned in Chemistry

A fact: Breathing oxygen keeps you alive.

The question: When you feel "dopey" will breathing *more* oxygen make you "*more* alive"? Think this over and then *write* your answer to the question.

The test by experiment: When you feel "dopey," breathe fresh air deeply and rapidly a few times, rest a moment, and repeat the process at least six times. At the end of five minutes do you feel any different? Is your mind clearer?

Why not make this plan a preliminary practice for every study session and for every class if your work becomes uninteresting.

Test this idea thoroughly and write a better conclusion than this one: Oxygen is free for the taking. Why be "dopey" when you can be "snappy"?

Putting Chemistry to Work

A

(1) Oxygen is the destroyer element as well as the life sustainer. Explain. (2) Why do substances burn more rapidly in 100 per cent oxygen than in air? (3) Why do fish require so little oxygen in proportion to their weight? (4) For what purposes do auto repair shops use oxygen compressed in steel cylinders? (5) The air you breathe contains nitrogen as well as oxygen. What happens to the nitrogen when it is taken into the lungs? What happens to the nitrogen if a person is under high pressure? (6) Why is water that

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

has been boiled and cooled not suitable for filling fish bowls? How could such water be made suitable?

B

(7) Select five different uses of oxygen and state what property each use depends upon. (8) What form of oxygen (free or combined) do the fish use? (9) A living plant oxidizes by respiration. After it is dead it continues to oxidize by decay. Explain how these two processes differ. (10) What is a balanced aquarium? (Consult a biology instructor or text.) (11) More than 250 years before the work of Lavoisier, it was written: "Animals cannot live where flames cannot live." What does this statement mean? Is it strictly true? (See Boy Scout handbook concerning chemistry merit badge.) (12) Some aquariums are large and require much work to change the water. Devise a plan to oxygenate the water. (13) Some plants live entirely under water. Do they use oxygen? If so, how is it obtained?

Research and Activities That You Will Enjoy

Reporting on a "worn-out" theory: In a few well-chosen words give to the class the main ideas of the phlogiston theory of burning. Contrast it with the accepted idea of burning. Refer to an encyclopedia or to Leonard, J. N. *Crusaders of Chemistry.*

An interpretation: After getting your topic well in mind by extensive outside reading and thought, write a short but carefully worded interpretation of the importance of the work of Lavoisier.

Problem 9

IN WHAT WAYS IS IT NECESSARY TO OVERCOME THE ACTION OF OXYGEN?

Why do you can fruits or paint your houses? Oxygen often unites with substances that we do not want oxidized. It may attack apples and other fruits and cause decay. This decay is aided by bacteria. In order to preserve fruit, it is heated to destroy the bacteria and sealed in containers to keep it away from both oxygen and living bacteria. When this is properly done, both bacterial action and oxidation are prevented.

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In a somewhat similar manner paint is put on houses or on metals in order to seal out the oxygen in the air and thus prevent the rusting of metals or the decay of woods. The farmer puts a layer of grease on the smooth surfaces of his plows and other tools when they are not in use in order to protect them from the "unfriendly" action of oxygen.

How can you put out dangerous fires? Fire is a wonderful friend to us. But it can also be a terrible enemy. Each year fires in the United States cause the loss of hundreds of human lives and millions of dollars of property.

How can dangerous fires be controlled? To answer this question you must keep in mind that combustion is fast oxidation and that it is a result of more than one factor. In other words in order to have a fire, three things are necessary: (1) a substance that can and will burn (you can't burn sand); (2) a supply of oxygen; and (3) a sufficiently high temperature. The first two of these items are fairly easy to understand. Everyone knows that certain substances will not burn; and you understand also that oxygen is necessary to combustion. But just what part does temperature play in this process of combustion?

The kindling point. Before any combustible substance can burn, its temperature must be raised to a certain definite point called the kindling point or kindling temperature. Dry leaves surrounded by air do not take fire until a match or other source of heat has been applied to them. Each burnable substance has its own specific kindling point which may be far greater or far less than the kindling point of some other substance. For example, one reason you can start wood burning more easily than hard coal is because the coal must be made hotter than wood before it bursts into flames. Most coal has a higher kindling point than wood.

When we say that three conditions are necessary for combustion, we mean that *all* of them are necessary—fire cannot burn with only two of these conditions or only one of them. Hence the elimination of any one of these three conditions will put out a fire.

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Water is used in fighting fires to cool the burning materials below their kindling temperatures.

Certain turn-over types of fire extinguishers use chemicals to generate carbon dioxide. When this carbon dioxide, which is approximately 1½ times as heavy as air, covers a fire, it excludes oxygen from the fire.

Clearing fire lanes in forests is one method of removing combustible material from the reach of fire. Do you see why city firemen sometimes dynamite certain buildings in the path of a conflagration? Why does turning off the gas stop the fire in your Bunsen burner?

How can "dust" explosions be eliminated? It is not unusual to read reports of "dust" explosions in starch factories, sugar factories, grain elevators, and other similar places. Explosions are due to very rapid combustion. When you place a log in a fireplace, only the outside of the log is exposed to the oxygen in the air. However, if the log is cut into sticks, a greater amount of the wood surface is exposed to oxygen, and the sticks burn more rapidly than the log. If you cut the wood sticks into tiny splinters, combustion is still more rapid. If you grind the wood into fine powder, float the powder in air, and then kindle it, the combustion will be rapid enough to produce an explosion—if each burning particle is near enough to another to raise its temperature to the kindling point.

The speed of combustion of a substance may be increased by increasing the amount of surface exposed to oxygen—the finer the burning particles, the more rapid is the combustion, providing there is an adequate supply of oxygen. How does this enable you to explain how "dust" explosions may occur?

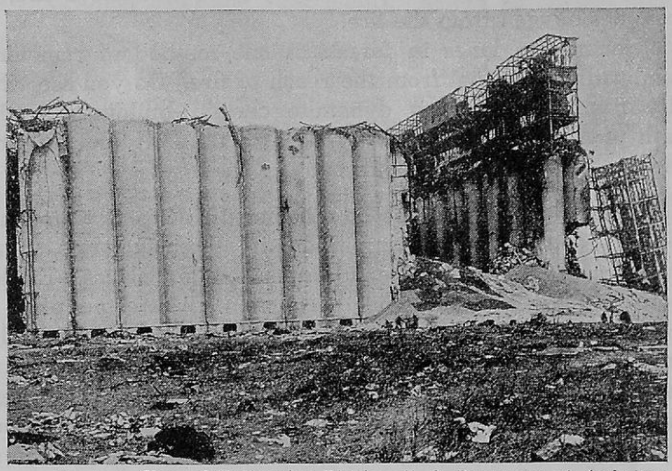
In general, the speed of combustion may also be increased by raising the temperature—the higher the temperature, the greater is the speed of combustion.

In order to eliminate dust explosions:

1. Obey that "No Smoking" sign; don't raise the dust to the kindling temperature.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

2. Use "air conditioning" to keep the dust moist and cool—it is then more difficult for it to reach the kindling temperature.
3. Eliminate as much dust as possible by proper machinery.



Courtesy, Chemical Engineering Division, U. S. Department of Agriculture

27. EFFECTS OF A DUST EXPLOSION. Combustible materials, finely divided and sufficiently distributed in air (oxygen), can produce an explosion by rapid combustion—if only a *spark* is furnished.

How can "spontaneous combustion" be eliminated? Fires sometimes "start themselves." Slow oxidation becomes more rapid with a sufficient rise of temperature. When grass clippings from a lawn are left in a pile, the moist material continues to respire (oxidize). This slow oxidation liberates a certain small amount of heat. If the heat of slow oxidation cannot escape as fast as it is formed, the interior of the pile becomes quite hot after a few hours. When insufficiently dried hay is placed in a barn, this same action takes place and the temperature finally may be brought up to the point where the hay begins to burn with a flame. This self-acting way of raising the temperature of a substance to its kindling point is called *spontaneous combustion.*

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

In the same way that hay in a barn may start spontaneous combustion, certain kinds of coal sometimes ignite automatically. Cotton waste or rags used to wipe up paint or *drying* oils become a menace if they are left covered or in a tight locker where the heat of oxidation in the drying process cannot escape as fast as it is formed. If the oils are non-drying, such as should be used on dusting cloths and mops, there is no danger of self-ignition. But they might be ignited easily by heat from some other source.

To eliminate the danger of spontaneous combustion:

1. Don't leave oily rags or similar materials in the basement, in closets, or in lockers.
2. Don't put hay in barns before it is sufficiently dry.
3. Put iron tubes in large coal piles to conduct away any heat which may be formed by oxidation.

How should you treat burns? Who of you has not been burned? It was not only very painful but highly dangerous if severe or extensive.

There are three degrees of burns which you should learn to recognize quickly: If the skin is only reddened, it is a *First Degree* burn; if the skin is blistered, it is a *Second Degree* burn; if tissue is charred or cooked, it is a *Third Degree* burn.

These "*do* and *don't*" rules should be kept in mind:

DO:

1. Remove all clothing touching a burned area *unless* cloth sticks to skin. If it sticks, cut away the loose cloth with scissors. Let a doctor take care of the cloth that sticks.
2. Be sure to summon a doctor if the burn is severe.
3. Do one of the following:
   (a) Soak gauze or clean cloth (sterile if possible) in a lukewarm 5 per cent solution of tannic acid. Apply gently to burned area.
   To make a 5 per cent solution of tannic acid: Half fill a sterile (or at least clean) jar with tannic

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acid powder. Add enough lukewarm water (sterile if possible) to fill the jar.

(b) If you do not have tannic acid, apply picric acid gauze or clean cloths soaked in a solution of picric acid.

(c) If you have neither tannic acid nor picric acid, soak gauze or clean cloth in a lukewarm solution of common baking soda (not baking powder) and apply to burned area.

To make baking soda solution: Add a number of heaped tablespoonfuls of baking soda to one quart of warm water (sterile if possible).

(d) If the burn is not severe, a "commercial" ointment may be used successfully. Carron oil, made by mixing equal volumes of linseed oil and limewater, is helpful.

DON'T:

1. *Don't* apply "iodine" to a burn.
2. *Don't* use absorbent cotton; it sticks to the burn.
3. *Don't* pull off wax or metal which has stuck to skin after burning it.
4. *Don't* open large blisters. Let the doctor do this.
5. *Don't* use soiled cloths or bandages.
6. *Don't* use ointments or oils on any second or third degree burns. *Good* burn ointments should be used *only* on *First Degree* burns.

How can you "de-oxidize" substances that already have been oxidized? When an element combines with oxygen (either rapidly or slowly), a compound of the element and oxygen is formed. This compound is known as an oxide. Some oxides are gases, such as carbon dioxide which is a compound of carbon and oxygen; some are liquids, such as water which is a compound of oxygen and hydrogen; some are solids, such as mercuric oxide which is a compound of oxygen and mercury.

Nature has allowed oxygen to unite with a number of elements to form compounds for which there is little use. For

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Courtesy, Lockheed Aircraft Corp.

ABOVE THE CLOUDS. Mastery of air travel is one of the great developments of recent years.

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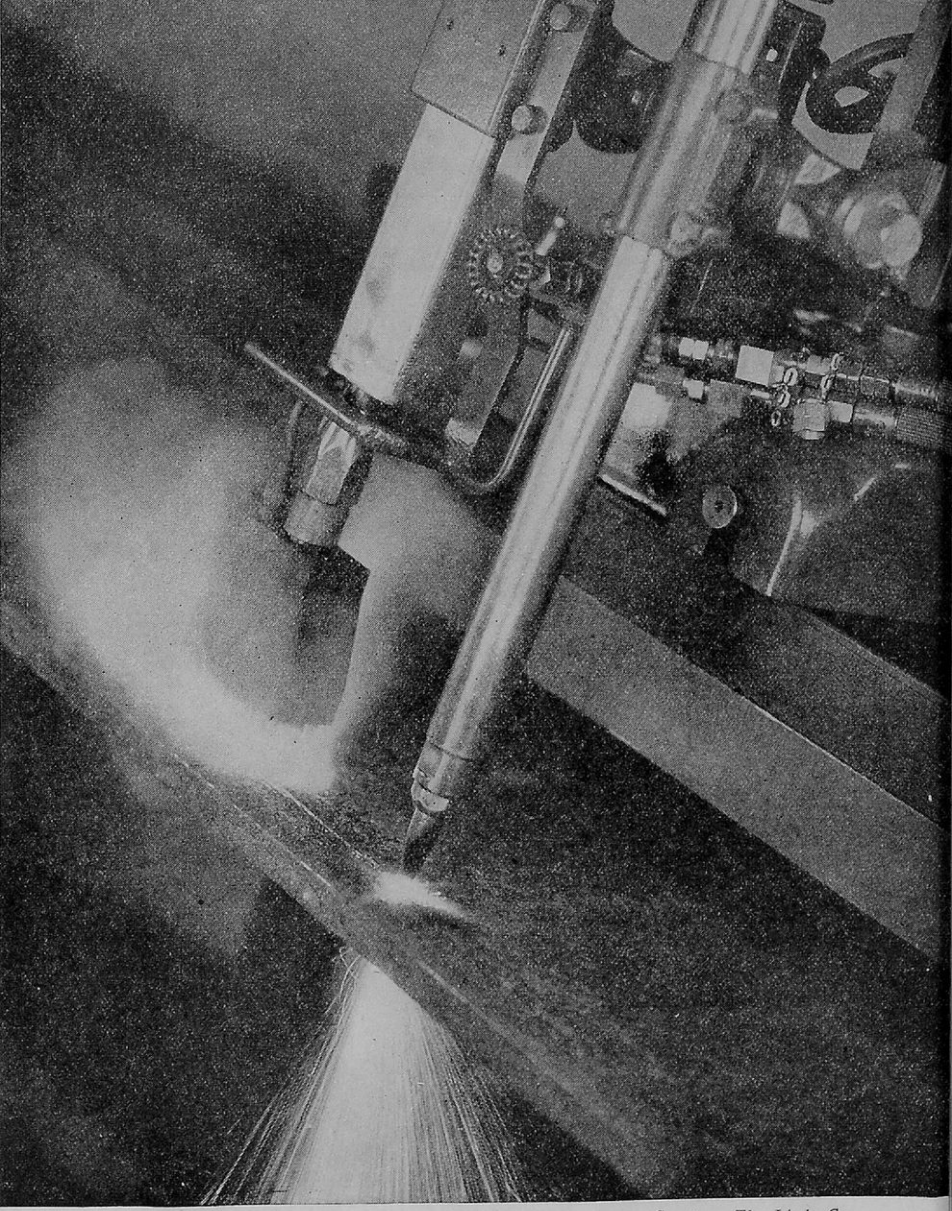

Courtesy, The Linde Co.

CUTTING STEEL WITH "WHITE HEAT." Oxyacetylene or oxyhydrogen blow pipes perform prodigious tasks with heavy plates of steel. They are cut to proper size and the edges are trimmed true for joining.

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example, ferric oxide is a compound of iron and oxygen. It has very few uses. However, the iron is needed to build bridges and to use in industries. Some method must be used to "de-oxidize" this compound and other compounds. One of the following problems in this unit will give you an insight into how the element hydrogen may be used for this purpose.

Applying in Life What You Have Learned in Chemistry

Jim Jones had studied about dust explosions and had begun to think about the finely divided coal in their basement. Should he have been concerned?

Just what conditions are required to make a dust explosion possible? Why must the material be finely divided? Why must it be scattered out in the air? Why must the particles not be too far apart?

Have you ever blown on glowing embers of a campfire to make it burn more brightly? Does the same action cause a candle flame to burn more brightly? Explain any difference. Why does a strong wind blow out the flame of a lantern?

Putting Chemistry to Work

A

(1) With reference to the kindling point, explain the use of paper and wood to start a fire of hard coal. (2) Since powdered coal has a greater surface, why does fine coal burn so slowly in a furnace? (3) A campfire out-of-doors usually dies out leaving unburned charcoal. Why is wood usually completely burned in a fireplace? (4) Is the danger of careless action confined to the careless person only? (5) Why do factories sometimes deaerate water by heating it nearly to boiling before permitting it to circulate in iron pipes? (6) Why does excelsior (shredded wood) burn so rapidly while a book burns very slowly? (7) Why is water usually ineffective in extinguishing burning oil?

B

(8) When a match is lighted, why does it not all burn at once? (9) Dust explosions are unexpected happenings. May they be classed as spontaneous combustion? Explain. (10) How have fish globes set fire to window curtains? (11) What are the two products of ordinary burning? To what general class of compounds do they

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

belong? (12) Why is it very difficult to ignite wood while it is wet or green?

Research and Activities That You Will Enjoy

A safety council: Organize a small group of students to plan and present topics on "Fire Prevention." One student might give government statistics on annual fire losses. Another might give the results of an interview with firemen on the causes of recent fires. Another might make a list of most likely causes of fires, etc. Finally draft all the reports into a brief summary.

A helpful chart: Look in magazines and newspapers for pictures that show different methods of fighting fires. Make a chart by mounting the pictures on large cardboard.

Problem 10

HOW IS IT POSSIBLE TO LEARN THE QUALITIES OF HYDROGEN?

Where are the "hide-outs" of hydrogen? Nature has provided us with very little free hydrogen. Traces of free hydrogen are in the atmosphere but these traces are very scant. Indeed, in 30,000 parts of air there is only about 1 part of this gas; only by very careful experiment can it be detected.

In order to find the "hangouts" of hydrogen, you must search for it in compounds where it has united chemically with other elements. In these compounds hydrogen is widely distributed.

Approximately 90 per cent of all known compounds contain hydrogen as a constituent. The water you drink, the foods you eat, the fuels you burn, plant life, and even your own body are composed in part of hydrogen.

Water is 11 per cent hydrogen by weight.

Petroleum and a host of derivatives, including benzine, gasoline, kerosene, and lubricating oils, are composed of various hydrocarbons which are compounds of hydrogen and carbon.

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Hydrochloric acid, sulfuric acid, nitric acid are composed of hydrogen and other elements. In fact, every acid and every base has hydrogen as a constituent.

Which of all the sources of hydrogen can you use for obtaining this gas? Your next problem is to find a way to separate it from one or more of its compounds.

After you find its "hide-outs," how can you "round up" hydrogen for use? In order to obtain hydrogen from one of its compounds, it is necessary to use some substance which will unite with the other element or elements in the compound, thus setting hydrogen free.

Water is a compound of hydrogen and oxygen—how can you use a metal to unite with the oxygen and thus set hydrogen free? In order to free the hydrogen in water, it is necessary to use some element that will unite with the oxygen that is combined in the water, thus setting the hydrogen free. You know that iron unites chemically with free oxygen when the temperature is raised sufficiently. Perhaps iron will also combine with the oxygen that is a constituent of water. If so, the problem is solved. You can prove by experiment that this suggestion really does solve the problem, for when you heat iron red hot and pass water in the form of steam over it, the iron does unite with the oxygen to form iron oxide, thus setting hydrogen free. This is an efficient method of preparing hydrogen in large quantities.

The chemical action that takes place can be expressed by the following word equation:

$$\text{iron} + \underset{\substack{\text{hydrogen}\\\text{oxygen}}}{\text{water}} \rightarrow \text{hydrogen} + \underset{\substack{\text{iron}\\\text{oxygen}}}{\text{iron oxide}}$$

Iron is not the only substance that can be used for this purpose. Coke or charcoal (carbon) can be used in a similar manner. Certain metals including *sodium, potassium,* and *calcium* can be used without raising the temperature as we did for iron. *Sodium, potassium,* and *calcium* are called very active metals because they unite very easily with the oxygen that is combined in water—even at ordinary temperatures.

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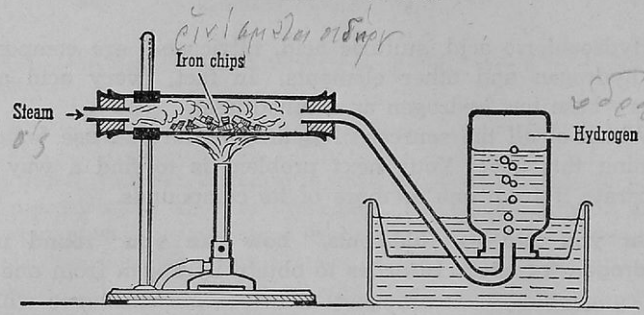


28. HEATED METAL REACTING WITH STEAM. Heated red-hot iron takes oxygen from steam, leaving the hydrogen free.

The following word equations express the chemical action that occurs when these metals come in contact with water:

General equation:

$$\text{water} + \text{metal} \rightarrow \text{hydrogen} + \text{metal hydroxide}$$

hydrogen
oxygen

metal
oxygen
hydrogen

If the metal is sodium, substitute the word *sodium* wherever the word *metal* appears in the general equation:

$$\text{water} + \text{sodium} \rightarrow \text{hydrogen} + \text{sodium hydroxide}$$

hydrogen
oxygen

sodium
oxygen
hydrogen

What will be the word equation if potassium is used? if calcium is used?

Note in these word equations that not all of the hydrogen in water is set free when these metals are used. Half of it is set free; the other half combines with the metal and the oxygen.

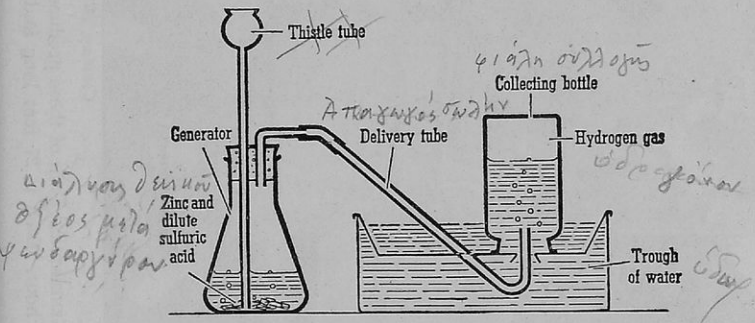
You have found how to release hydrogen from water. Is it possible to make other hydrogen compounds release hydrogen?

Acids contain hydrogen—how can you use a metal to "oust" hydrogen from an acid? All acids are compounds containing hydrogen, and they are much more active chemically than water. The problem in obtaining hydrogen from an acid is

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

similar to the problem of obtaining it from water in that you use a metal which will unite with all the elements in the acid except the hydrogen, thus setting the hydrogen free.

Zinc and iron are able to "drive off" or replace hydrogen from solutions of most acids at a rapid rate without being heated. This method has become the standard laboratory method of preparing hydrogen. Iron is the cheapest metal but its impurities are carried over into the hydrogen, so zinc is the metal generally used.



29. LABORATORY PREPARATION OF HYDROGEN. Ordinary active metals displace hydrogen from dilute acids.

The chemical action that takes place can be expressed by the following word equations:

active metal + acid → hydrogen + a salt of the metal

zinc + sulfuric acid → hydrogen + zinc sulfate

hydrogen sulfur oxygen — zinc sulfur oxygen

or zinc + hydrochloric acid → hydrogen + zinc chloride

hydrogen chlorine — zinc chlorine

Try writing word equations for iron reacting with sulfuric acid and with hydrochloric acid.

How you can get hydrogen from sodium hydroxide. A few metals (aluminum, zinc, and silicon) react with sodium hydroxide:

aluminum + sodium hydroxide → hydrogen + sodium aluminate

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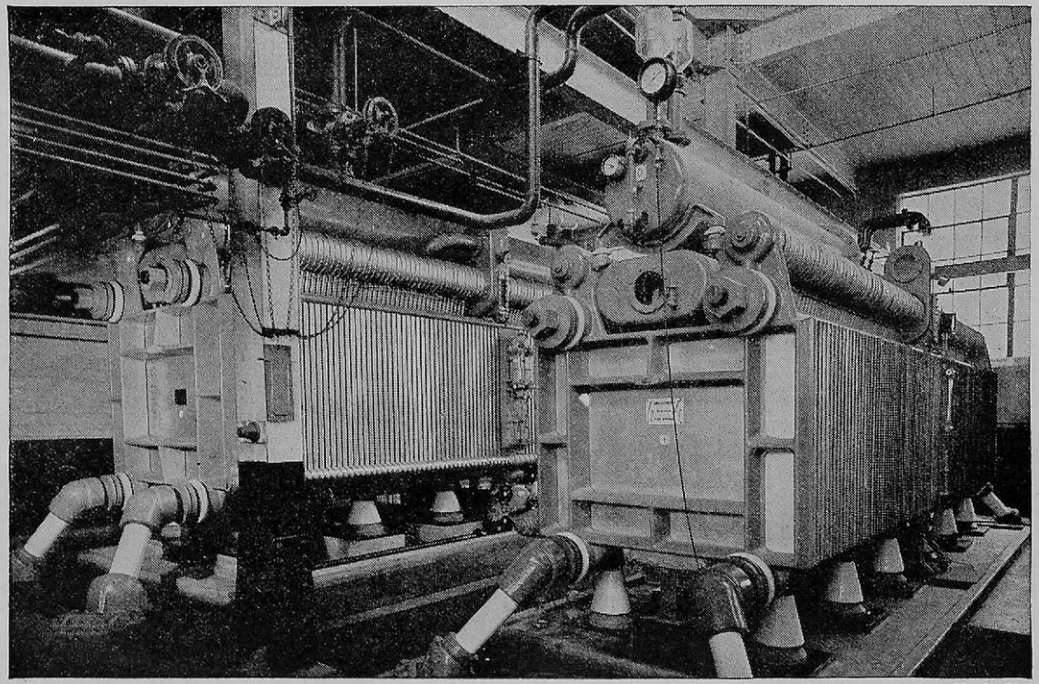

Courtesy, Albert H. Bruecke, New York City

30. LARGE ELECTROLYTIC HYDROGEN-OXYGEN GENERATORS. Each of these produces 8800 cubic feet of hydrogen and 4400 cubic feet of oxygen per hour. Each is 27 feet long and weighs 207,000 pounds.

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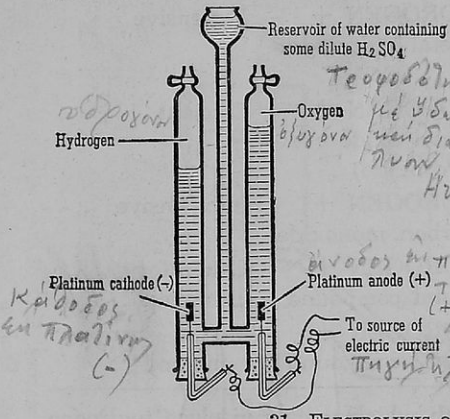
How can you obtain hydrogen by decomposing water with electricity? Water is a very stable compound and, therefore, a great deal of energy must be applied to it in order to decompose it. This can be done by passing a direct current of electricity through it after adding a little acid. The acid enables the water to conduct an electric current.



Positively charged hydrogen is attracted to the cathode and changed into gaseous hydrogen. The oxygen becomes gaseous at the anode. The volume of the hydrogen obtained is twice the volume of the oxygen. Sulfuric acid is used to make the water a conductor of electricity. Sodium hydroxide could be used in place of the sulfuric acid to give a conducting solution.

31. ELECTROLYSIS OF WATER

In industry hydrogen is usually produced by the electrolysis of water or by passing steam over red-hot iron or through very hot coke (carbon). When steam is passed through red-hot coke, the oxygen of the water combines with the carbon of the coke, forming carbon monoxide and hydrogen. When this mixture of carbon monoxide and hydrogen is subject to great pressure, the carbon monoxide liquefies, and the hydrogen is obtained in a relatively pure state.

Summary of methods of obtaining hydrogen. A review of the foregoing methods shows that water is either directly or indirectly the common source of hydrogen. Electrolysis and the displacement of hydrogen by a metal illustrate the methods of preparing hydrogen directly from water. In the reactions between an acid and a metal (or a base and a metal), the liberated hydrogen may be regarded as coming originally from water, since neither an acid nor a base can be formed without water.

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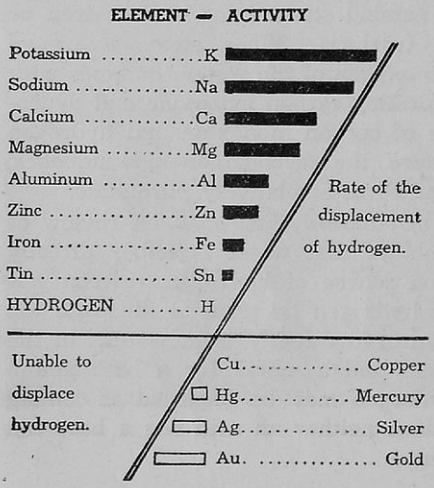
METHODS OF OBTAINING HYDROGEN

Substances Used	*Products Formed*	*Effectiveness*
1. Hydrogen oxide (water) (electrolysis) →	HYDROGEN + oxygen	Pure hydrogen
2. Water + very active metal (cold) →	HYDROGEN + metal hydroxide	Expensive
3. Water + active metal (heated) →	HYDROGEN + metal oxide (or hydroxide)	Efficient
4. Water + carbon (heated) →	HYDROGEN + carbon monoxide	Inexpensive
5. Acid (diluted) + active metal →	HYDROGEN + metal compound	Laboratory method
6. Base (solution) + active metal →	HYDROGEN + metal compound	Mobile—army method

The relative activity with which metals displace hydrogen from its compounds is shown in Fig. 32.



32. ACTIVITY SERIES OF COMMON METALS

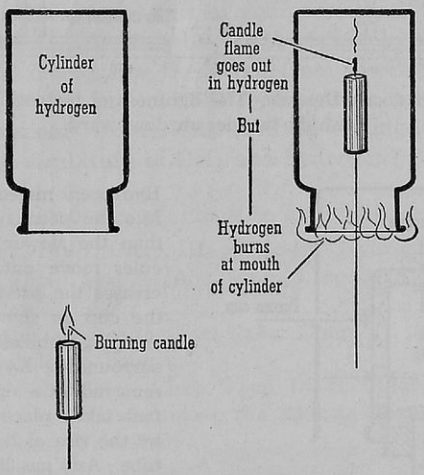
Metals above hydrogen will displace hydrogen from compounds such as acids and water. Metals below hydrogen will not displace hydrogen. Elements higher in the series will displace elements lower in the series. For example, copper will displace silver from silver nitrate solutions, forming copper nitrate and crystals of silver.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Taking hydrogen's "fingerprints": how does it differ from other substances? Important properties of hydrogen are as follows:

Physical properties.

1. When pure, it is colorless, odorless, tasteless.
2. Solubility: slightly soluble, 1.8 vols. dissolve in 100 vols. of water at 20° C.



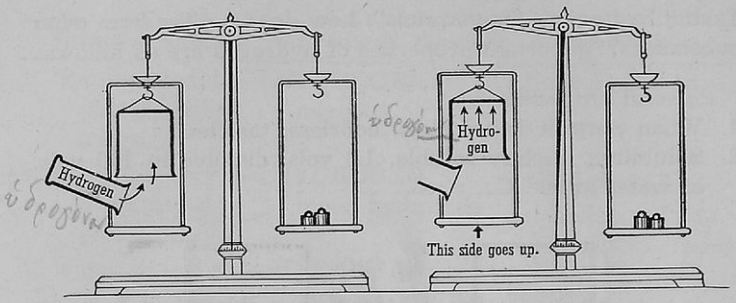
33. HYDROGEN BURNS BUT WILL NOT SUPPORT COMBUSTION

3. Density: air is 14.4 heavier. One liter weighs 0.09 g.
4. Liquefiability: becomes liquid at a temperature of —240° C. and a pressure of 13 atmospheres.
5. Adsorption: some metals condense hydrogen on their surfaces.
6. Diffusion: diffuses more rapidly than any other gas.

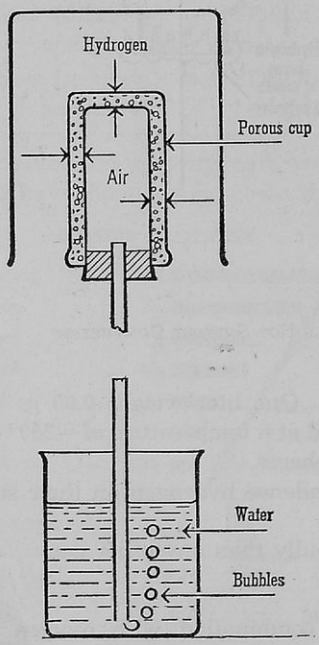
Chemical properties.

1. Combustibility: burns by combination with oxygen or chlorine. Its very high heat of combustion makes it a good fuel.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



34. POURING HYDROGEN UPWARD. The lightness of hydrogen permits it to push the heavier air downward.



Hydrogen molecules move into the porous cup faster than the slower air molecules move out. This increases the pressure inside the cup as shown by the escaping bubbles. When the surrounding hydrogen is removed, the opposite effect takes place as shown by the rise of liquid in the tube. Any gas lighter than air shows a similar behavior, but hydrogen, being the lightest gas, shows this behavior more strikingly than other gases. Light molecules must move with greater velocity than heavy molecules to exert the same pressure. What will happen if the cup is surrounded by carbon dioxide? (Carbon dioxide is about one and a half times as heavy as air.)

35. UNEQUAL DIFFUSION OF HYDROGEN AND AIR THROUGH A POROUS CUP

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2. Combines readily with several elements, particularly the nonmetals such as oxygen to form water (H_2O), chlorine to form hydrogen chloride (HCl), and sulfur to form hydrogen sulfide (H_2S).

How to identify hydrogen. (1) As a pure gas: When pure, it burns quietly with a very hot, colorless or pale blue flame. Impurities may make the color of the flame more visible.

(2) In combination with other elements; in mixtures with other combustible gases; and in compounds: When burned, water is formed. This can be made visible by some means of cooling and condensing the vapor from the hot flame. The formation of water proves that hydrogen is present in the burned substance. Would this method distinguish between pure CH_4 and a mixture of CH_4 and hydrogen?

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. III, pp. 52-56, "Hydrogen."

HAYNES, WM. *This Chemical Age.* Chap. I, pp. 3-19, "Not Difficult nor Dangerous."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. VI, pp. 66-72, "The Lightest Substance Known."

JAFFE, BERNARD. *Crucibles.* Chap. V, pp. 73-92, "Henry Cavendish."

KENDALL, JAMES. *At Home among the Atoms.* Chap. IX, pp. 131-140, "Hydrogen, 'Nize Baby.'"

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XIV, pp. 242-245, "Hydrogen."

WEEKS, MARY ELVIRA. *The Discovery of the Elements.* Chap. IV, pp. 29-33, "Hydrogen."

Applying in Life What You Have Learned in Chemistry

How discoveries are made: We owe our modern comforts and conveniences to many great men—past and present—who have labored long hours to learn Nature's secrets.

The most frequent partner of oxygen has served the human race since the first man. Yet hydrogen was unknown until Henry Cavendish discovered it. Cavendish gave little thought for himself as to what he would eat or wear. He had great wealth, but his sole desire was to seek out new truths. You will find out more about this remarkable man in: Jaffe, *Crucibles,* Chapter V.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Putting Chemistry to Work

A

(1) Why does the hydrogen prepared in the laboratory usually have an odor? (2) Is it necessary to use a water pan in collecting hydrogen? Explain your answer. (3) When you prepare hydrogen in the laboratory, what fact indicates to you that hydrogen was obtained from the acid and not from the metal? (4) Oxygen and hydrogen are very similar in what two properties? very different in what two properties? (5) Show how the funnel tube in the hydrogen generator acts as a safety tube. (6) Could hydrogen be stored without loss in a jar inverted over water? (7) How can the preparation of hydrogen be used to measure the activity of metals? (8) Why is there no danger of an explosion in lighting an oxyhydrogen blowpipe?

B

(9) Give two reasons why zinc is commonly used for the preparation of hydrogen in the laboratory. (10) Why did Cavendish call this gas which he had discovered, "inflammable air"? (11) How would you prepare hydrogen quickly? How would you prepare it in moderate quantity? How would you prepare it in large quantities? (12) By what constituent do hydroxides differ from oxides? (See the formulas.) (13) State how four factors can affect the rate of preparation of hydrogen. (14) What is wrong with this reasoning? "Sodium reacts violently with water. Your body contains about an ounce of sodium. Therefore, you take a chance every time you go in swimming." (15) Why were only metals of low activity known to the ancient world? (16) Pilatre De Rozier, an early French chemist, surprised his friends by inhaling hydrogen and lighting it as he exhaled. On one occasion it exploded in his mouth, burning him badly. Can you explain what happened?

Research and Activities That You Will Enjoy

"It-floats-through-the-air" demonstration: Blow soap bubbles filled with hydrogen. Study their density and their flammability and discuss lighter-than-air craft. CAUTION: *Remember the Hindenburg!*

Cavendish: An eccentric man and a true scientist in the twilight days of alchemy was Henry Cavendish. Report the interesting story of the discovery of hydrogen.

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Courtesy of Major H. Lee Wells, Jr., Omaha, Nebr.—Copyright, 1935

36. READY FOR A FLIGHT INTO THE STRATOSPHERE. Captains Stevens and Anderson rose 72,395 feet on November 11, 1935. This flight started in the Black Hills and ended near Kimball, South Dakota. Valuable scientific information concerning conditions in the stratosphere was secured during this ascent.

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Problem 11

HOW DOES HYDROGEN SERVE YOUR DAILY NEEDS?

Hydrogen helps man to rise in the air. Hydrogen enables scientists to explore the upper atmosphere. No other gas will make a balloon rise so far into the stratosphere as hydrogen. This is because it is the lightest gas. One liter of air weighs 1.29 grams under standard conditions, but the same volume of hydrogen weighs only 0.09 gram. The difference in the weight of the two gases (1.29 —0.09 = 1.2 g per liter) is the lifting force of hydrogen.

Until recently hydrogen was used extensively in dirigibles. Its use for this purpose, however, is very dangerous since it is highly flammable. A number of catastrophes have occurred to dirigibles filled with this gas. Helium which is nonflammable is, therefore, rapidly taking the place of hydrogen in lighter-than-air craft. But hydrogen, since it is the lightest gas, will no doubt continue to be used for stratosphere flights.

Hydrogen helps you to travel; it helps to manufacture goods by furnishing heat. When you drive your car to a filling station and purchase gasoline, you really purchase compounds of hydrogen and carbon, for gasoline is a mixture of hydrocarbons. The hydrogen helps you to travel. When you ride on a train pulled by a locomotive burning coal or oil, hydrogen is helping you to travel, for coal and petroleum also contain both hydrogen and carbon. When hydrogen burns or oxidizes, it furnishes more than four times as much heat per gram as carbon does. These two elements, uniting with oxygen, furnish much of the energy that is used to heat homes, to travel, and to manufacture industrial products. It is interesting to note that when hydrogen burns, it unites with oxygen to form water (steam), which is used to extinguish flame. Hydrogen also burns in (unites with) chlorine to form hydrochloric acid (HCl) and it unites with sulfur to form hydrogen sulfide (H_2S).

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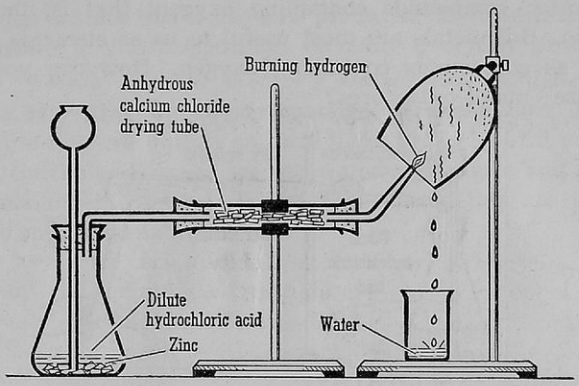


37. BURNING HYDROGEN FORMS WATER. Water is hydrogen oxide.

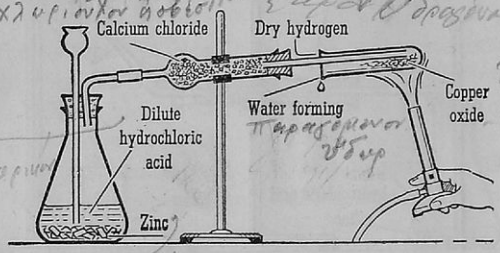
Hydrogen furnishes very high temperatures. When hydrogen burns in oxygen it produces a temperature of approximately 2000° C. But this high temperature could not be used to melt or "cut" iron, steel, or other metals till the oxyhydrogen blowpipe was invented. With the oxyhydrogen blowpipe most metals can be cut or welded easily.

In recent years acetylene gas (C_2H_2) has taken the place of hydrogen in blowpipe use where particularly high temperatures of about 3000° C. are required. Hydrogen, however, again has recently taken the lead in the production of high temperatures. When hydrogen gas is blown through an electric arc, the hydrogen absorbs energy—and when this hydrogen unites with oxygen just outside the electric arc, not only is the absorbed energy released as heat, but the burning hydrogen releases much heat also. A temperature of about 4,200° C. is produced. This is one of the highest temperatures obtainable in the laboratory. The temperature of the sun's surface is approximately 6,000° C.

Hydrogen can be used to remove oxygen from metallic compounds. Oxygen, as you have seen, is a very sociable element. It combines readily with many other elements including many of the metals. For this reason the metal ores

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

are often compounds containing oxygen; that is, they are oxides. But metals are most useful to us as elements rather than as compounds containing oxygen. How can you "de-oxidize" metal oxide ores?



38. REDUCING COPPER OXIDE WITH HYDROGEN

With the exception of compounds like mercuric oxide, you cannot "de-oxidize" metal ores by heat alone, for they are too stable. Hydrogen can help you. If you want to get the copper that is in copper oxide, you can heat it in the presence of hydrogen. The hydrogen unites with the oxygen of the copper oxide, thus freeing the copper.

The chemical action of this process may be shown as follows:

$$\underset{\substack{\text{copper}\\\text{oxygen}}}{\text{copper oxide}} + \text{hydrogen} \rightarrow \text{copper} + \underset{\substack{\text{hydrogen}\\\text{oxygen}}}{\text{water}}$$

A Principle for You to Remember

The removal of oxygen from a compound is called reduction. Substances from which oxygen has been removed are said to be reduced.

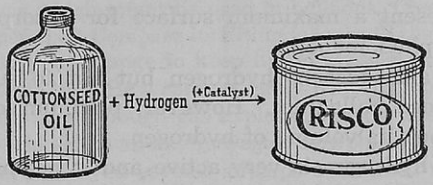
Reduction might be called the opposite of burning or oxidation. When a substance oxidizes, oxygen unites with it; when a substance is reduced, the oxygen leaves it to unite with the reducing agent.

Hydrogen and carbon are our chief reducing elements.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Hydrogen enables you to use new products. Hydrogen is used extensively in the preparation of many everyday products.

The "Crisco" in your mother's kitchen was hardened by the use of hydrogen. Crisco contains vegetable fats. Many vegetable fats are liquids and are undesirable as lard substitutes. By the addition of hydrogen under pressure and aided by finely divided nickel as a catalyst, liquid fats are transformed into solid fats.



39. HYDROGEN ENABLES US TO MAKE SOLID FATS FROM OILS

Fish oils may also be hydrogenated and by this process they lose their objectionable odor and become suitable for use in making soap.

The "ammonia" used in your kitchen for cleaning purposes contains hydrogen. Both ammonia and "wood" alcohol may be prepared synthetically and both contain combined hydrogen. Ammonia can be prepared by combining hydrogen with nitrogen under great pressure. "Wood" alcohol (chemically called methanol) is now made by combining hydrogen and carbon monoxide.

Hydrogen makes it possible to get a greater quantity of gasoline from crude oil. Through the use of hydrogen, the yield of gasoline from petroleum is now being increased. Petroleum, or crude oil, contains a relatively small amount of gasoline in its natural state. But crude oil can be broken down by heat and pressure and combined with hydrogen to increase the yield of gasoline. This process will be explained further in a later unit. Synthetic gasoline also has been produced by a somewhat similar treatment of coal with hydrogen, but our great supply makes this process unprofitable in this country.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Hydrogen makes it possible to have self-lighting gas lamps—adsorption. A few metals act as "hangouts" for hydrogen, for they concentrate hydrogen on their surfaces. This process is called *adsorption.* When a metal adsorbs hydrogen, the hydrogen "collects" on the surface of the metal. The element palladium adsorbs approximately 500 times its volume of hydrogen. It is hard to imagine that 1 cc of palladium can adsorb half a liter of hydrogen. Palladium for this purpose is used in the form of a very fine powder and in this condition its particles present a maximum surface for adsorption, which is a surface phenomenon.

Platinum also adsorbs hydrogen but not to such a great extent as does palladium. However, platinum does adsorb about 50 times its volume of hydrogen.

Adsorbed hydrogen is very active and it begins to "burn" below its usual kindling point upon exposure to oxygen. The heat from this burning can be used to ignite gas lamps, thus making the lamps "self-lighting."

Hydrogen combined with oxygen forms one of the most important chemical compounds in the world: water. In the next unit of this book you will study water: a substance that frequently furnishes power; a substance without which you could not live; a substance that is most important in chemistry.

Readings for Pleasure and Profit

HOLMES, HARRY N. *Out of the Test Tube.* Chap. VI, pp. 72-78, "The Lightest Substance Known."

HOWE, H. E. *Chemistry in Industry.* Vol. II, Chap. I, pp. 1-11, "Catalysis—A New Factor in Industry."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XIV, pp. 239-241, "Hydrogen."

Applying in Life What You Have Learned in Chemistry

Mr. Crandall looked up from his evening paper.

"Son, here's an article that says helium is about twice as heavy as hydrogen gas."

"No wonder Piccard used hydrogen," answered young Allen. "You see, Dad, since helium is twice as heavy as hydrogen, a

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

helium-filled balloon has to be twice as large as a hydrogen-filled one to go the same height."

"Wait a minute, son. Let's check on that."

Is Allen's statement correct or incorrect? How will a knowledge of the lifting ability of gases answer the question?

Putting Chemistry to Work

A

(1) How could you prove that fuel gas contains hydrogen in some form? (2) Hydrogen is flammable; helium is expensive. Select some other gas which might be used in balloons. (See list of gases, page 771, appendix.) Compare its lifting force with that of hydrogen. (3) How could you arrange to keep hydrogen securely in a jar for use the next day? (4) How can we safely heat our homes and cook our foods with gas although gas explosions often wreck buildings? How can we use safely an oxyhydrogen blowpipe although burning hydrogen has destroyed several airships and killed many people? (5) How could the apparatus shown in Fig. 38 be changed and used to determine the ratio by weight in which oxygen combines with hydrogen to produce water? (6) A laboratory assistant filled one jar with hydrogen, another jar with oxygen, and left a third jar containing air. They were not labeled. How did the instructor identify the gases by a simple test without interfering with their further use in experiments? (7) Make a list of all the substances in your home which you think might have hydrogen as a constituent. (8) Water collects on the outside of a glass filled with ice water. It also collects on the inside of a cold dry glass inverted over a burning candle. Explain the source of the water in each case.

B

(9) What relation has the process of oxidation to that of reduction? the burning of hydrogen to that of the electrolysis of water? (10) An oxyacetylene welder says that he must have "reducing conditions" to get strong joints. What does he mean, and why is this precaution necessary? (11) When a careless student asserted that "air is a mixture of oxygen and *hydrogen*," he was warned never to strike a match, for if he were not killed by the explosion, he was sure to be drowned! Explain. (From Holmes and Mattern.) (12) Predict what would happen in each of the following experiments: A lighted splint is put into (a) a bottle of hydrogen; (b) a bottle of oxygen; (c) a mixture of air and oxygen; (d) a mixture of air and hydrogen.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

How Good Are You at Solving Problems?

(1) If 32.5 grams of zinc are required to "push" 1 gram of hydrogen out of an acid, how many grams will be required to prepare 10 liters of hydrogen from an excess of sulfuric acid?

(2) What weight of hydrogen would be obtained by displacing all the hydrogen from 4.9 grams of sulfuric acid? (The percentage of hydrogen in sulfuric acid is $2 \div 98$.) How many liters would this weight of hydrogen occupy?

(3) Approximately 10 per cent of the weight of your body is due to hydrogen. Compute the weight of hydrogen in your body from your weight. If it were gaseous hydrogen, would it have sufficient lifting ability to take the "remainder of yourself for a ride"?

(4) The rates of diffusion of gases are inversely proportional to the square roots of their densities (Graham's Law). Compare the rates of the diffusion of hydrogen and air, having densities of 1 and 14.4.

Research and Activities That You Will Enjoy

A trip: Visit a welding shop or other shop where oxyacetylene welding is done. Learn all you can about the apparatus and the types of work done. Report the information to your class.

A report: By outside reading or by asking an industrial or engineering chemist, learn more about an atomic hydrogen flame and tell the class about it.

Looking Back into Unit 2

Be sure you know the purpose of this unit. Read again the material on page 22, "Looking Ahead into Unit 2." Then study the following Summary Test.

Summary Test

1. *What is air?*
   (a) How do you know that air is a mixture rather than a compound?
2. *How are you affected by the gases of the atmosphere?*
   (a) In what ways is carbon dioxide an important gas?
   (b) How are you dependent on water vapor in the air—
   (1) For food? *(2)* For comfort?
   (c) How are two other gases in air important to you?
   (d) How are the inert gases in the air useful?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

3. *How does a study of air and other substances indicate that matter is composed of tiny moving molecules?*
   (a) In what ways does diffusion lead us to believe in molecules?
   (b) What simple demonstrations show that there is space between the molecules of a gas?
   (c) How do changes in state strengthen our belief in molecules?
   (d) What are the main points in our theory of moving molecules?

4. *How is it possible to learn the characteristics of the colorless, odorless, tasteless element—oxygen?*
   (a) Where is oxygen found?
      (1) What difficulties were overcome in its discovery?
      (2) What problems confront you in its preparation?
   (b) How is oxygen prepared—
      (1) In your laboratory?
      (2) On a commercial scale?
   (c) How does oxygen differ from other substances? What are its properties?

5. *Why is oxygen a most useful element in your world?*
   (a) What is the first essential of living beings? How is it essential?
   (b) How is oxygen related to sanitation?
   (c) What is the explanation of burning?
   (d) What are other valuable uses of oxygen?

6. *In what ways is it necessary to overcome the action of oxygen?*
   (a) Why do you can fruits and paint your homes?
   (b) How can you put out dangerous fires?
   (c) How can dust explosions be eliminated?
   (d) How can spontaneous combustion be eliminated?

7. *How is it possible to learn the qualities of hydrogen?*
   (a) Where is hydrogen found?
   (b) How is hydrogen prepared—
      (1) Commercially?
      (2) In your laboratory?
   (c) How does hydrogen differ from other substances? What are its properties?

8. *How does hydrogen serve your daily needs?*
   (a) What quality of hydrogen makes it useful in balloons? What quality makes its use dangerous?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

(b) What qualities of hydrogen make it valuable in industrial processes?
(c) How is hydrogen useful in reduction?
(d) What useful products are related to hydrogen?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

In this unit you discovered that the *atmosphere* abounds in free, raw materials upon which Nature and Man are continually drawing for their use. Nature's achievements in *photosynthesis* and Man's utilization of the *lazy, inactive gases—helium, neon,* and *argon*—are fascinating. Man and Nature both find ways to put *oxygen* and *nitrogen* to work effectively.

You breathe *oxygen* and live because it converts your food into *heat* and *muscular energy.* Under ordinary circumstances you can go on living because vegetable and animal wastes decay instead of piling up layer on layer; the *carbon dioxide* that results from this decay is sent back into the atmosphere to be used over again by plants as food. Man has learned to adapt the energy from *burning* (*oxidizing*) fuels to his use, and we have the steam engine, the auto, the airplane, the Diesel engine. And now we *liquefy* the *air,* recover the oxygen, and ship it in cylinders or tanks for a variety of uses—welding, cutting metals, aiding the patient in severe cases of pneumonia, and a variety of other practical and worth-while uses.

You have been given much *oxygen*—much of your body is oxygen and over 46 per cent by weight of all the earth is oxygen. You owe much to the pioneers who worked with oxygen—to *Priestley* and to *Lavoisier* whose exact work made *chemistry* a *science.*

Perhaps you are not quite so impressed with *hydrogen,* for here you have an element that is furnished naturally only in compounds, but chemists have found ways to obtain it in a free state. Because it produces so much energy when it burns and because it likes oxygen so well, man has found many ways to use it. Combined with *carbon, hydrogen* serves in many *fuels*—natural and artificial gases, gasolines, and fuel oils. Man uses hydrogen to fill balloons because it is the lightest gas, but here the behavior of hydrogen is tricky because of its great explosiveness when mixed with oxygen.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

You remember *hydrogen* as an excellent *reducing agent,* ready in many cases to withdraw oxygen from compounds. *Hydrogen* is in turn *oxidized* to form *water.* Here you learn the interrelation between *oxidation* and *reduction.*

Oh, yes, you were introduced to *molecules—fast, moving particles* in *gases,* less fast in *liquids,* and comparatively slow, but vibrating, in *solids.* These invisible bodies behave according to some very definite laws; your study of them perhaps gives you a new conception of matter. You learned that matter is not only in motion but also that there is a great deal of space between the tiny particles that compose it.

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Looking Ahead into

Unit Three

Your first personal need in life is oxygen; your second is water. Water is also an economic necessity. It is the lifeblood of the nation. It is a means of transportation, a source of steam power, a raw material in industry, a standard of comparison, a necessary part of many solutions.

Your continued good health requires pure drinking water. How can water be purified for you? The answer to this problem is one in which every citizen is interested—an answer which science has produced.

Water is essential in chemistry. It has been said that if we knew all the chemistry of a single drop of water, we would know a great deal more chemistry than we now do. What is water? Its composition has long been an interesting problem, the determination of which has engaged the best efforts of several notable chemists. You will be interested in the composition of water because it throws light on the nature of some of the smallest things in the world—molecules and atoms.

Note how our chemical story is carried forward in the following problems concerning your world of water and solutions.

Problem 12. *You Cannot Live without Water—How Is Water Made Pure for You?*

Problem 13. *What Properties of Water Make It Your Useful Friend and Servant?*

Problem 14. *What Is Water?*

Problem 15. *What Is a Solution?*

Problem 16. *When You Make a Solution, What Factors Affect the Speed of Dissolving and the Degree of Solubility?*

Problem 17. *How Are Substances Recovered and Purified by Crystallization?*

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Water: The World of Water and Its Importance to You; Its Use in Solutions

Problem 12

YOU CANNOT LIVE WITHOUT WATER—HOW IS WATER MADE PURE FOR YOU?

Water is the most common chemical compound. The large amounts which occur in nature make it very familiar to everyone. The oceans, lakes, and rivers cover nearly three-fourths of the earth's surface. Water falls from the clouds as rain and condenses from the air as dew. All plant and animal bodies, including our foods, contain much of it. In fact, plant and animal life cannot exist without water.

In spite of the fact that it occurs in such large quantities in nature, natural water is not chemically pure. Sea water contains nearly four per cent of dissolved solids as impurities; spring water, well water, river water, and lake water all contain dissolved mineral matter, and even rain water contains dissolved gases and dust from the air.

Water may contain harmful bacteria—how can you kill bacteria in water? Certain impurities in water *may* be very objectionable and in some cases have an injurious effect upon health, as in the case of water in which bacterial or other organic growth has taken place. Moderately safe water for drinking purposes may be provided by *boiling* the water for about ten minutes. However, such a procedure should be used only as a temporary measure. It is well to remember that water often gives no outward sign, either by color, odor, or taste, as to its bacterial content or its fitness for household purposes.

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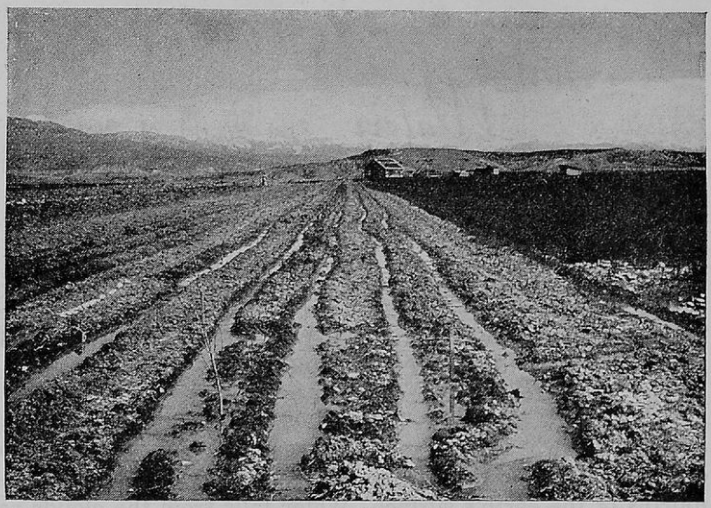

U. S. Bureau of Reclamation Photograph

40. THE DESERT BECOMES A GARDEN. Irrigation makes this fine farm possible.

Water may contain mud or other suspended materials—how can you remove these materials from water? Impurities in water may be present either *in solution* or *in suspension.* Water containing suspended matter is not clear but is more or less cloudy. Such impurities may be removed partially by filtration, which consists of passing the water through porous materials, such as paper, porcelain, beds of charcoal, or sand and gravel. In the laboratory the filter may be made of paper. Charcoal, porous plates, and sand are used to remove suspended matter from large amounts of water.

A "ring around the bathtub" may be a sign that the water is "hard"—how can you eliminate dissolved matter from water? The method mentioned above does not remove dissolved impurities from water. Although small amounts of dissolved substances are not seriously objectionable in water to be used for drinking and other household purposes, too large quan-

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

tities of such impurities may give to the water an unpleasant taste. Again, water in certain localities may contain large enough amounts of dissolved compounds of calcium, magnesium, and similar metals to give the water other undesirable qualities. Such water is known as *hard water*. Extremely hard water feels harsh and unpleasant to the skin. With soap it will not produce a quick and suitable lather when it is used for bathing and laundry purposes. The soap reacts with the compounds in the water to produce a curdy scum which collects on the clothes or leaves a "ring around the bathtub." Hard water is also objectionable for use in boilers and teakettles because boiling the water causes some of these compounds to deposit as boiler scale on the sides and bottoms of the vessels. This not only reduces the heating efficiency, since the scale is a poor conductor of heat, but also damages the boilers by corrosion.

You can eliminate the objectionable dissolved compounds from hard water by the addition of washing soda or borax. A more complete consideration of this subject of hard water properly belongs in a study of calcium and magnesium compounds.

How can all types of impurities be removed from water in one operation? For laboratory uses and some commercial purposes, dissolved impurities are removed from water by a process called *distillation*. This consists of vaporizing the water by heating and then condensing it in a tube, called a condenser, which is surrounded by cold water or air. All suspended matter and all dissolved matter which has a higher boiling point than the water, are left behind. The distillate, which is the water coming from the inner tube of the condenser, will contain only gases and other easily evaporated (volatile) liquids which the original water may have contained. These may usually be removed by discarding the first portion of the distillate.

Two common types of laboratory apparatus used in distilling water and other substances on a small scale are shown in Figures 41 and 42. The first shows an air condenser

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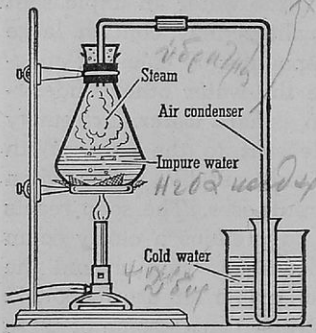
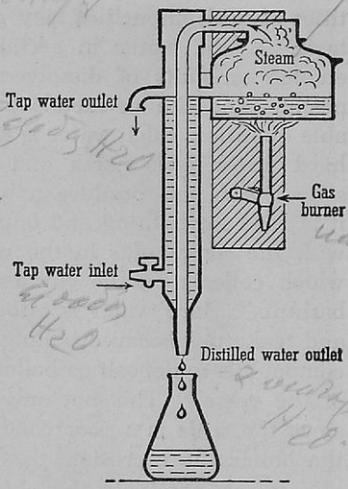


41. SIMPLE DISTILLATION. The liquid in the flask vaporizes and leaves behind any solid impurities. The vapor is then condensed by the water-cooled tubes and the air.



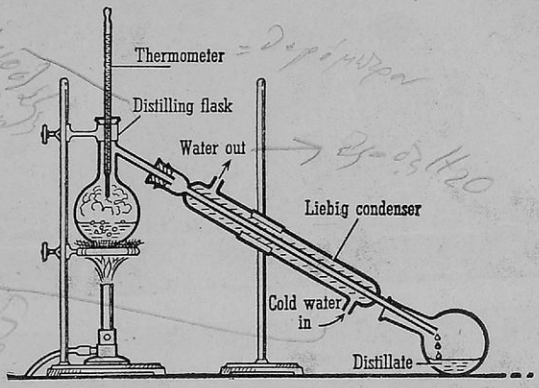
42. LABORATORY DISTILLATION

which is a very simple, though not very effective, device for distilling substances. A more effective setup employs the Liebig condenser (Fig. 43), in which an outer jacket of cold running water serves to condense the steam or other vapor. The upward flow of cold water against the downward flow of the distillate is worthy of notice here, since this "counter current system" is a principle often employed in chemistry. This arrangement permits a more efficient exchange of heat. The colder water in the lower part of the condenser withdraws heat from the coolest portion of the distillate, while the warmer water condenses the hot vapor in the upper part of the condenser.

Most gases are completely removed from water by boiling it. Volatile liquids may be removed by a process of *fractional distillation,* although this process is not usually applied in the purification of water. Fractional distillation is useful in separating a mixture of liquids having different boiling points, such as a mixture of alcohol and water. A more or less complete separation is accomplished by boiling the mixture of

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

liquids at a temperature near the boiling point of the most volatile liquid. The first fractions contain a large proportion of the liquid with the lowest boiling point.



43. DISTILLATION WITH A LIEBIG CONDENSER. The Liebig condenser is more efficient than the air condenser. The cold water surrounds the vapor tube and cools the vapor so it condenses.

The same result may be obtained by using a tall fractionating column through which the vapor passes. The less volatile liquid condenses in the fractionating column while the more volatile liquid passes on into the condenser. In this manner the separation can be made in a single distillation.

How are cities able to provide you with healthful water? Suspended material in water is often in such a fine state of subdivision that it passes through the pores of an ordinary filter. The supply of water for such cities as Kansas City, Cincinnati, and Cleveland is drawn from the rivers (or lake) on which these cities are located and this water contains large amounts of finely divided clay in suspension. In cases of this kind, a solution of aluminum sulfate (known as filter alum) is frequently added to the water. The aluminum sulfate reacts with the dissolved alkaline impurities in the water to form aluminum hydroxide. If sufficient quantities of natural lime or other alkaline substances are not present in the raw

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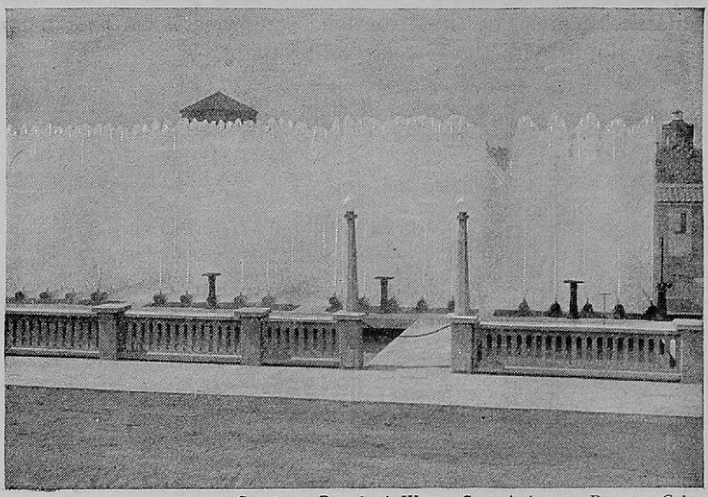

Courtesy, Board of Water Commissioners, Denver, Colo.

44. AERATION SYSTEM USED IN DENVER, COLORADO. In this large western city, water is sprayed into the air. Some undesirable gases are removed in this way; some air is also dissolved in the water. How does this improve the water for drinking purposes?

water, lime must also be added. This method of treating the water removes the greater part of the suspended impurities by *coagulation*. The equation for the reaction is as follows:

$$\begin{matrix}\text{aluminum} \\ \text{sulfate}\end{matrix} + \begin{matrix}\text{calcium} \\ \text{hydroxide}\end{matrix} \rightarrow \begin{matrix}\text{aluminum} \\ \text{hydroxide}\downarrow\end{matrix} + \begin{matrix}\text{calcium} \\ \text{sulfate}\end{matrix}$$

The aluminum hydroxide, known as the *coagulum*, is an insoluble, gelatinous compound which becomes thoroughly mixed with the raw water in the mixing chambers. Then in large chambers, known as sedimentation (settling) chambers, into which the water passes, the aluminum hydroxide settles out and drags down with it finely divided suspended matter. The clearer water is drawn from the top of these chambers and passed through large filter beds, composed of sand and gravel. The combination of coagulation, sedimentation, and

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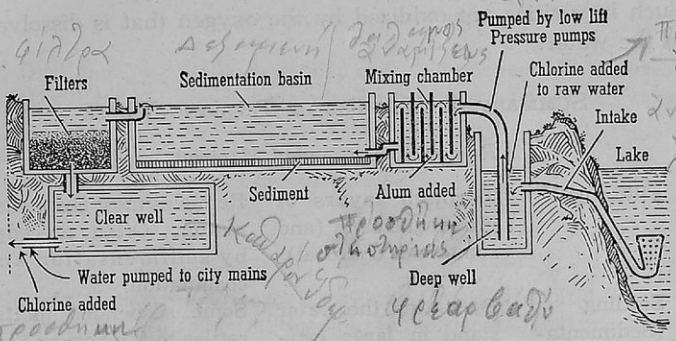

45. HOW WATER IS MADE FIT FOR DRINKING. This is a diagram of a city water plant supplying large quantities of water to a city.

filtration is very effective in removing suspended impurities from water. However, in the complete treatment of water, chlorine usually is added to destroy any bacterial growth which remains in the treated water.

How does nature battle impurities in water? It is interesting to remember that Nature herself has provided for the purification of water on a vast scale. Surface water often is contaminated with much suspended organic matter, such as decaying plants and animals, sewage, and bacteria. As this water settles through the ground, the thick beds of rocks, gravel, and sand act as huge natural filters, removing much of the suspended impurities. In this way deep wells and springs in some localities may become excellent sources of water for household purposes. If a simple chemical analysis of the water shows an unusual amount of chlorides or ammonia, a possible contamination from human wastes and sewage is indicated. As a precautionary measure the purity and fitness of such natural untreated water for drinking purposes should be tested and certified by local or state health authorities.

Nature also provides for the destroying of organic matter (dead fish and refuse) that is in lakes and rivers. If this were not true, bodies of water would become filled with impurities.

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Such impurities are oxidized by the oxygen that is dissolved in the water.

SUMMARY OF METHODS OF TREATING WATER

	Removing Suspended Material	
1. Filtering	Through layers of gravel and sand (and sometimes charcoal)	Removes most suspended matter. Often preceded by sedimentation and coagulation.
2. Settling (Sedimentation)	By letting the water stand in large containers	Some suspended matter settles to the bottom.
3. Coagulating (Coagulation)	By adding "alum" to water, aluminum hydroxide is formed.	Sticks smaller suspended particles together and makes settling and filtering more effective.
	Sterilizing Water to Kill Bacteria	
1. Boiling	From 10 to 15 minutes.	Kills dangerous bacteria and drives off dissolved gases.
2. Ultraviolet light	In sunshine or from mercury arc lamps	Kills practically all bacteria.
3. Chemical treatment	With chlorine, chloride of lime, ozone, or oxygen from the air	Oxidizes much organic matter thereby killing most bacteria. Chlorine treatment is common.
4. Freezing	In winter	Not dependable for killing bacteria. Removes most dissolved solids.
	Removing Hardness from Water	
1. Heating	To boiling point	Removes only carbonate hardness by precipitating compounds which cause it.
2. Adding softening agents	Washing soda, trisodium phosphate, household ammonia, or borax	Precipitates objectionable dissolved calcium compounds by changing them to insoluble compounds.

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Complete Purification of Water

1. Distilling (Distillation)	Boiling and then condensing vapors. First distillate containing volatile impurities may need to be discarded.	Removes all impurities. Very effective but expensive.

Readings for Pleasure and Profit

HOLMES, HARRY N. *Out of the Test Tube.* Chap. VII, pp. 79-89.

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry, Second Series.* Art. 7, pp. 41-48, "Purer Water Supplies." Art. 8, pp. 49-55, "Water; Some Interpretations."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. II, pp. 43-48; 65-74, "Water Purification."

Applying in Life What You Have Learned in Chemistry

"The Rangers" of Hillside School had spent a most enjoyable week of camping, swimming, and fishing at a beautiful site on Lowneck Creek.

During their next-to-last night rain had fallen in torrents and the camp awoke to find that the swollen creek had backed up into the creek-bank spring which was their only source of drinking water. The spring, usually clear and cool, now had a layer of mud on the bottom.

Some of the boys insisted that since the mud had settled the water was safe to drink. Others suggested that the water be filtered through clean canvas. One timid youngster wanted to break camp. What would you have suggested? Justify your recommendations by your knowledge of water purification.

You are an assistant in a laboratory. A question arises as to whether a bottle of water has been distilled or not. What could you do to give a quick answer? What could you do to give a more certain answer?

Which side would you take on the following question: Are the small household filters attached to water faucets a protection or a menace? Explain the stand you take.

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Putting Chemistry to Work

A

(1) A certain household decided to substitute boiled water for distilled water. To what extent and for what purposes was it justified? (2) Tell fully what you would do to make the following kinds of water fit for the purposes indicated: (a) ocean water for drinking; (b) muddy river water for a steam boiler; (c) rain water for drinking; (d) hard water for the laundry; (e) "questionable" well water for washing dishes; (f) hydrant water for a storage battery; (g) lake water for chemical analysis; (h) spring water for drinking. (3) How could the total amount of solid material in a sample of water be determined? (4) Why would you favor a microscopic examination of drinking water? (5) What can be said of the past history of a sample of water that gives positive tests for dissolved ammonia or nitrates?

B

(6) What differences can you point out between *purified* water, *distilled* water, and *sterilized* water? (7) In what sense is water distilled in nature? (8) Explain by means of a diagram the cycle of changes through which water at the earth's surface is continuously passing. Show how the water may be contaminated and purified in its journey. (9) Two-tenths of a pound of chlorine per million pounds of water is usually sufficient to sterilize it. A tank of liquid chlorine contains 25 pounds and costs $4.50. How long would such a tank of chlorine last a city treating 1,500,000 gallons (about 8 pounds per gallon) of water daily? What would be the cost per year? Is this expense justifiable?

Research and Activities That You Will Enjoy

A forum: What are the possible sources of impurities in your city water? How can these dangers be eliminated or decreased?

A report: Explain to the class what this prominently displayed sign means: "This water supply is approved by the State Board of Health."

A discussion: Is the cost of maintaining state and local boards of health justifiable from the standpoint of water supply? How would you go about having a source of drinking water certified?

A demonstration: Materials which are easily oxidized will decolorize a very dilute pink solution of potassium permanganate slightly acidified with sulfuric acid. How would you apply this fact

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in detecting certain impurities in drinking water? (To what types of impurities would this test apply?)

Problem 13

WHAT PROPERTIES OF WATER MAKE IT YOUR USEFUL FRIEND AND SERVANT?

You know, of course, that no one can live without water. It is such a common substance, however, that you may easily overlook its properties and the important everyday uses that *depend on* these properties.

Water in liquid form is used all over the world as a standard of comparison. Why? Water is found in almost all parts of the globe. Its abundance, its wide distribution, its stability, and ease of purification are the reasons for its adoption as a standard for the measurement of several physical units.

Water is used as a standard in expressing weight. The gram is the weight of one milliliter of water. (See page 762.) The metric system of weights, therefore, uses water as a standard. When we speak of water as a standard in expressing weight, we mean water at a temperature of 4° C. This temperature was chosen because, contrary to what one might expect, water shows its greatest density, or weight, at 4° C.

Water is also used as a standard in expressing weight by comparing the weight of a specific volume of some material with the weight of an equal volume of water. The number which expresses the relation between the two weights is known as specific weight, or *specific gravity*. By saying that the specific weight of gold is 19.3, we mean simply that gold is 19.3 times as heavy as an equal volume of water.

Water is used as a standard in determining temperatures. The fixed points on the centigrade thermometer scale were chosen with reference to water. Zero degree centigrade is the freezing point of *water* and 100° C. is the boiling point of *water* under normal atmospheric pressure (760 mm of mercury).

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Effect of pressure on boiling point. The boiling point of water (and all liquids) is noticeably changed by the pressure on its surface. When the pressure is lowered, the boiling point is also lowered because steam or vapor can escape more easily. On the other hand if the pressure is increased, the boiling point is correspondingly higher. Under reduced pressure rapid evaporation of a sugar solution occurs without danger of scorching the sugar. The pressure cooker, a familiar device in many homes, employs an increase in pressure to permit a higher temperature and hence more rapid cooking of foods. Its use is especially desirable in mountainous country where the atmospheric pressure and consequently the boiling point of water is low.

Water is used as a standard in expressing amount of heat. Temperature alone is *not* an indication of how much heat a substance contains or is able to give up. You know that a teacup of boiling water at 100° C. thrown into a snowdrift will not melt as much snow as a gallon of water at room temperature, 20° C. In other words, a thermometer measures the intensity of heat but it does not measure the amount of heat.

The amount of heat (and other forms of energy as well) depends on *two* factors, an *intensity* factor and a *capacity* factor. Your studying is somewhat similar. The amount of studying you do depends not only on *how long* you study (capacity factor), but also on *how hard* you study (intensity factor). In the case of heat, the intensity is determined with a thermometer and is indicated as temperature. Heat *capacity* differs for different substances. The heat capacity of water is greater than the heat capacities of other substances. *One gram of water* was chosen as the standard for comparing the heat capacity of different substances.

Amount of heat is measured in calories, abbreviated *cal.* The calorie, often called the small calorie, is the *amount of heat required to raise the temperature of one gram of water one degree centigrade.* It takes less than one calorie of heat to raise a gram of other substances one degree centigrade.

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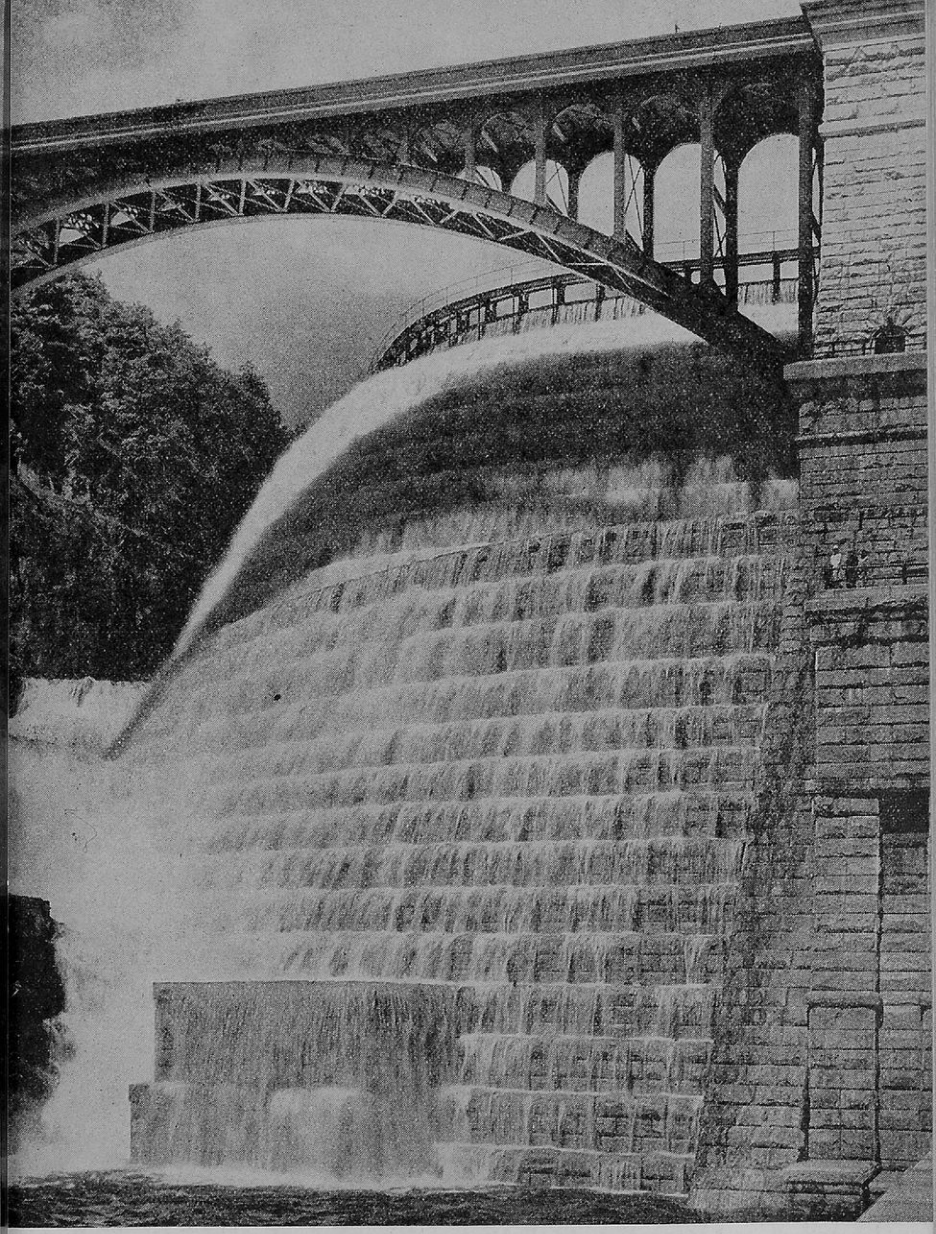

Ewing Galloway

MAN'S GREAT BLESSING. Pure water is an essential for health. The building of water systems to provide wholesome drinking water for crowded metropolitan areas is one of the most difficult problems of modern life. Here is the Croton Dam which helps to purify water for New York City by allowing it to flow in thin streams over the dam.

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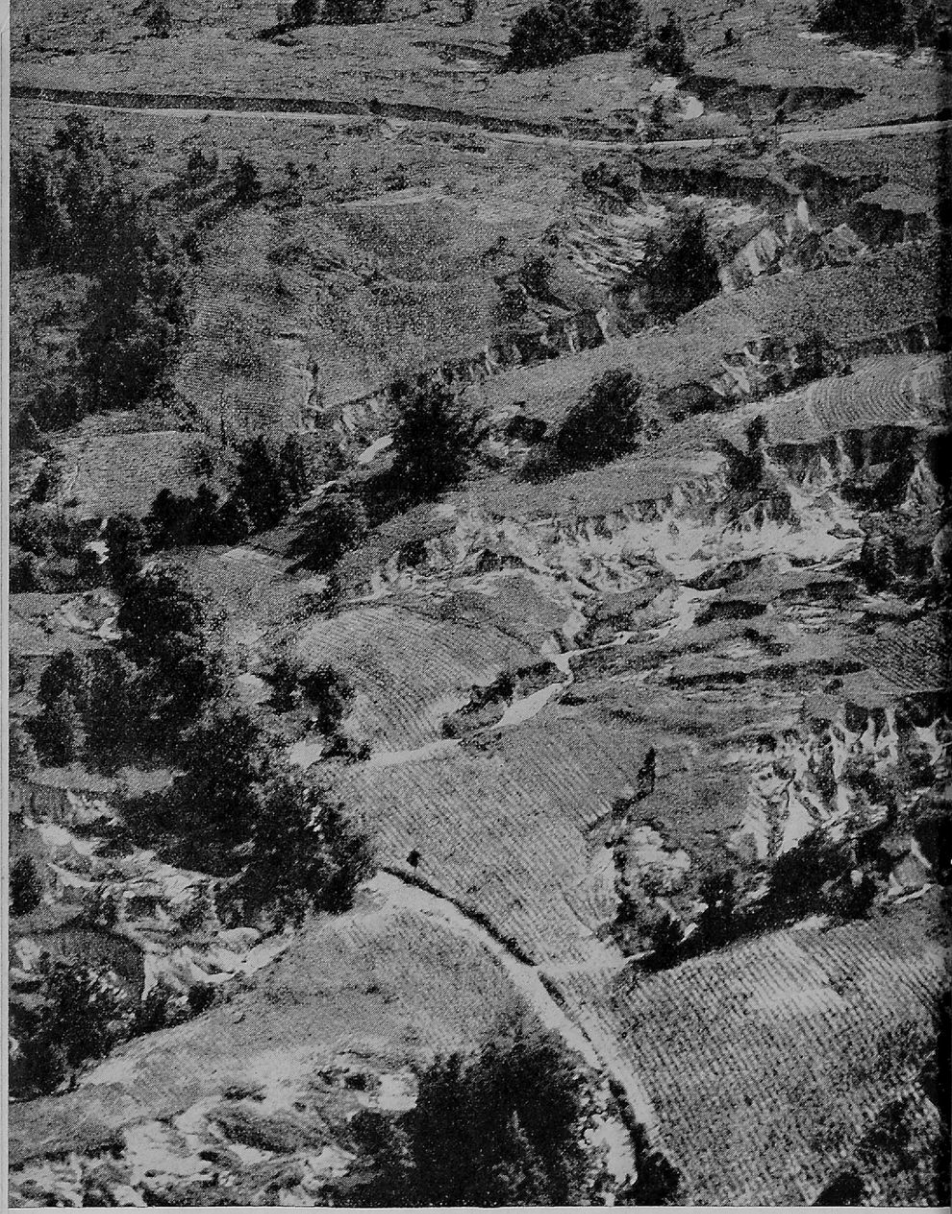

Courtesy, Bureau of Agriculture

WATER DOES DAMAGE. Many people have acted as if soil is indestructible. Here is a view of how it may be ruined by running water. When vegetation is removed, erosion often carries away the soil which nature took millions of years to make. "These things ought not to be."—Eccles.

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The calorie is a metric unit. The English unit of heat is the British thermal unit, abbreviated B.T.U., which similarly is the amount of heat needed to raise the temperature of one pound of water one degree Fahrenheit. One B.T.U. is equivalent to 252 calories. The large calorie, abbreviated Cal., is the kilogram-calorie. It is equal to 1000 small calories. The large calorie is used in expressing the heat value of foods.

Water in the form of steam runs many machines. Why? When water is changed to steam by heating it, a very great increase in volume occurs. Steam under one atmosphere of pressure occupies about sixteen hundred times as much space as the same weight of water. Confining steam produces the very great pressures utilized by steam engines.

Water and steam are used in radiators to heat many of your homes. Why? The amount of heat required to warm water or the amount of heat which water liberates when it cools is greater than the heat exchange of any other common substance. The heat that is required to warm one gram of water will warm to the same extent about 5 grams of aluminum, about 10 grams of zinc or copper, about 20 grams of silver or tin, or about 30 grams of mercury or lead. Also one gram of water cooling one degree will liberate about five times as much heat as one gram of aluminum undergoing the same temperature change.

This is one reason why hot water is often used in the radiators of heating systems in homes or automobiles. On the other hand, water is the cheapest and also is the most efficient cooling agent in auto radiators. It is well known that a large body of water has a distinct influence on the climate of adjacent land areas.

If you have been so unfortunate as to receive a burn from steam, you know that such a burn is often more painful and serious than one caused by hot water. This suggests that steam has more heat in it than hot water even though the temperature is the same. These illustrations perhaps may be better understood by noting the following paragraph and the accompanying chart.

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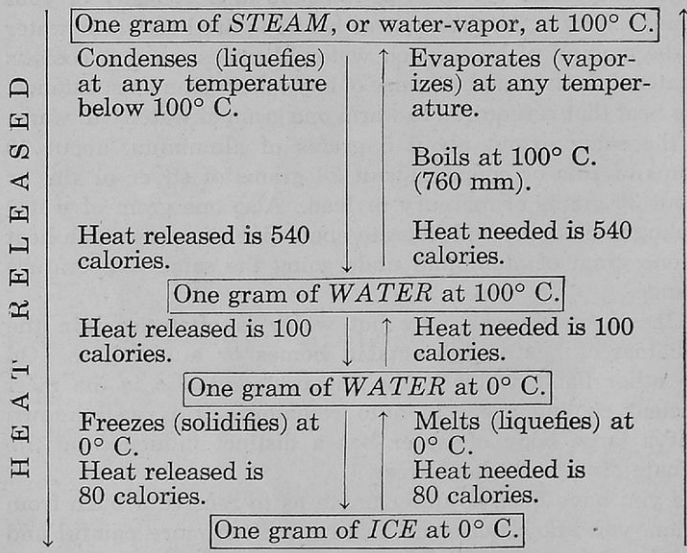
Ice ⇄ Water ⇄ Steam: How much heat is involved? Having learned to measure heat in calories, you are ready to see how much heat is required to melt ice and to vaporize water. If a small piece of ice is dropped into some water, the ice will melt by withdrawing heat from the surrounding water. It can be calculated that each gram of ice requires 80 calories to melt it. This quantity of heat is needed to melt one gram of ice at 0° C. to one gram of water at 0° C. Eighty calories is the *heat of fusion* of ice. In a similar manner, 540 calories are required to convert one gram of water at 100° C. to one gram of steam at 100° C., so 540 calories is the *heat of vaporization* of water. These ideas are brought out in the accompanying diagram.



Water in the form of ice cools and preserves foods. Why? You can hardly imagine dropping a piece of ice-cold steel in a glass of water to cool it for drinking purposes. Yet, a chunk of ice-cold steel would not cool a glass of water nearly so

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much as a piece of ice with the same weight and the same temperature. This is perfectly understandable when you note the preceding paragraph and see that it takes 80 calories of heat just to melt one gram of ice, without raising its temperature a fraction of a degree. This capacity for absorbing heat is utilized in ice refrigerators. As the ice melts it absorbs heat from the comparatively warm food.

What happens when water freezes? When it is cooled sufficiently, water (freezing point, 0° C.) changes to ice and in so doing expands about one-ninth of its volume. For this reason, ice is lighter than water and therefore floats.

However, both above and below 4° C., water expands slightly and is correspondingly less dense. This relation between the temperature and the density of water has a profound bearing upon aquatic life by hindering the complete freezing of a deep body of water in the winter. As water cools to 4° C. it becomes heavier and settles. Consequently, when the water temperature is higher than 4° C., the coldest water is always at the bottom. On the other hand, as water cools *below* 4° C., it becomes lighter. As a result, the coldest water is now at the top, and when it begins to freeze, the ice always forms at the surface, not at the bottom.

It is interesting to note that the downward movement of dense water carries a supply of dissolved oxygen to the living organisms at lower levels.

Water dissolves many substances—this is one of its most important uses. One of the most familiar characteristics of water is its ability to dissolve many substances, thus forming solutions. As you know, the majority of the reagents in your laboratory are aqueous solutions—substances dissolved in water. Solutions play an important part in your everyday life and in industry. The interesting story of how solutions are made and used comes later in this unit.

The importance of solutions is further emphasized by the fact that the vast majority of chemical changes occur in solution. Many substances which react slowly, if at all, in the dry state show a marked tendency to react when in solution.

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Water combines chemically with many substances. *With metals.* The more active metals such as sodium, potassium, and calcium react with water. When the reaction occurs, half of the hydrogen combined in the water is liberated; the other half unites with the metal, forming the hydroxide of the metal.

With metallic oxides. Water combines directly with many metallic oxides to form a class of compounds known as *bases,* such as sodium hydroxide (lye) and calcium hydroxide (lime-water). For this reason, metallic oxides are known as *basic anhydrides* ("bases without their water"). Soluble bases all have similar properties and turn litmus paper blue.

Calcium oxide + water → calcium hydroxide, a *base*
Sodium oxide + water → sodium hydroxide, a *base*

The general word equation is:

Metallic oxides + water → metallic hydroxides, or *bases*

With nonmetallic oxides. A similar reaction occurs when water combines with the oxides of the nonmetallic elements such as carbon and sulfur. In this case the products turn litmus paper red and are known as *acids.* Nonmetallic oxides are *acidic anhydrides.*

Carbon dioxide + water → carbonic acid
Sulfur dioxide + water → sulfurous acid
Phosphorus pentoxide + water → phosphoric acid

The general word equation is:

Nonmetallic oxides + water → nonmetallic hydroxides, or *acids*

Hydrates. Often when substances separate from solutions as crystals, they may take from solution a definite proportion of water to help form an essential part of their crystalline structure. The water is combined so loosely that it may be released with gentle heating. This water is known as *water of hydration* and the crystals are called hydrates. Blue crystalline copper sulfate, $CuSO_4 \cdot (H_2O)_5$, is an example of a hydrate.

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Water often acts as a catalyst. In many chemical reactions water acts as a catalyst. It is well known that dry iron will not rust easily, but when moisture is present it rusts rapidly. Later you will learn of other chemical reactions in which water serves as a catalyst. Among these is the reaction of hydrogen and chlorine. A mixture of hydrogen and chlorine with a trace of water as a catalyst will unite explosively when brought into the sunlight, but will not combine if the gases are perfectly dry.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XII, pp. 168-177, "Water."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. VII, pp. 99-103, "Water and Its Properties."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. VII, "The Elixir of Life."

Applying in Life What You Have Learned in Chemistry

Mrs. Keppler was worried. It was bad enough for the ice bill to go "sky-high" during the last few torrid days of July. But it was worse to have all the ice in their small icebox melt by the middle of the afternoon and then find that the milk had soured during the night. Mrs. Keppler turned the vexing problem over to her daughter, Janet.

Janet made a recommendation. "You see, Mother," she explained, "all we need to do is to wrap the ice in several layers of newspaper. That will keep the ice from melting so fast." So it was done.

The next morning they were pleased to find a large piece of ice remaining in the icebox. But imagine their disappointment to find the milk sour as usual!

How would a knowledge of water have helped Janet from making such a common error?

The news goes around at your summer cottage on the lake that several cases of typhoid fever have developed presumably from drinking well water. Your parents decide to boil all drinking water. You find, however, that the water has a "flat" taste. What is the cause of the different taste, and what will you do about it?

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Putting Chemistry to Work

A

(1) Why are tubs of water sometimes placed in unheated vegetable cellars in the winter? (2) Why is a burn from steam likely to be more painful than a burn from boiling water? (3) How is it possible for a "three-minute" egg to become a "six-minute" egg in mountainous country? (4) Serious accidents have occurred when pressure cookers have been opened without first permitting them to cool. Explain what happens. (5) Is water which is boiling vigorously hotter than water which is boiling slowly? Explain your answer.

B

(6) From the standpoint of absorbing heat, give two reasons why water is usually a good fire extinguisher. (7) Explain how melting ice keeps the food in a refrigerator cool. (8) The temperature of boiling water at atmospheric pressure does not rise as heating is continued. What becomes of all the heat that is added? (9) Directions for a certain chemical procedure say that a solution should be boiled for 20 minutes. Chemists in the Rocky Mountain States fail to obtain satisfactory results unless the solution is boiled 25 minutes. Can you explain this?

How Good Are You at Solving Problems?

(1) How many calories of heat are needed to change 10 grams of ice at 0° C. to water at 0° C.? to change 10 grams of ice at 0° C. to water at 17° C.?

(2) How many calories of heat are involved in changing 10 grams of water at 100° C. to steam at 100° C.? What becomes of the heat absorbed?

(3) How many *large* calories of heat are involved in changing 100 grams of ice at 0° C. to steam at 100° C.?

(4) A quart of milk (1074 g) at room temperature (20° C.) is placed in an ice refrigerator. Approximately how many grams of ice will melt in cooling the milk to 8° C.? (What assumptions do you make in order to solve this problem?)

Research and Activities That You Will Enjoy

A discussion: On the basis of the kinetic-molecular theory, explain the changes in the physical state of water.

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A report: The albumin in milk coagulates at 66° C. In making evaporated milk how is the water removed without coagulating the albumin?

A demonstration: Plan and perform a demonstration to show that the boiling point of water changes with changes in pressure.

Problem 14

WHAT IS WATER?

You already have learned some of the reasons why scientists believe that matter is made up of molecules. Scientists also believe that molecules of matter are composed of smaller particles called atoms. Chemical changes are very largely due to the characteristics of atoms. Your next unit in this book indicates some of the reasons why scientists believe that there are such things as atoms. This problem gives you an interesting foundation for a better understanding of the next unit.

Water is a stable compound of oxygen and hydrogen. Water is a very stable compound; that is, it is not easily decomposed by heating. At very high temperatures, however, water decomposes slightly into its constituent elements.

$$\text{Water} \rightleftarrows \text{hydrogen} + \text{oxygen}$$

At 2000° C. and under ordinary pressure, fewer than 5 molecules in every 500 molecules of water vapor are decomposed. And as the temperature is lowered, the oxygen and hydrogen recombine unless they have been separated from each other before cooling. The reaction shown by the above equation is a *reversible one,* indicated by the double arrow.

Water is a combination of 2 parts hydrogen and 1 part oxygen —by volume. There are two methods of determining the composition of a compound. One is to tear the compound apart (analysis) to see of what elements it is composed and the amounts of these elements. The other method is to permit

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the elements to unite (synthesis) in order to determine in what ratio they combine. The first method is more frequently used, but the latter is probably more fascinating and convincing. If the compound is composed of elements which ordinarily are gases, we may express its composition *by volume* (volumetrically), by determining the volumes of the gases which are united. A more common expression of the composition of a compound is *by weight* (gravimetrically), since this method may be applied to any compound.

Analysis of water by volume. You have already seen on page 71 (Fig. 31) that water may be decomposed by using an electric current and that this process is known as electrolysis. If an allowance is made for the unequal solubility of hydrogen and oxygen in the water, a careful measurement of the volumes of the gases produced by this reaction shows twice as large a volume of hydrogen as of oxygen. This shows that water is composed of hydrogen and oxygen in the ratio 2:1 *by volume.*

Synthesis of water by volume. The decomposition of water may be reversed by permitting the hydrogen and the oxygen to combine. This is done in a graduated hard glass tube called a *eudiometer tube* (Fig. 46). This tube is fitted with the proper connections for passing an electric spark through the mixture of gases to cause them to combine. When two volumes of hydrogen are mixed with one volume of oxygen and the mixture ("electrolytic gas") is exploded, the steam formed by the reaction condenses to water and the hydrogen and oxygen are completely used up.

In actual practice, however, the gases are not mixed in the exact ratio in which they combine since the explosion, without a cushion of remaining gas to take the shock, might break the eudiometer tube. Suppose 20 ml of hydrogen and 18 ml of oxygen under the same conditions of pressure and temperature are mixed and exploded in the eudiometer. After the volume of the remaining gas is corrected to the above conditions, it will be found to occupy exactly 8 ml and a test will show that only oxygen remains. The slight volume

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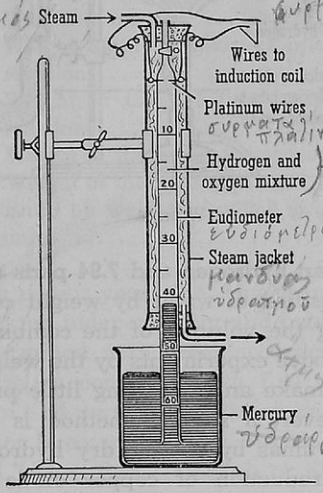
of the condensed water is negligible. This is further proof that hydrogen and oxygen combine in the ratio of 2:1 by volume.



Hydrogen and oxygen combine in the ratio of two volumes of hydrogen to one of oxygen. This mixture shrinks one-third in the combination leaving two volumes of water vapor. The mixed gases are collected over mercury. The eudiometer (gas-measuring tube) is surrounded by a steam jacket so that the water produced by the reaction will be in the form of gas (steam). A spark between two short platinum wires attached to an induction coil ignites the mixture.

46. SYNTHESIS OF WATER BY VOLUME

A striking fact can be learned if the eudiometer tube is surrounded by a steam jacket so the reaction can be carried out at 100° C. and the product of combination (steam) will remain in the gaseous state. Again suppose a mixture of 20 ml of dry hydrogen and 10 ml of dry oxygen (both at 100° C.) is exploded in the eudiometer. You may be greatly surprised to find that 20 ml of gas remain, a volume equal to the volume of the hydrogen and twice as large as the volume of oxygen. Since you know by the above experiments that the hydrogen and oxygen are completely used up, the remaining gas must be steam. Then you can extend the volume relation to:

$$\underset{2\text{ vols.}}{\text{hydrogen}} + \underset{1\text{ vol.}}{\text{oxygen}} \rightarrow \underset{2\text{ vols.}}{\text{water (steam)}}$$

What volume of oxygen will combine with 7.5 l of hydrogen? What volume of steam will result?

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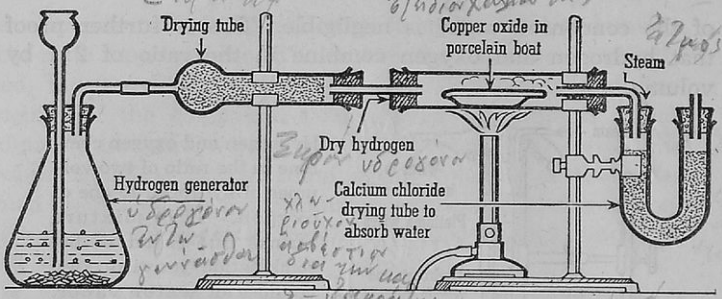

47. SYNTHESIS OF WATER BY WEIGHT

Water is a combination of 1 part hydrogen and 7.94 parts oxygen—by weight. The composition of water by weight could be determined by multiplying the volumes of the combining hydrogen and oxygen in the above experiments by the weights of these gases, which would make an interesting little problem for you to solve. However, a simpler method is one employed by Berzelius and Dumas by passing dry hydrogen over heated copper oxide (reduction of copper oxide by hydrogen). See page 80 and Fig. 38. Think through this method of determining the composition of water. Answer the following questions; then on a separate sheet of paper use the following data to solve the problem for yourself.

1. What materials would you use to generate hydrogen?
2. Why should the hydrogen be purified?
3. How is the hydrogen dried?
4. What reaction occurs in the glass tube containing the heated copper oxide?
5. What is the purpose of the second calcium chloride tube?
6. Will the weight of the material of heated copper oxide in the glass tube increase or decrease as the hydrogen passes over it and what will this change of weight be equal to?
7. How will the second calcium chloride tube change in weight and what will the change in weight be equal to?
8. How will the weight of combined hydrogen be found?

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DATA

(a) Weight of copper oxide before reaction..... 52.869 grams
(b) Weight of the copper oxide and the copper after reaction ..... 44.869 grams
(c) Weight of oxygen ..... _____ grams
(d) Weight of the calcium chloride tube before the reaction ..... 80.483 grams
(e) Weight of the calcium chloride tube after the reaction ..... 89.483 grams
(f) Weight of the water formed..... _____ grams
(g) Weight of the hydrogen used..... _____ grams
(h) Ratio by weight in which hydrogen and oxygen unite ..... _____ : _____

In recent years the American chemists, Morley and Noyes, working independently and using more refined methods, have determined with great accuracy that *one part by weight of hydrogen combines with 7.94 parts by weight of oxygen* to form 8.94 parts by weight of water. Expressed as percentages, water is composed of $1 \div 8.94 = 0.1119$, or 11.19% hydrogen and $7.94 \div 8.94 = 0.8881$, or 88.81% oxygen by weight.

It has been shown that any amount of water that you may think of is composed of 1 part of hydrogen to 7.94 parts of oxygen by weight. Do you not think, therefore, that the smallest possible particle of water, the molecule, is also composed of 1 part of hydrogen to 7.94 parts of oxygen by weight? Some interesting points concerning this question will be discussed in your next unit.

Applying in Life What You Have Learned in Chemistry

Ernest Invenit had just put the finishing touches to his great scheme to revolutionize the power question. He looked over it approvingly. Wouldn't he show his Dad a thing or two even though Dad was an engineer? Wonder why someone hadn't thought of it before!

"You see, Dad," explained Ernest enthusiastically, "all I have to do is to boil water at a very high temperature—under pressure, of course—and separate the gases by letting the hydrogen pass through porous plates. Our chemistry instructor demonstrated

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that this morning. You know hydrogen molecules will go through the walls of a porous cup because hydrogen molecules bounce much faster than other molecules do. Then I'll burn the hydrogen under the boiler to make the water boil and probably have plenty of hydrogen to spare. Isn't that a good idea? Will you patent it for me?"

"Now wait just a minute, son," replied the unenthusiastic father. "Haven't you overlooked a small point here? Didn't you also learn in that chemistry class of yours something about the stability of water? So I'm afraid your plan won't work."

Putting Chemistry to Work

A

(1) How does a mixture of one gram of hydrogen and eight grams of oxygen differ from nine grams of water? (2) In determining the composition of water by the electrolysis method, why are the first results slightly misleading? What can be done to eliminate this slight error? (3) Water is approximately eight-ninths oxygen by weight. Then why is it not a good oxidizing agent? (4) In determining the composition of water by the synthetic method, why do we usually disregard the volume of water formed? (5) Someone objected to the use of water for putting out very hot fires because the water would decompose and thus release hydrogen which would burn and increase the fire. What do you think about this?

B

(6) Interpret the following statements so they will be in agreement: "Water is composed of 2 parts of hydrogen and 1 part of oxygen"; "The composition of water is approximately 1 part hydrogen and 8 parts oxygen"; "The composition of water is H, 11.19 and O, 88.81." (7) When hydrogen and chlorine combine to form hydrogen chloride, the reaction is shown by, $H_2 + Cl_2 \rightarrow 2\,HCl$. What does this equation show about the volumes of the gases involved? (8) When sodium oxide (Na_2O) reacts with water, why is no hydrogen set free? (9) How is it possible for 10 ml of hydrogen to combine with 5 ml of oxygen to form only 10 ml of steam?

How Good Are You at Solving Problems?

(1) An electric spark is permitted to pass through a mixture of 8 grams of oxygen and 4 grams of hydrogen. How many grams of

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water will be formed? Will either gas remain? If so, how much by weight?

(2) A mixture of 20 ml of oxygen and 10 ml of hydrogen is exploded in a eudiometer tube. After the steam condenses, will a quantity of either gas remain? If so, how much?

(3) If you have not already done so, find the composition of water from the data given on page 111.

(4) When ammonia was passed over hot copper oxide in an apparatus similar to the one shown in Fig. 47, the copper oxide was reduced as shown:

$$3\,CuO + 2\,NH_3 \rightarrow 3\,Cu + 3\,H_2O + N_2$$

During the reaction the copper oxide lost 17.91 grams in weight, while the calcium chloride tube gained 20.16 grams in weight. What is the composition of water according to these data?

(5) Calculate the composition of air by volume from the following data: a mixture of 100 ml of hydrogen and 100 ml of air is exploded in a large eudiometer. 137 ml of gas remain.

Research and Activities That You Will Enjoy

A demonstration: Set up the apparatus and demonstrate for the class how to determine the composition of water by weight.

A report: Through outside reading prepare a report on the life and work of Edward Morley.

A chart: Make a chart picturing how two volumes of hydrogen combine with one volume of oxygen to produce two volumes of steam. (What assumption do you make here?)

Problem 15

WHAT IS A SOLUTION?

The most important physical property of water is its ability to dissolve many substances. There is scarcely a substance that does not dissolve in water to some extent. In fact, it often is called the "universal solvent." Pure distilled water that has stood in glass for a short time shows definite tests for substances dissolved out of the glass. As you would expect, these tests are delicate.

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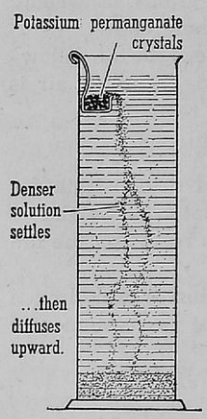
A substance which is dissolved is called a *solute*. A substance which does the dissolving is a *solvent*. The resulting mixture is a *solution*. A knowledge of what happens when a substance goes into solution, and of the nature of the solution formed, is most helpful in understanding many of the problems in everyday activities.

A solution is a uniform mixture; a sample taken from the top of a sugar solution is just as sweet as a sample taken from the bottom. You perhaps know from experience that any part of a sugar solution tastes the same. The uniform taste is one indication that the sugar solution is a uniform mixture. In this connection note also the following: If a few crystals of potassium permanganate are suspended in a paper stirrup in a cylinder of water just below the surface (Fig. 48), soon streams of a purple solution will be seen settling to the bottom. This shows that the density of this solution is greater than the density of the solvent. After settling, the colored solution begins to diffuse through the whole volume of water. In a short time the entire volume of water is uniformly colored. It will remain so indefinitely since there is no tendency on the part of the solute to settle out. In other words, a solution contains the solute uniformly distributed throughout the solvent. Unless the solute is highly colored, the solution is clear and transparent. If the solution is colored by the solute, the depth of color may be used as a rough indication of the amount of solute.



48. CRYSTALS HANGING IN SOLUTION

A solution is a molecular dispersion; for example, in a sugar solution the molecules of sugar are separated from each other and mixed uniformly with the water molecules. Although you cannot see the molecules of a substance, you know that the dissolved particles in a sugar solution are very small because the solution is clear.

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Even a very small amount of potassium permanganate imparts a deep purple color to a liter of water. Although this solution can be diluted to one hundred liters, the purple color is still plainly visible. It is quite evident that the solute is in an extremely minute state of division. It is estimated that the dissolved particles in solutions are probably at least as small as molecules. This is what the chemist means when he calls a solution a molecular dispersion (scattering) of one substance in another substance.

Later we shall find that the dispersed particles vary in size, extending from those which are smaller than molecules to those which consist of groups of molecules bound together.

The temperature falls when ammonium nitrate is dissolved in water; the temperature rises when ammonia gas is dissolved in water. Why is this? During the process of solution there are energy changes. If a handful of ammonium nitrate is stirred into about 200 ml of water, the temperature of the solution will drop about 20° C. This shows that energy is needed to overcome the forces which hold the molecules together in the solid state. The water supplies this energy and the temperature of the solution is lowered.

On the other hand, if ammonia gas is passed into water, there is a decided rise in temperature. In this case about 800 ml of gas dissolve in 1 ml of water. It is evident that the solution of this large volume of gas in water must liberate energy in the form of heat due to compression of the gas.

Many solids behave like ammonium nitrate, and many gases act as ammonia does; but sometimes opposite results are obtained when solutions are formed.

Fifty ml of alcohol dissolved in fifty ml of water make only ninety-six ml of solution. On the other hand, several small lumps of sugar will dissolve in a beaker of water without increasing the volume of the water. A solution of ammonium chloride has a *greater* volume than the sum of the volumes of the solvent and the solute. There is no satisfactory explanation to account for the volume changes that occur during solution.

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The freezing point of a solution is lower than the freezing point of the solvent; the boiling point is higher—unless the solute is a volatile one. In general, these changes in a solution are proportional to its concentration. If, for example, a certain quantity of sugar dissolved in a liter of water lowers the freezing point of the solution a certain number of degrees, twice the amount of sugar will lower the freezing point twice as much. Application is made of this principle in the "antifreeze" solutions used for auto radiators. Very careful measurements show that this effect depends on the number of dissolved particles present; that is, an equal number of dissolved molecules causes an equal lowering of freezing points of two solutions. One gram-molecular weight (molecular weight in grams) of sugar dissolved in a liter of water lowers the freezing point 1.86° C. and raises the boiling point 0.52° C. In advanced work this furnishes a method for estimating molecular weights.

It is interesting to note here that the freezing point of a solution of an acid, a base, or a salt is lower and its boiling point is higher than you might expect from the concentration of the solute. Later you will find an interesting explanation for the "abnormal" freezing points and boiling points of solutions of these three classes of substances.

What is a dilute solution? a concentrated one? a ten per cent solution? Since solutions are mixtures, the ratio of quantities of solute to solvent may vary to any degree up to the point of saturation. In general, when the amount of solute is relatively small, the solution is said to be *dilute.* A solution containing a relatively large quantity of solute is a *concentrated* one. Most of the solutions in the reagent bottles in your laboratory are dilute solutions. The acids in the large stock bottles may be concentrated. The term "strong" is not used in this connection but is reserved for another condition.

The words dilute and concentrated do not refer to very definite amounts of solute. A more precise way of expressing concentration is by the use of percentages by weight. A 10 per cent solution of sulfuric acid contains 10 grams of hydro-

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gen sulfate and 90 grams of water in 100 grams of solution. Ordinary hydrogen peroxide is a 3 per cent solution of hydrogen peroxide in water. Vinegar is about a 4 per cent solution of acetic acid in water.

What is a saturated solution? Suppose a small amount of powdered potassium chlorate is added to 100 ml of water in a small flask and it is shaken to hasten the dissolving. It is found that the compound readily dissolves. If more of the solute is added and the shaking repeated, a point is finally reached when no more will dissolve—the conditions of the experiment (temperature and pressure) remaining the same. The solution is then said to be *saturated.* A saturated solution is one which contains all the solute that it can hold in the presence of undissolved solute of the same kind. An *unsaturated* solution contains less solute than is required to form a saturated solution at the same temperature and pressure.

Heating the above saturated solution in the absence of undissolved solute will cause it to become unsaturated at a higher temperature. To saturate it again it is necessary to add more of the potassium chlorate until all dissolves that will at the higher temperature. The solution will now contain more than eight times as much solute at 100° C. as was necessary to saturate it at 20° C. If the solution is cooled rapidly by holding the flask under the cold-water tap, a mass of fine crystals forms until only the amount of dissolved material needed to form the saturated solution at the lower temperature is left in the solution. Cooling the solution more slowly will cause larger crystals to form, but the quantity of material which crystallizes out of the solution is the same in both cases. Rapid cooling results in the formation of small crystals like fine granulated sugar; a longer time permits larger crystals to grow like coarse sugar or rock candy.

A saturated solution is in equilibrium. When table salt is placed in water, at first the salt dissolves rapidly, then more slowly, until the solution becomes saturated. Crystallization will occur when the saturated solution is cooled. While solution and crystallization may be thought of as opposite changes,

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both are taking place at the same time—but often at different speeds. When the rate of dissolving is greater than the rate of crystallizing, the solution is an unsaturated one and the change can be indicated as:

$$\text{Solid salt} \underset{\text{(crystallizing)}}{\overset{\text{(dissolving)}}{\rightleftharpoons}} \text{Dissolved salt}$$

As more salt dissolves, the speed of solution (shown by the upper arrow) becomes less while the speed of crystallizing (lower arrow) becomes greater. Presently, the rate of dissolving and the rate of crystallizing become equal and at this point the solution becomes a saturated one.

$$\text{Solid salt} \underset{\text{(crystallizing)}}{\overset{\text{(dissolving)}}{\rightleftharpoons}} \text{Dissolved salt}$$

More accurately, then, a saturated solution is a solution in which the speeds of dissolving and crystallizing are equal. A saturated solution aptly illustrates *physical equilibrium* (balance).

Can you make a solution more than saturated? When saturated solutions of certain substances (such as sodium sulfate, sodium acetate, and sodium thiosulfate or "hypo") are cooled, crystallization may not occur as you might expect. Since these solutes are much less soluble at low temperatures than at higher temperatures, you have here examples of solutions containing greater quantities of solutes than they normally would. Such a solution is known as a *supersaturated solution.* If a small crystal of the solute is dropped into the solution, rapid crystallization takes place and the same amount of heat is liberated that was absorbed during solution. This is an interesting sight which your instructor may wish to demonstrate for you. Since a supersaturated solution is in an unstable condition, it is rather difficult to form and to keep one.

Many solutions do not contain water. Solutions containing solvents other than water behave much like water solutions. Some of the more common solvents are *alcohol, ether, glycerin,* and light petroleum oils like *benzine* and *naphtha.* Essential

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oils which are found in flavoring extracts and perfumes come to us as alcoholic solutions. Alcoholic solutions of nonvolatile substances are known as *tinctures*. Tincture of iodine is an example. Fats and greases are soluble in naphtha. Dry cleaning consists of dissolving such substances in solvents other than water and thus removing them from the clothing.

There are also solutions of one molten metal in another. When such solutions cool and solidify, we have *alloys*. The low melting point of some bismuth alloys is due to the fact that the metals dissolved in the bismuth lower its freezing point (melting point) just as salt lowers the freezing point of water. The term "solid solutions" often is applied to alloys.

Some mixtures only resemble solutions. If some very fine sand is stirred in water, the largest grains of sand will settle most rapidly when the water becomes quiet. The medium-sized grains will settle more slowly, while the smallest grains may require several minutes or longer to settle. Muddy water will settle fairly completely if given time. Since muddy water is not uniform, and since the mud may be removed by filtering, it is not a "true" solution. Such mixtures as fine particles of mud in water are called *suspensions*, and the mud is said to be suspended in the water.

Alcohol and water dissolve in each other in all proportions; they are said to be *miscible*. On the other hand, oil and water do not dissolve each other; they are *immiscible*. But if the oil is shaken with the water, the oil droplets for a short time will remain suspended in the water. Soon, however, the droplets will coalesce (run together) and separate as a layer of oil. If each droplet is surrounded with a film of some material like soap which holds the droplets apart and prevents them from running together, they will remain suspended in water some time. Such a suspension of one liquid in another is known as an *emulsion*. The material which causes the separation to be more complete is the emulsifying agent. The cleansing action of soap depends on the formation of an emulsion of the oil or grease (dirt) so it may be washed away more easily by the water.

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If you examine some starch paste in water, you will find that starch does not settle; neither can it be filtered out of the solution. On the other hand, if you pass a strong beam of light through it, you can see the path of the light because the particles of starch are large enough to scatter the light. A solution of sugar does not show the path of light; dissolved sugar particles are not large enough to scatter light. Here then you have a mixture containing particles which are not large enough to act like a suspension or small enough to behave as a solution would. Such a mixture is called a *colloidal dispersion*. The study of the colloidal state is an important part of chemistry which will be taken up in Unit 10.

Applying in Life What You Have Learned in Chemistry

Poor Susan! She had sat down on a wad of chewing gum. It looked as if her new dress were ruined.

"I've ruined my dress!" cried Susan. "I've tried everything I know to get it off. I scraped as much off as I could and tried soap and water but the rest won't come off. What can I do?" she asked Jane.

Jane remembered about solvents for gums.

"Come over to my Dad's store and I'll have it off in a jiffy," she promised.

What did Jane probably have in mind? What would you have done?

"I wouldn't use that tincture of iodine," warned Henrietta. "The bottle has been sitting there several days with the stopper out."

"Oh, it's surely all right; it's still iodine, isn't it?" returned her classmate.

The next day Henrietta's friend not too proudly displayed a blistered finger. What probably happened?

Putting Chemistry to Work

A

(1) Why is distilled water preferred to tap water in the preparation of laboratory solutions of reagents? (2) How is it possible for a boric acid solution to be saturated and dilute at the same

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time? (3) What would you do to follow the laboratory directions, "Concentrate by evaporation"? (4) Directions for a certain varnish remover called for a hot 8 per cent solution of trisodium phosphate. How would you prepare such a solution?

(5) What would you do to obtain solid material from a hot saturated solution? from a cold unsaturated one? (6) How can you determine whether a solution is *saturated, unsaturated,* or *supersaturated* after dropping a crystal of the solute into the solution? (7) Why should bottles of emulsions used as medicines be shaken before being used? (8) What is a saturated solution?

B

(9) Tell how a solution differs from water in respect to three physical properties. (10) Give a molecular explanation for the fact that the volume of a mixture of water and alcohol is less than the sum of their volumes before they are mixed. (11) What characteristics are shown by an ideal solution? (12) What is the chemist's idea of a saturated solution from the molecular standpoint? (13) Apply accurately the terms *saturated, unsaturated,* and *supersaturated* to sugar solutions in your home.

Research and Activities That You Will Enjoy

A display: Prepare in small labeled bottles different kinds of solutions. Explain to the class how you prepared each solution and why you think each is correctly labeled.

A report: See if you can learn either by a visit or by outside study how drug manufacturers prepare extracts. Report the information to the class.

Problem 16

WHEN YOU MAKE A SOLUTION, WHAT FACTORS AFFECT THE SPEED OF DISSOLVING AND THE DEGREE OF SOLUBILITY?

In everyday life we deal constantly with solutions containing solids, liquids, or even gases. Why not make lists of all the solutions you can think of which are used in your homes, in industry and the trades, and in medicine? (Start with a large sheet of paper.)

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How can you make a solution quickly? You know, of course, that many of the substances which you use in your laboratory work are in solution. Frequently you will have to prepare other solutions of solids in liquids. Suppose you need to make a solution of copper sulfate as quickly as possible. What can you do?

You might drop several large lumps of copper sulfate into a beaker of water. Certainly some of the copper sulfate would go into solution at once, but you would have to wait some time before you would have a saturated solution. Almost without thinking, you would *stir the solution* and this action would hasten dissolving. Recalling that granulated sugar dissolves faster than lump sugar would suggest *pulverizing* the copper sulfate before adding it to the water. Finally you might also remember that sugar dissolves faster in hot tea than in cold lemonade; this suggests *heating the solution.* Can you now tell how to make a solution of copper sulfate quickly? Would the same points necessarily apply to common salt?

Most solids behave as the copper sulfate did in the preceding experiments, although the *amount* dissolved must not be confused with the *speed* of dissolving. The speed of solution may be increased in three ways: (1) Stirring, shaking, or suspending the solute increases the speed of dissolving by helping the solute to scatter faster through the solvent. (2) If the solute is more finely powdered, it presents a greater surface to the dissolving action of the solvent and thus increases the speed of solution. (3) Raising the temperature increases the speed of dissolving in the case of most solids by increasing the solubility and creating convection currents.

How is the solubility of a substance indicated? If you wish to indicate roughly the solubility of a substance you may say that it is *very soluble, moderately soluble, slightly soluble,* or *insoluble.* It should be remembered that these terms are relative and that no substance is absolutely insoluble. The above terms may be given approximate values to show the number of parts by weight of solvent dissolving *one* part of solute, as follows:

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		Examples (in water)
Very soluble	Less than 1 part	NaOH
Freely soluble	From 1 to 10 parts	NaCl
Soluble	From 10 to 30 parts	$Na_2SO_4 \cdot (H_2O)_{10}$
Sparingly soluble	From 30 to 100 parts	$NaIO_3$
Slightly soluble	From 100 to 1000 parts	$CaSO_4$, $Ca(OH)_2$
Very slightly soluble	From 1000 to 10,000 parts	$Ca_3(PO_4)_2$
Insoluble	More than 10,000 parts	$BaSO_4$, AgCl

The above figures and examples are given only to show the wide variation in the solubility of substances. You are not expected to memorize them.

The *degree of solubility* (ordinarily called solubility) of solids and liquids is usually given as the *weight in grams needed to saturate 100 grams of the solvent at a given temperature.* Thus 36.0 grams of sodium choride saturate 100 grams of water at 20° C. The solubility of gases is usually given as the volume in milliliters which will dissolve in 100 ml of the solvent at a given temperature.

You can easily see that *solubility is a definite term* which states (1) the amount of solute, (2) the amount of solvent, and (3) the temperature. In general, the solubility of solids is increased by a rise in temperature. However, the figures in the table below show that the relative increase in solubility is not the same for all solids. Furthermore, a few solids (such as calcium sulfate and calcium hydroxide) are less soluble at higher temperatures. Heating a saturated solution of calcium sulfate causes some of the solute to come out of solution.

SOLUBILITY OF SOME SOLIDS

Name	0° C.	20° C.	40° C.	60° C.	80° C.	100° C.
Potassium chlorate	3.3	7.4	14.0	24.5	38.5	57.0
Potassium nitrate	13.3	31.6	63.9	110.0	169.0	246.0
Sodium chloride	35.7	36.0	36.6	37.3	38.4	39.8
Lead nitrate	38.8	56.5	75.0	95.0	115.0	138.8
Barium chloride	31.6	35.7	40.7	46.4	52.4	58.8

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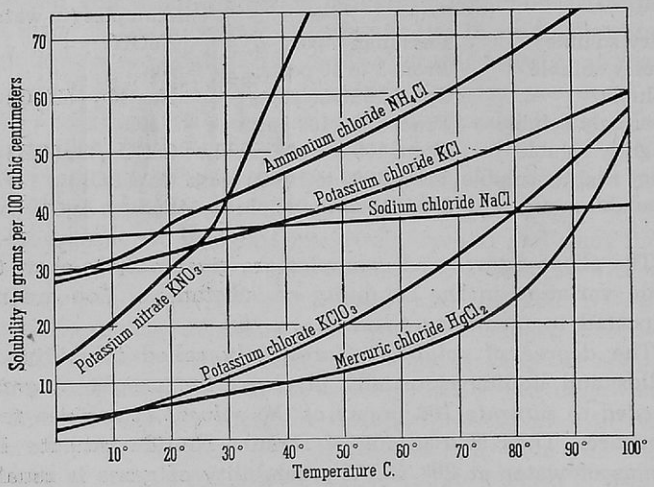

49. SOLUBILITY REPRESENTED BY CURVES. An understanding of solubility is more easily gained by curves than by columns of figures. Nearly straight lines show that the increase in solubility is regular with the rise of temperature.

How to use solubility curves. The difference in the solubility of solids at various temperatures can more simply be shown by using solubility curves as shown in Fig. 49. In this way, a curve rising steeply to the right shows a great increase in solubility with rising temperature. A nearly horizontal curve shows a slight change in solubility.

It is interesting to notice that the solubility of potassium chlorate at 100° C. is more than seventeen times its solubility at 0° C. On the other hand, the solubility of common table salt (sodium chloride) shows only a very slight increase (less than 15 per cent) for the same temperature change.

How solubility rules will help you. In laboratory work it is frequently necessary to know whether a substance is soluble or not. A table of solubilities similar to the one given in the appendix (page 781) is usually employed for this purpose. An examination of the table will show that the general

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rules preceding the table are approximately true. These simple rules are very useful and getting them well in mind at this time will save you the trouble of referring frequently to a table of this sort.

How do temperature and pressure affect the solubility of gases? Thus far you have been concerned mainly with solutions of solids in liquids. But you will also frequently have to consider solutions of gases in liquids. In this connection it is helpful to divide the gases into three groups on the basis of their solubility in water.

Very soluble gases: ammonia, hydrogen chloride, sulfur dioxide

Fairly soluble gases: hydrogen sulfide, chlorine, and carbon dioxide

Slightly soluble gases: oxygen, hydrogen, nitrogen

The degree of solubility of several gases is given in the appendix on page 771.

Why are some gases collected over hot water? Although heat usually increases the solubility of solids, with gases the results are just the opposite. Gases are much less soluble at high temperatures than at low temperatures. Some gases, therefore, are collected over *hot* water in order to keep them from going into solution so readily.

Boiling will completely expel the gas from most gas solutions. Ammonia, carbon dioxide, oxygen, and sulfur dioxide can be driven out of solution by boiling. A few gases, such as hydrogen chloride, cannot be completely driven off, but instead form solutions with constant boiling points. In general, then, a rise in temperature increases the solubility of a solid but decreases the solubility of a gas.

Effect of pressure on dissolving gases. Pressure has little effect on the solubility of a solid, but it greatly influences the solubility of gases. This may be shown by letting a little sodium sulfite react with some hydrochloric acid in a test tube. By this reaction sulfur dioxide gas is liberated. If the test tube is closed tightly with the thumb, the gas pressure in the test tube increases. Suddenly removing the thumb will

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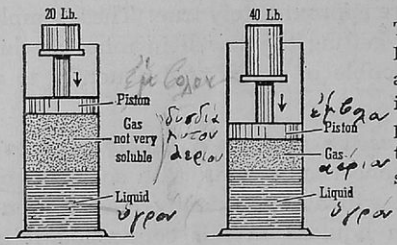

The solubility of a gas, unlike a solid, is decreased by a rise in temperature, but increased by an increase in pressure. Pressure crowds the molecules closer and some are forced into the solvent. (Henry's law.)

50. EFFECT OF PRESSURE ON THE SOLUBILITY OF A GAS

reduce the pressure on the surface of the liquid and cause the solution to foam up as the dissolved gas escapes. *The solubility of a gas* (unless it is very soluble) *is directly proportional to the pressure which is applied to it.* This is a statement of *Henry's law.*

Readings for Pleasure and Profit

FINDLAY, ALEXANDER. *The Spirit of Chemistry.* Chap. XV, "Solutions."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. IX, pp. 169–175, "Solutions."

Applying in Life What You Have Learned in Chemistry

Donald Gray's uncle was exasperated. He had planned to spray several hundred of his fruit trees this morning and even the copper sulfate solution was not ready yet.

"I don't understand it," said the uncle. "Yesterday morning I dumped all the 'blue stone' into the barrel of water and it hasn't dissolved yet. Of course, the crystals were a little larger than usual, but I didn't want to bother to pound them up."

"Next time, uncle," suggested Don, "why don't you hurry up the dissolving by putting the crystals in a cotton bag and . . .?"

Can you finish Donald's excellent suggestion?

"New Company Being Formed to Make Effervescent Water—Great Success Predicted for 'Nitrogenated' Water—Huge Profits Promised for Stock Purchased Now!" . . . and the article continued with an explanation of how the soft-drink industry would be revolutionized by the use of an effervescent water containing

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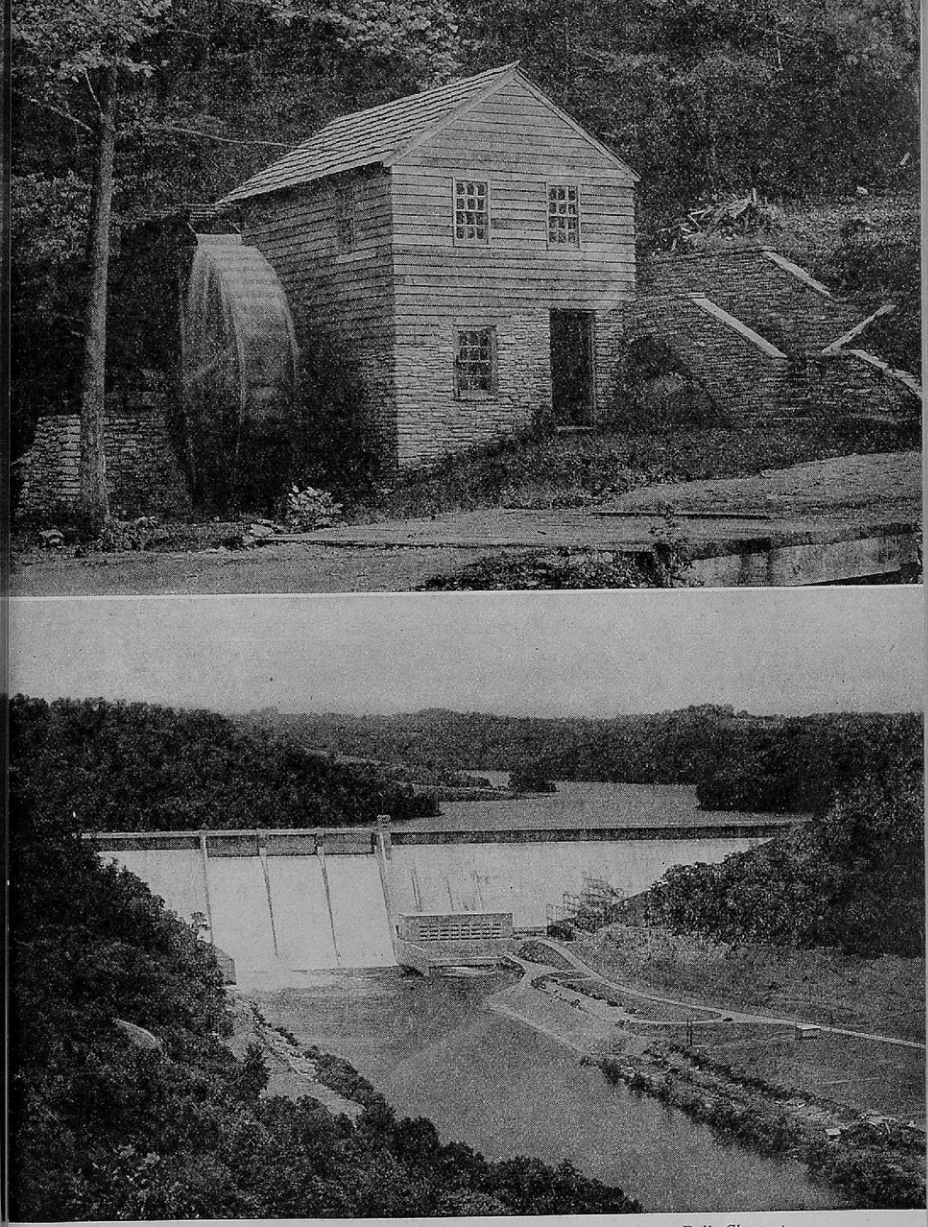

Rell Clements

WATER POWER IN EARLY DAYS AND WATER POWER TODAY. Early settlers used running water to drive machinery. The top picture shows an old-time mill for grinding grain. The lower picture shows the modern Norris Dam.

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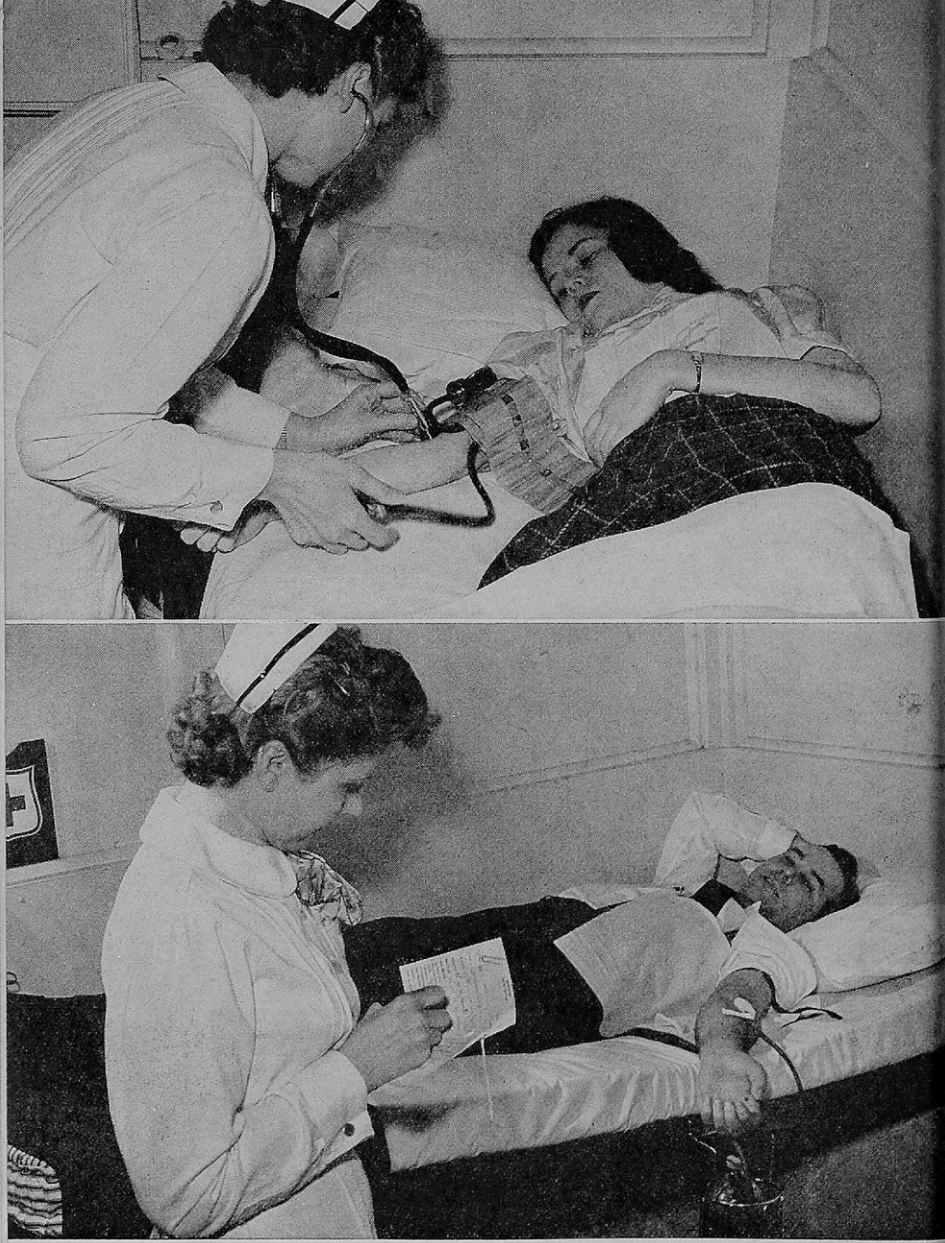

Courtesy, Monsanto Chemical Co.

BLOOD DONORS SAVE LIVES. Severe injuries frequently cause death by shock and loss of blood. Blood plasma from healthy persons is evaporated and the plasma stored under aseptic conditions. When this plasma is mixed with sterile water, it can be used at once to save lives. Prospective blood donors are checked carefully.

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nitrogen instead of the carbon dioxide found in the usual carbonated water. Would you invest your savings in stock of the company? Analyze the possibilities from a chemical standpoint.

An item in a "Household Hints" column pointed out the usual waste of sugar in sweetening iced tea and suggested using sugar sirup instead of granulated sugar. Do you think this plan would effect a saving? When sugar sirup is used, does sugar crystallize out of the cold solution? Why not try the plan to determine if it is efficient?

Putting Chemistry to Work

A

(1) Explain why gas bubbles gather on the inside of the glass when a glass of cold water stands for a short time in a warm room. (2) Why does shaking boiled water with air remove the "flat" taste? (3) If you were trying to prepare a saturated solution of table salt as quickly as possible, would you heat it? Explain your answer. (4) If you desire to prepare a 10% solution of alum as quickly as possible, how would you proceed? (5) A farmer must dissolve 25 pounds of copper sulfate in a barrel of water. How can he do it with the least effort? (6) Do you think you could prepare a 32 per cent solution of common salt? (Careful!) Explain your answer.

B

(7) Name four factors which may affect the solubility of solutes. Give at least one application of each. (8) Does carbonated water (carbon dioxide dissolved in water) effervesce when it is inside the fountain or only when it is drawn from the tap? (9) Using the table of solubilities on page 123, construct on graph paper solubility curves for potassium chlorate, lead nitrate, and barium chloride.

How Good Are You at Solving Problems?

(1) If one liter of water at 80° C. is saturated with potassium chlorate, how many grams of the solute would you expect to crystallize when the solution is cooled to 20° C.?

(2) 500 ml of water are saturated with potassium nitrate at 25° C. Approximately how many more grams of the solute will dissolve when the solution is heated to 40° C.?

(3) Make a solubility curve for barium chloride and for lead nitrate. (See table on page 123 and Fig. 49.)

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(4) Compute the solubility of sodium chloride at 30° C. from the following data:

(a) Weight of empty dish .....55.876 grams
(b) Weight of dish and saturated solution .....73.452 grams
(c) Weight of dish and solute after evaporation..60.564 grams

(5) If a solution of potassium nitrate in 100 grams of water saturated at 80° C. is cooled to 20° C., how many grams of the salt would you expect to come out of the solution?

(6) From the following experimental data, determine the solubility of potassium chlorate at 20° C.:

(a) Weight of evaporating dish ..... 93.56 grams
(b) Weight of dish and saturated solution.....110.19 grams
(c) Weight of dish and residue after evaporation. 94.69 grams

Research and Activities That You Will Enjoy

A chart: Make a large wall chart showing the solubility curves of several solids with widely differing solubilities in water. Explain to the class how you will use such a chart.

A demonstration: After outside preparation, demonstrate and explain the process of osmosis. Point out its importance to the class.

Special reports: (a) Antifreeze solutions for auto radiators (b) Industrial solvents and their uses (c) Standard solutions in chemical analysis (d) Vapor pressure of solutions.

Problem 17

HOW ARE SUBSTANCES RECOVERED AND PURIFIED BY CRYSTALLIZATION?

How solutions may produce crystallization. The amount of solid solute that can be held in solution is decreased by evaporation of the solvent or by a drop in temperature. When this occurs the excess material comes out of solution as a solid. It is usually in crystalline form. Crystals are solids bounded by plane faces at definite angles. The crystalline form of a substance is one of its distinguishing physical properties and this may be used in identifying it. Sodium chloride forms

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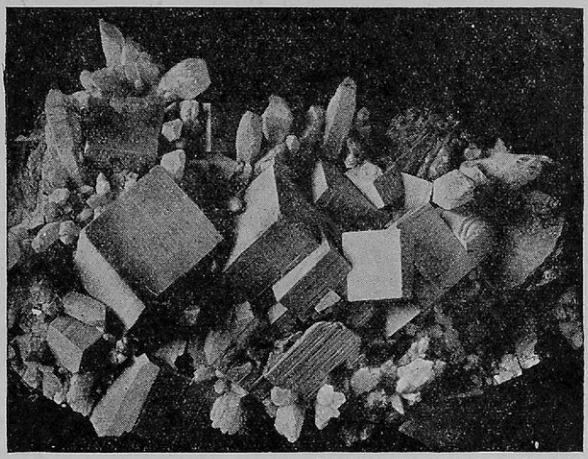
crystals which are cubes. Potassium sulfate crystals are hexagonal prisms (needle-shaped). Crystals grow by the addition of material from the outside. From its very beginning, a crystal retains the same shape unless it is distorted by crowded conditions or other disturbing influences.



Courtesy, U. S. National Museum

51. NATURAL CRYSTALS. The cubes are pyrites (FeS_2) and the prisms are quartz (SiO_2). Molecules of the same kind arrange themselves in orderly forms to make the different shapes of crystals.

• *How are the particles arranged in some crystals?* The structure of crystalline solids has been determined by the use of X rays. (See page 204.) A crystal, such as a sodium chloride crystal, has been shown to consist of particles arranged in orderly rows forming a definite pattern known as its space-lattice. The particles which form the space-lattice are *not* molecules of sodium chloride as we might expect, but they consist of electrically charged sodium particles (ions) and electrically charged chlorine particles (ions) arranged alternately. In the center of a crystal each sodium ion is surrounded by six chlorine ions and each chlorine ion is surrounded by six sodium ions. Nowhere do we find a *molecule* which consists of one sodium atom united to a definite chlorine atom to the

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52. THREE GRADES OF CHEMICALS. "Tech" means technical or commercial grade. "U.S.P." means United States Pharmacopoeia, a grade of sufficient purity to be used as medicine. "C.P." means chemically pure.

exclusion of others. The *ions* are held together in orderly rows, but they have not selected definite partners. This notion of the arrangement of the particles in solid sodium chloride makes it unnecessary to believe that molecules of sodium chloride exist in crystals of salt. But we continue our use of the term molecule for two reasons: (1) when gaseous atoms of sodium and chlorine react, we believe that molecules are formed; (2) the molecular weight of sodium chloride, which is the sum of the weights of one sodium ion and one chlorine ion, is very convenient to use as expressing the chemical unit of mass.

Substances are often purified by recrystallization. The separation of a mixture can often be brought about by using the differences in the solubility of its components. Table salt may be obtained from sea water in this manner. As soon as the solution becomes more concentrated by evaporation, the salt

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begins to crystallize, leaving behind in the mother liquor the more soluble or less plentiful components of the mixture.

A single crystallization usually produces impure crystals, but they may be purified by recrystallizing. The more nearly the components resemble each other, the greater will be the number of recrystallizations required to produce the desired purity. Absolute purity of chemicals is not possible; they are labeled *"C. P."* to show a high degree of purity; *"U. S. P."* for medicines; *"tech"* for low-grade chemicals. (See Fig. 52.)

Some pure crystals contain water. When certain substances separate from solutions as crystals, they take from the solution a definite proportion of water to help form the crystal. This water is known as *water of hydration* and is an essential part of the crystal. Crystals which contain this water of hydration are known as *hydrates*. Water of hydration is chemically combined in the crystal and should be distinguished from water which is sometimes mechanically inclosed within crystals. When crystals containing droplets of inclosed water are heated, miniature explosions may occur as the steam escapes. This is called *decrepitation*. When hydrates are heated, they lose their water quietly.

The quantity of water contained in hydrates is definite and often quite large. The formulas for a few hydrates are listed in the table below.

FORMULAS FOR SOME HYDRATES

Calcium sulfate	$CaSO_4 \cdot (H_2O)_2$	Strontium chloride	$SrCl_2 \cdot (H_2O)_6$
Barium chloride	$BaCl_2 \cdot (H_2O)_2$	Sodium carbonate	$Na_2CO_3 \cdot (H_2O)_{10}$
Copper sulfate	$CuSO_4 \cdot (H_2O)_5$	Aluminum sulfate	$Al_2(SO_4)_3 \cdot (H_2O)_{18}$
Sodium sulfate	$Na_2SO_4 \cdot (H_2O)_{10}$	Potassium alum	$KAl(SO_4)_2 \cdot (H_2O)_{12}$

The formula[1] of copper sulfate hydrate, $CuSO_4 \cdot (H_2O)_5$, indicates that there are *five* molecules of water attached to *each* molecule of copper sulfate. The dot in the formula denotes the loose attachment of water and is *not* a sign of multiplication.

[1] This method of expressing the formulas of hydrates is the one adopted by the Division of Chemical Education of the American Chemical Society.

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Courtesy, Dow Chemical Company

53. SPRINKLING CALCIUM CHLORIDE ON THE ROAD. Calcium chloride is used quite extensively for keeping down dust on roads, tennis courts, and in mines. It absorbs moisture from the air, forming a concentrated solution. This solution moistens the fine grains of dust. The dust protects the calcium chloride by slowing down the solvent action of rain.

What happens when hydrates lose water? Since the water of hydration is not held very firmly in hydrate molecules, it can be driven out by gentle heating. When a hydrate loses water, it loses its crystalline form. A substance which has lost its water content is *anhydrous* (without water). Removing water from a substance is *dehydration.* Some hydrates, washing soda crystals for example, will lose water on exposure to air at ordinary temperatures. At first the crystals become covered with a white powder, and finally crumble to powder. Such substances are said to be *efflorescent.* Other hydrates, such as magnesium chloride crystals, will absorb water from the air and become quite wet. In some cases enough water is absorbed to dissolve the substance. Calcium chloride behaves in this way. Such substances are said to be *deliquescent.*

Some hydrates are useful; others are troublesome. A number of uses of materials depends on the relation of the

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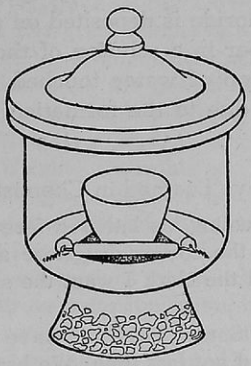
substances to their water of hydration. Gypsum is a natural hydrated calcium sulfate. On being heated, it loses three-fourths of its water and forms a new hydrate known as plaster of Paris.



The lower part of this vessel contains calcium chloride which absorbs water, thus keeping the air dry in the space above. Desiccators are used in quantitative analyses, where accurate weights of substances must be obtained. Substances which may absorb water from the air are kept dry in desiccators before the analyst weighs them.

54. A DESICCATOR

Natural table salt contains as an impurity magnesium chloride, $MgCl_2 \cdot (H_2O)_6$, which is deliquescent. In damp weather it absorbs moisture from the air, thus causing the salt "to cake." To prevent this "caking" and to keep the salt in a "free-running condition," the deliquescent substance is removed or substances like sodium phosphate and sodium bicarbonate are added to keep the salt dry. It is believed that these substances convert the deliquescent magnesium chloride to anhydrous materials.

Calcium chloride often is scattered on tennis courts, on dirt roads, and in mines to keep down the dust. It is also scattered on fresh concrete pavements to prevent too rapid drying. Can you suggest what action takes place in these cases?

How can you make a test for water? Copper sulfate crystals (hydrate) are dark blue. The anhydrous copper sulfate is white. So this substance can be used to test for the presence of small quantities of water in substances such as alcohol. A little of the anhydrous white salt is added to the liquid to

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be tested. If water is present, it is taken up to form the blue hydrate. The change in color is quite evident and easily shows the presence of water.

Cobalt chloride likewise can be used in testing for water since anhydrous cobalt chloride is blue while the hydrate is red. A little anhydrous cobalt chloride is deposited on a strip of filter paper by dipping the paper in a solution of the compound and then drying it. A drop of water touched to the blue paper causes it to turn red due to the formation of the hydrate.

Applying in Life What You Have Learned in Chemistry

"Jack," called Mr. Thomsen, thrusting his lathered face out of the bathroom door, "run down to the corner drugstore and get me a few large lumps of alum. Tell the clerk I want the same as I got the last time."

At the drugstore the clerk said, "Sorry, Jack, but we're all out of the *U.S.P.* alum crystals your Dad got last time. We have *C.P.* alum crystals."

Was the clerk trying to sell a "cheap substitute"? Should Jack take the alum?

Putting Chemistry to Work

A

(1) How can you be certain that a colorless, tasteless, odorless liquid is really water? (2) What is the reason for placing small open bottles of calcium chloride in large clocks and fine chemical balances? (3) Which is cheaper to buy: crystals of washing soda (sodium carbonate) that have been kept in a closed can or crystals that have been kept in open cans (if the price per pound is the same)? Explain your answer. (4) When sugar is heated, a large quantity of water comes off and a black mass remains. When washing soda crystals are heated, a large quantity of water also comes off, but a white powder remains. How are these two processes alike? How are they different?

B

(5) In general, which indicates a higher degree of purity, *C.P.* or *U.S.P.*? (6) Why should bottles of calcium chloride be kept tightly stoppered? (7) How does a hydrate illustrate the Law of Definite Composition? State the law in your own words. (8) How

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could you prove that water of hydration is chemically combined in a hydrate?

How Good Are You at Solving Problems?

(1) Calculate the percentage of water in Epsom salt, $MgSO_4 \cdot (H_2O)_7$. (Hint: $126 \div 246 = ?\%$).

(2) A 1.04-gram sample of a hydrated salt weighed 0.6656 gram after heating. What was the percentage of water?

(3) Determine the percentage of water in a hydrate from the following experimental data:

(a) Weight of crucible .....23.408 grams
(b) Weight of crucible and hydrate .....25.988 grams
(c) Weight of crucible and anhydrous salt .....25.606 grams

How does the determined value compare with the value calculated from the formula $BaCl_2 \cdot (H_2O)_2$? ($36 \div 244 = ?\%$)

(4) The directions for an experiment called for exactly 10 grams of *anhydrous* potassium alum, but only the crystals were available. (See formulas of hydrates, page 131.) How many grams of the hydrated salt should be used?

(5) Which is the better buy: anhydrous washing soda (sodium carbonate) at 8 cents per pound or washing soda crystals at 5 cents per pound? Show your reasoning.

Research and Activities That You Will Enjoy

A demonstration: Try to grow some large crystals; bring them before the class to show the effect of slow evaporation. Compare them with a sample of the same substance obtained by rapid crystallization and point out the application to smooth or "grainy" fudge.

A discussion: Show the class how a desiccator is constructed and used. Call for a class discussion on its importance and call for suggestions on the kind of dehydrating agents.

A paper: Prepare and present to the class a paper on "Crystallography." The formation of crystals on a slide under a microscope presents a beautiful sight. Such tiny crystals may be shown to the class by means of a microprojector.

Looking Back into Unit 3

Be sure you know the purpose of this unit. Read again the material on page 88, "Looking Ahead into Unit 3." Then study the following Summary Test.

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Summary Test

1. *How is water made pure for you?*
   (a) How can you kill harmful bacteria in water?
   (b) How can you remove suspended materials from water?
   (c) How are dissolved materials removed from water—
      (1) By the addition of softening agents?
      (2) By distillation?
   (d) How are cities able to provide you with healthful water?
2. *What properties of water make it your useful friend and servant?*
   (a) How is water used as a standard—
      (1) In expressing weight?
      (2) In determining temperature?
      (3) In expressing amount of heat?
   (b) How do the physical changes of water make it useful?
   (c) How do we use the chemical properties of water?
3. *What is water?*
   (a) What demonstrations show you the composition of water?
   (b) What is the composition of water—
      (1) By volume?
      (2) By weight?
4. *What is a solution?*
   (a) How do you know that a solution is a uniform mixture?
   (b) What do you mean when you say that a solution is a molecular dispersion?
   (c) In what ways can you express the concentration of a solution?
   (d) Give examples of solutions in which water is not the solvent.
   (e) What mixtures only resemble solutions? How do they resemble solutions?
5. *When you make a solution, what factors affect the speed of dissolving and the degree of solubility?*
   (a) How can you make a solution quickly?
   (b) How is the solubility of substances indicated?
   (c) How does temperature affect the solubility of solids?
   (d) What factors affect the solubility of gases? How?
6. *How can you recover and purify substances by crystallization?*
   (a) What happens during crystallization?
   (b) How are substances purified by crystallization?
   (c) What are hydrates? What uses are made of them?

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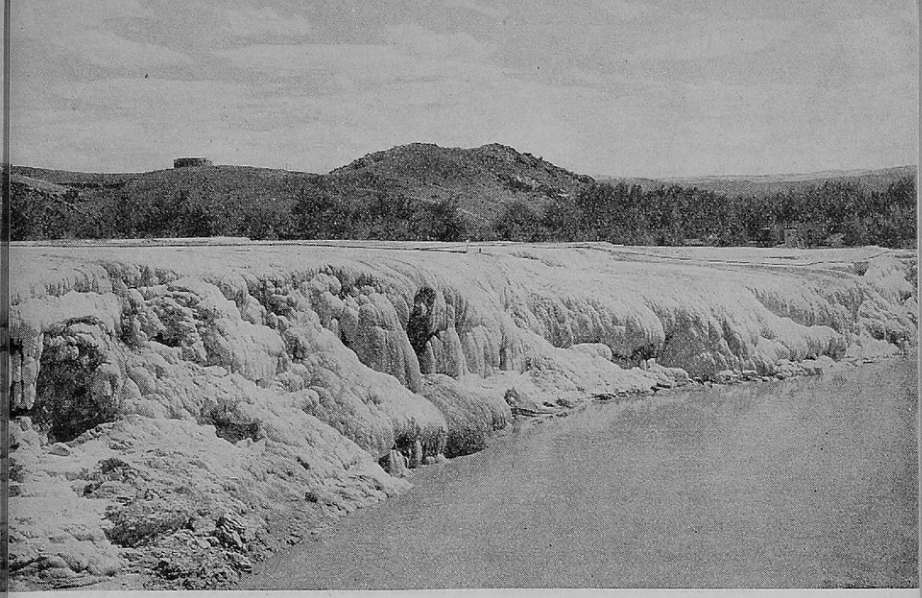

Courtesy, Dept. of Commerce & Industry, Cheyenne, Wyoming

MINERAL FALLS AT THERMOPOLIS, WYOMING. The water in these hot springs dissolves minerals that are underground and deposits them at the surface.

Closing the Unit

You cannot say with the Ancient Mariner "*Water, water,* everywhere, and not a drop to drink" for the chemist shows how to make the *salty ocean,* the *sewage*-infested *river,* and *water* from any other source fit for any purpose. In this unit you learn a respect for purity in water, whether it be for healthful use about the home or for laboratory work in chemistry.

Our weights are based on *water* (1 ml of water at 4° C. weighs 1 g); the intensity of heat is indicated with *thermometers* whose degrees are based on the *boiling point* and *freezing point* of water; the amount of *heat energy* is measured in *calories;* indeed, *water* is an excellent *standard*—it is stable and uniform and dependable in behavior.

Famous chemists have made accurate measurements in the *synthesis* and *analysis* of *water;* they have found that *water* conforms ideally to the *fundamental law of definite composition.*

Water is an excellent *solvent* and it seems to be necessary for many *chemical reactions.*

Thus you learn that a very familiar and common compound holds for you a vast wealth of valuable scientific information which aids you in obtaining a fundamental concept of chemistry.

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Looking Ahead into

Unit Four

A wise man once said that a person is not becoming mature unless he is learning to "see" the invisible—to use his mind to "see" things that his eyes cannot see. In this unit you have several opportunities to use your imagination in order to "see" the smallest things in the world—molecules, atoms, protons, electrons.

Even before you started your study of science, you no doubt heard of and wondered about these small particles of which everything in the world is made. You may have wondered how it is possible to know about them. You may even have doubted that such particles as atoms exist. This is a proper attitude to assume in science study. You are fully justified in asking for evidence before accepting an idea as being true. On the other hand, when the evidence has been presented carefully, it is only fair that you should make a serious effort to understand it, and if it is acceptable, make it a part of your thinking.

The problems listed below will act as your guideposts to show you where you are going as you explore and discover for yourself more about one of the most fundamental theories in chemistry—the atomic theory.

Problem 18. *Why Do Scientists Believe That Molecules Are Composed of Tiny Units of Matter—Atoms?*

Problem 19. *What Discoveries Enable Scientists to Determine the Molecular Weights of Substances?*

Problem 20. *How Have Scientists Determined Atomic Weights? How May You Use Atomic Weights in Chemical Computations?*

Problem 21. *What Are Atoms Made of and How Are They Constructed?*

Problem 22. *How Do the Atoms Hook Up with Each Other to Form Compounds?*

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Units of Matter:

Molecules, Atoms, Electrons, Protons, Neutrons, Positrons

Problem 18

WHY DO SCIENTISTS BELIEVE THAT MOLECULES ARE COMPOSED OF TINY UNITS OF MATTER—ATOMS?

In Unit 2 of this book you learned some good reasons for believing that matter is composed of molecules. Molecules are *units* of matter; generally speaking, molecules of the same kind have equal weights.

Molecules are not the only units of matter. Scientists now know that molecules are composed of still smaller units called atoms. No one ever has seen an atom; perhaps no one ever will see one because atoms are exceedingly small. Why do scientists think that such tiny particles exist? Here is a simple illustration that may show the reasonableness of scientific investigation. This illustration shows what the sense of *hearing* can teach you about an unseen object which is inclosed in a small box.

If the object rolls freely like a marble in any direction when the box is tilted, you know that the object is spherical. If it rolls freely in only one direction but slides on an incline at right angles to the first direction, you know at once that the object is cylindrical like a crayon. If it only slides in any direction as the box is tilted, the object has a flat base. If the object rolls bumpily, it is an irregular solid and the kind of bumps "tells a story" of its irregularities.

If you perform this simple experiment, you might say that you "hear" the shape of the object. Really, you use your imagination and your sense of reason to interpret the shape of the object from what is heard. In many such ways all of us use our senses to obtain information.

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What is a scientific hypothesis, a scientific theory, and a scientific law? The true scientist does not believe that "things just happen." He wants to know *how* and *why* things occur; he believes that specific conditions lead to specific results. Consequently, when the scientist is confronted with a group of unexplained facts which he has encountered, he studies these facts from every possible point of view and attempts to derive a plausible explanation. If the explanation looks reasonable, it becomes known as a *hypothesis.*

A hypothesis is subject to change. If facts appear which show that the hypothesis is wrong, it either must be changed to fit the facts or discarded. A hypothesis is somewhat like a scaffolding around a new building. It is useful in constructing the finished building, but it can be discarded if it becomes useless. However, if further investigation shows that a hypothesis agrees with all known facts, it may be "promoted to a higher rating" as a *theory.*

You can easily understand that if a theory is conclusively proved to be true, it becomes a *scientific law.* Note also that if all new facts bearing on the case can be explained by a theory, and the theory points the way to new discoveries, it may be considered a satisfactory statement of truth after an adequate period of thorough testing.

The electrolysis of water indicates that molecules are made up of smaller particles. You already have found that, under the action of an electric current, water can be decomposed into hydrogen and oxygen. This indicates that each water molecule is made up of particles of hydrogen and oxygen which of necessity must be smaller than the molecules of water. These particles of hydrogen and oxygen are called *atoms.*

The Law of Definite Composition indicates that atoms are units of matter. Water, as you know, is composed of 1 part hydrogen and 7.94 parts oxygen by weight. In general *all compounds are composed of two or more elements chemically combined in a definite ratio by weight.* This is the Law of Definite Composition—it has been proved over and over in the laboratory. This truth suggests that the particles (atoms) which combine

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to form compounds are units, each kind of atom having a definite weight.

The Law of Multiple Proportions is perhaps the most convincing evidence of the existence of atoms. Water is composed of 1 part hydrogen and 7.94 parts oxygen by weight. Hydrogen peroxide is composed of 1 part hydrogen and 15.88 (2×7.94) parts oxygen. In other words, the ratio between the weight of the oxygen in water and the weight of the oxygen in hydrogen peroxide is 1 to 2.

Oxygen also forms different compounds with nitrogen. Definite weights of these two elements unite as follows:

Nitrous oxide:	1 part N and 0.571	(1×0.571) part O
Nitric oxide:	1 part N and 1.14	(2×0.571) parts O
Nitrogen trioxide:	1 part N and 1.71	(3×0.571) parts O
Nitrogen dioxide:	1 part N and 2.28	(4×0.571) parts O
Nitrogen pentoxide:	1 part N and 2.85	(5×0.571) parts O

In the preceding table note the weights of *oxygen.* These weights of oxygen are in the ratio of small whole numbers (1 : 2 : 3 : 4 : 5). There are no intermediate values. Whenever there is more than the smallest weight (an atom) of an element found combined, the larger weight of the element is some multiple of the smallest weight. These units were named atoms because the word, atom, means *unbroken.* John Dalton's statement of these facts is known as the *Law of Multiple Proportions: when any two elements, A and B, combine to form more than one compound, the different weights of B, which unite with a fixed weight of A, bear a small whole-number ratio to each other.*

What is the atomic theory? Dalton in his statement published in 1803 made several assumptions concerning atoms which, in general, are still held:

1. Atoms are exceedingly small. (Modern calculations show that the diameter of an atom is less than one ten-millionth of an inch.)

2. Atoms of the same element are alike in properties; atoms of different elements are unlike in properties.

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3. Each kind of atom has its own definite weight that differs from the weight of any other kind of atom.

4. Atoms of most of the elements are able to enter into combination with other atoms to form compounds. In this combination the atom loses its characteristic properties.

5. Atoms in chemical combination are not entirely altered. (The study of the structure of atoms will make this clear. Information concerning the structure of atoms is given later in this unit.)

Dalton and his followers made no distinction between atoms and molecules. While Dalton's work was of the greatest value in organizing the great science of chemistry, its full value was not realized until 1858 when Cannizzaro, who is affectionately known as the Father of Italian Chemistry, formulated clearly our present ideas of the true relations of atoms to molecules.

Readings for Pleasure and Profit

DARROW, F. L. *The Story of Chemistry.* Chap. II, pp. 25-34, "Atoms and Molecules."

GOLDBLATT, L. A. *Collateral Readings, Second Series.* Art. 5 "The Atomic Hypothesis."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Article 9A, pp. 51-55, "Cannizzaro and the Atomic Theory"; Article 9B, pp. 56-60, "The Size and Shape of Molecules."

JAFFE, BERNARD. *Crucibles.* Chap. VII, pp. 114-135, "John Dalton."

KENDALL, JAMES. *At Home among the Atoms.* Chap. VI, pp. 75-90, "The Mighty Atoms."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. XIX, pp. 255-266, "Into the Atom."

Applying in Life What You Have Learned in Chemistry

A study hint: "One-story intellects, two-story intellects, three-story intellects with skylights. All fact-collectors who have no aim beyond their facts are one-story men. Two-story men compare, reason, generalize, using the labours of the fact-collectors as well as their own. Three-story men idealize, imagine, predict; their best illumination comes from above, through the skylight."

—OLIVER WENDELL HOLMES

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Putting Chemistry to Work

A

(1) The first step in learning is seeing or observing. Give some suggestions for insuring accuracy in this process. (2) Another step in learning is testing hypotheses to be sure of their correctness. Give some examples to show how you have proved or disproved a saying or belief. (Consider some superstition or weather saying.) (3) In 1845 Sir John Franklin, searching for the Northwest Passage, perished with his party of 128 men in the frozen wastes of northern Canada. Admiral Byrd made four polar expeditions and reached the North and South Poles without the loss of a single human life. In your opinion, to what factors was his success due? (4) *Dalton, Berzelius:* The painstaking work of John Dalton and John J. Berzelius form an important link in the "growing up" of chemistry. Investigate and report the old and the new chemical symbolism.

B

(5) What unit of matter is represented by the symbol? by the formula? (6) What is an axiom, an adage, a forecast, a fable, a rumor, a maxim, a prophecy? (7) How is the truth of natural laws determined? (8) Of what value is a knowledge of natural laws? (9) How do hypotheses grow into laws? (10) How do we know that the molecules of any compound are alike? (11) How did Dalton obtain the evidence which led to his formulation of the laws of definite and multiple proportion?

Problem 19

WHAT DISCOVERIES ENABLE SCIENTISTS TO DETERMINE THE MOLECULAR WEIGHTS OF SUBSTANCES?

Suppose that you are a chemist in a large manufacturing plant. The purchasing department asks you how much salt must be purchased by the company to produce 5,000 kilograms of chlorine. Your job depends upon your being able to find this information. But you cannot give the information without knowing molecular weights and atomic weights. How scientists were able to determine molecular weights is shown in this problem.

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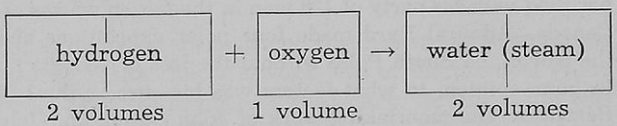
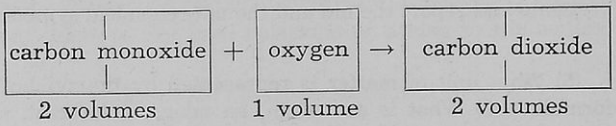
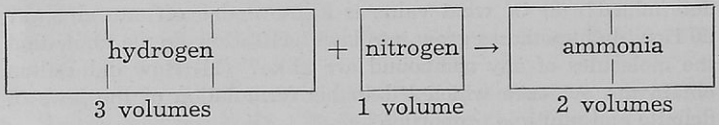
What two important laws made it possible for scientists to determine molecular weights?—Gay-Lussac's law and Avogadro's law. You learned in Unit 3 that exactly two volumes of hydrogen combine with exactly one volume of oxygen to form two volumes of water vapor. Similar experiments with other gases show some interesting facts concerning their combining volumes. A few of these results are shown here:







In looking over the results of a series of experiments like these, the French chemist Gay-Lussac was struck with the fact that the relation between volumes of combining gases is a simple one. He expressed this fact in 1808 in the statement which we now know as *Gay-Lussac's law—The ratio between the volumes of combining gases and of the product, if gaseous, can be expressed in small whole numbers.*

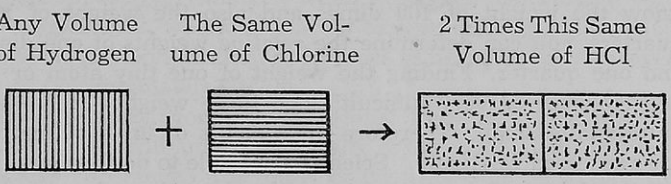
What is Avogadro's law? In a paper published in 1811 the Italian scientist Amadeo Avogadro made a few observations concerning the volumes of combining gases. He contended that since one volume of hydrogen combines with one volume of chlorine to produce hydrogen chloride and since neither hydrogen nor chlorine is left over, it must follow that the original volumes of hydrogen and chlorine contained equal

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

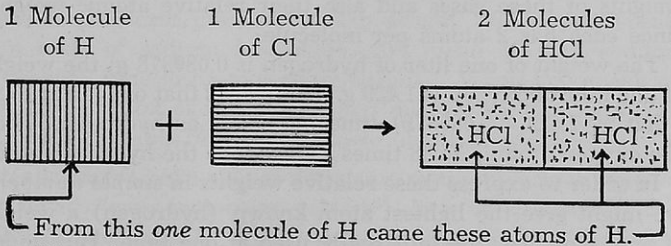
numbers of particles (molecules). After he had examined other cases of combining gases, he summarized his conclusions in the statement which is now known as *Avogadro's law—Equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules.*

The great value of Avogadro's statement was not realized until Cannizzaro cleared up the distinction between atoms and molecules. Likewise you will not see the significance of this statement until you, yourself, understand the difference between atoms and molecules.

Knowing the number of atoms in a molecule of a gas can aid in determining molecular weights—how many atoms are in a molecule of hydrogen? Scientists have found by experiment that:



By Avogadro's law (Equal volumes of gases under the same conditions contain equal numbers of molecules) you know that the volume of hydrogen contains the same number of molecules as the volume of chlorine. Suppose that each one of these equal volumes contains only one molecule.



From this *one* molecule of H came these atoms of H. What does this fact show about the number of atoms in a molecule of H?

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1. Hydrogen chloride is composed of hydrogen and chlorine. Each molecule of HCl contains a hydrogen atom.
2. There are two molecules of hydrogen chloride. Therefore these two hydrogen chloride molecules contain two hydrogen atoms, at least.
3. The two hydrogen *atoms* came from one *molecule* of hydrogen.
4. Therefore, one hydrogen molecule contains two hydrogen atoms.

By a similar line of reasoning, it can be shown that oxygen, chlorine, and nitrogen also have two atoms to the molecule.

From now on, use the formulas H_2, O_2, N_2, and Cl_2 whenever you write the molecular formulas for these gases.

Weights of units of matter are expressed relatively. If you know the weight of 100 dimes and also the weight of 100 quarters, you can determine the *relative* weights of one dime and one quarter. Finding the weight of one tiny atom or of one molecule is very difficult since these weights are so infinitesimally small. Therefore the weights of units of matter are expressed *relatively*. Scientists are able to do this because equal volumes of gases contain an equal number of molecules (Avogadro's law). This means that a liter of hydrogen contains the same number of molecules as a liter of oxygen or as a liter of any gas (under the same conditions). The weight of a liter of hydrogen when compared with the weight of a liter of oxygen therefore enables us to determine the relative molecular weights of these gases and also their relative atomic weights since *each* has 2 atoms per molecule.

The weight of one liter of hydrogen is 0.089878 g; the weight of one liter of oxygen is 1.429 g. This shows that oxygen is 15.88 (that is, 1.429 ÷ .089878) times as heavy as hydrogen. Then the oxygen atom is 15.88 times as heavy as the hydrogen atom.

In order to express these relative weights in *simple numbers*, we might give the lightest atom known (hydrogen) a weight of one. This was the unit really used at one time. But under such a system, oxygen had an atomic weight of 15.88. Oxygen enters into many compounds and this number

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was an awkward one to use, so the value 16 was arbitrarily given to oxygen to make computations involving oxygen easier. This gives the value of 1.008 for the atomic weight of hydrogen. The *approximate* atomic weight of hydrogen is still frequently given as one. Since hydrogen and oxygen each have 2 atoms per molecule, the molecular weight of hydrogen is approximately 2×1 or 2, and the molecular weight of oxygen is 2×16 or 32.

What is meant by "gram-molecular weight"? Keep in mind that atomic and molecular weights are only ratios. They have no denomination. When we say the atomic weight of sodium is 23, we do not mean 23 grams or 23 milligrams, but we mean that the weight of a sodium atom is 23/16 as heavy as the oxygen atom or 23 times the weight of the hydrogen atom (approximately). Similarly when we say the molecular weight of oxygen is 32, we mean that an oxygen molecule is twice as heavy as the oxygen atom or 32 times as heavy as the hydrogen atom (approximately).

In laboratory work chemists must know what quantity of a substance will unite chemically with a given quantity of another substance. The most convenient unit of weight for laboratory work is the *gram-molecular weight* (G.M.W.)—which is the molecular weight of a substance expressed in grams. For example, the gram-molecular weight of oxygen is 32 *grams* because, as you have seen, the molecular weight of oxygen is 32. Similarly, the gram-molecular weight of hydrogen is approximately 2 grams. The term *mole* is often used in place of the term gram-molecular weight. When you speak of a mole of sodium hydroxide, you mean 40 g of sodium hydroxide (one gram-molecular weight). When you speak of a *molar solution* of nitric acid, you mean a solution one liter of which contains 63 g or one mole of nitric acid.

Scientists have been able to determine many molecular weights by using "gram-molecular volume"—how is gram-molecular volume determined? When working with gases in the laboratory, it is much more convenient to use volumes rather than weights. A commonly used unit of volume for gases is the

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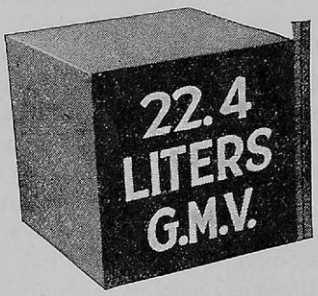
gram-molecular volume (G.M.V.)—which is the volume that one gram-molecular weight of a gas occupies under standard conditions. It has been found experimentally that 1 gram-molecular weight of *any* gas occupies approximately 22.4 liters under standard conditions. Therefore *22.4 liters* is the *gram-molecular volume* of any gas.



This block has a volume of 22.4 liters. It is the volume that one gram-molecular weight of any gas occupies at standard conditions of temperature and pressure (760 mm pressure and 0° C.). To find the gram-molecular weight of any gas or vapor, find the weight of this volume at 760 mm pressure and 0° C.

55. GRAM-MOLECULAR VOLUME

How have scientists determined molecular weights by using gram-molecular volume? From your study of the preceding paragraph you can see that the weight of 22.4 liters of any gas (under standard conditions) is the gram-molecular *weight* of the gas. This suggests a method for determining the molecular weight of any substance which is in the gaseous condition.

A Principle for You to Remember

The weight of 22.4 liters of a gas is its gram-molecular weight—that is the molecular weight of the gas expressed in grams.

If the gram-molecular weight of a gas is *32* g, the molecular weight of the gas is *32*.

Suppose you wish to determine the molecular weight of a gas. You may determine the weight of some measurable vol-

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ume of it, and then from this information you may compute the weight of 22.4 liters of the gas. *This weight will be the gram-molecular weight of the gas.*

Here are two specific examples:

1. A liter of acetylene gas at standard conditions is found to weigh 1.16 g. What is its molecular weight?

The gram-molecular weight can be determined by finding the weight of a gram-molecular volume (22.4 liters).

Therefore, the G.M.W. of acetylene is $1.16 \times 22.4 = 25.984$ g and the molecular weight is 25.984.

2. It is not always possible to get exactly one liter of gas in an experiment. It may be necessary to use smaller volumes. Then one more step is necessary in order to determine the weight of one liter.

250 ml of a gas weigh 0.41 g. What is the molecular weight of the gas?

$$\frac{0.41}{250} \times 1000 = 1.64 \text{ (weight of 1 liter)}$$

$$1.64 \times 22.4 = 36.736 \text{ g (the G.M.W. of the gas)}$$

The molecular weight of the gas is therefore 36.736.

Summary of operations for determining molecular weight.

1. Obtain a convenient volume of the pure gas.
2. Determine the weight of this gas and its volume under standard conditions.
3. Determine the weight of 1 liter of the gas.
4. Determine the weight of 22.4 liters or the gram-molecular weight.

By computations of this kind, it is possible to find the gram-molecular weight of any substance that is a gas or that can be put into the gaseous state without decomposition. Note that all experimental volumes must be reduced to standard conditions. (See appendix.)

This method of determining molecular weights can be used only with gases or with substances which will readily vaporize (without decomposition) and become gases. For other substances other methods must be used. These are usually methods

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based upon the principle that when a substance goes into solution, the freezing point of the solution is lowered and the boiling point is raised. For example, it is found that when one gram-molecular weight of a substance such as sugar is dissolved in one liter of water, the freezing point is lowered 1.86° C. Suppose you have a liter of water containing 20 g of the same kind of solute and careful measurement shows that it freezes at — 0.93° C. Since this is half the effect produced by dissolving one mole in a liter of water, you may conclude that you have only half of a mole in solution. The molecular weight of the solute must then be 40.

There is no method of accurately determining the molecular weight of such substances as starch, gelatin, and rubber which neither form true solutions nor vaporize without decomposition.

Readings for Pleasure and Profit

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Article 9A, pp. 51-55, "Cannizzaro and the Atomic Theory."

JAFFE, BERNARD. *Crucibles.* Chap. IX, pp. 157-174, "Amadeo Avogadro."

Putting Chemistry to Work

A

(1) Are there molecules of elements? If so, give an example. (2) Do compounds exist in atomic form? Explain your answer. (3) How does the composition of a molecule of an element differ from that of a molecule of a compound?

B

(4) Make a "picture" equation of the example in which hydrogen is combined with nitrogen to make ammonia. (5) By means of the "picture" equation in item 4 explain how three volumes plus one volume shows a shrinkage to two volumes. (6) Why was it worth while to determine the composition of water so accurately? (7) Are chemical formulas the result of careful experimentation or are they "built up" without experimentation? Explain.

How Good Are You at Solving Problems?

(1) A gas is found to be twice as heavy as oxygen. What is its molecular weight?

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(2) A liter of nitrogen is found to weigh 1.251 g (S.T.P.). Show *two* ways in which you can determine the molecular weight of nitrogen.

(3) Arrange the following gases in the order of their decreasing densities: CH_4, Br_2, CO_2, O_2, NH_3, Cl_2.

(4) What is the ratio among the weights of the molecules of three gases which weigh 1.25 g, 1.43 g, and 0.717 g per liter respectively?

(5) A liter of a certain gas weighs 1.17 g (S.T.P.). What is the molecular weight of the gas?

(6) What is the molecular weight of a gas if 400 ml (S.T.P.) of it weigh 0.792 g?

(7) What is the molecular weight of a substance if 15.5 g of it dissolved in 500 ml of water give a solution which freezes at $-0.93°$ C.?

(8) Give the method for determining the weight of a liter of gas whose formula is known.

(9) Calculate the weight of a liter of hydrogen sulfide (H_2S).

Research and Activities That You Will Enjoy

Avogadro and Cannizzaro: A quiet, unassuming teacher, Amadeo Avogadro, announced an outstanding hypothesis that should have revolutionized and clarified chemistry fifty years before Stanislac Cannizzaro successfully explained it to skeptical chemists. Read for yourself and report how atoms and molecules were "untangled."

Problem 20

HOW HAVE SCIENTISTS DETERMINED ATOMIC WEIGHTS? HOW MAY YOU USE ATOMIC WEIGHTS IN CHEMICAL COMPUTATIONS?

How scientists have determined many atomic weights experimentally. Many students are curious to know how atomic weights are derived. One method used to find atomic weights of elements may be understood by noting the table on the next page. This table shows measurements made in the laboratory.

Note the figures in the carbon column. The smallest figure is 12 and each figure in the column is either 12 or a multiple of 12.

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HOW THE WEIGHTS OF ATOMS MAY BE DETERMINED

Compound	Mol. Wt.	Portion of the Molecular Weight Due to C	H	O	Cl
Carbon dioxide	44	**12**		32	
Carbon monoxide	28	**12**		**16**	
Alcohol	46	24	6	**16**	
Butane	58	48	10		
Propane	44	36	8		
Acetylene	26	24	2		
Benzene	78	72	6		
Chloroform	119.5	**12**	1		106.5
Methyl chloride	50.5	**12**	3		**35.5**

It is reasonable to suppose that, among all of the compounds of carbon, there should be one or more containing only one carbon atom. This will appear in the table as the smallest weight of carbon contained in the molecular weight of any of its compounds. In the carbon column it is 12. Since 12 is the smallest weight of carbon in any carbon compound, this figure is taken as the atomic weight of carbon. In a similar manner, it has been found that 1 is the approximate atomic weight of hydrogen; 16, of oxygen; and 35.5, of chlorine.

A Principle for You to Remember

The atomic weight of an element equals the *smallest weight of the element found in 22.4 liters of any of its gaseous compounds.*

Note that from this table it also is possible to determine the formula of each compound given. The table shows that in the carbon dioxide molecule there is one atom of carbon and two ($32 \div 16 = 2$) atoms of oxygen. The formula of carbon dioxide, then, is CO_2. In chloroform there is one atom of carbon, one of hydrogen, and three ($106.5 \div 35.5 = 3$) of

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chlorine. Its formula, then, is $CHCl_3$. Try to write the formulas of the other compounds in the table.

In using this method, one precaution must be observed. A great number of compounds must be used. Suppose the last two compounds in the table had been left out. Then from the data at hand you might decide that *two* was the atomic weight of hydrogen. Scientists check this method by other methods before drawing final conclusions.

How to use formulas and atomic weights to compute molecular weights. Atomic weights are units of the greatest use to the chemist. He may use them to determine the formulas of compounds (as in the table on page 152). If he knows the formula of a compound, he may use atomic weights to determine its molecular weight. For example, the formula of ethyl chloride is C_2H_5Cl. This means that 2 atomic weights of carbon, 5 atomic weights of hydrogen, and one atomic weight of chlorine have entered into its composition. Since the atomic weights of carbon, hydrogen, and chlorine are 12, 1, and 35.5 respectively, the molecular weight of C_2H_5Cl is:

$$\underset{\text{carbon}}{2(12)} + \underset{\text{hydrogen}}{5(1)} + \underset{\text{chlorine}}{35.5} = 64.5$$

To find the molecular weight of a compound, add the atomic weights of all atoms in the compound. You will find a table of atomic weights in this book on page 772.

Find the molecular weights of the following compounds: sodium chloride ($NaCl$), aluminum chloride ($AlCl_3$), potassium chlorate ($KClO_3$), calcium hydroxide [$Ca(OH)_2$], sodium sulfate (Na_2SO_4).

How to use atomic weights and the formula of a compound to compute the percentage composition of the compound. Being able to determine the molecular weight from a formula also gives you a method to determine the percentage of any element in a compound. The formula of copper oxide is CuO. If you wish to find what per cent of copper is present in copper oxide, you may proceed as shown on the following page.

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1. Find the molecular weight of CuO

Atomic weight of Cu	64
Atomic weight of O	16
Molecular weight of CuO	80

Sixty-four eightieths of copper oxide is copper.

2. Divide the weight of the element by the molecular weight.

$$\frac{64}{80} = 80\%$$

Therefore 80% of copper oxide is copper.

This problem is similar to the problem of determining the percentage of girls in a class. Suppose your class has 32 pupils in it, and 12 of them are girls. Of course you can find the percentage of girls by dividing 12 by 32. $12 \div 32 = .375$ or 37.5%.

A Principle for You to Remember

To compute the percentage composition of a compound, divide the total atomic weight of each element by the molecular weight of the compound. Express the resulting decimals as per cents.

How to use atomic weights and the percentage composition of compounds to compute the formulas of compounds. The problem of finding the formula when the percentage composition is given is just the reverse of the preceding problem. Suppose you have a compound with the following percentage composition: Ba 58.81%, S 13.73%, O 27.46%. To determine the formula of this compound, divide each per cent by the atomic weight of the element.

First step:

Ba	*S*	*O*
137) 58.81	32) 13.73	16) 27.46
.43	.43	1.72

These quotients are in the same ratio as the numbers of atoms in the different molecules. This ratio can be determined usually by dividing these relative numbers by the smallest one.

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Second step:

Ba	*S*	*O*
.43) 0.43	0.43	1.72
1	1	4

The formula of the compound is $BaSO_4$.

Readings for Pleasure and Profit

KENDALL, JAMES. *At Home among the Atoms.* Chap. V, pp. 63-74, "A Few Figures."

Putting Chemistry to Work

A

(1) In your own words explain how the constant composition of a compound is a result of the existence of units of matter. (2) What further proof do we have in the laws of definite composition and multiple proportions that matter is indestructible? (3) How do weighing and other measuring help us to understand the working of nature? (4) If a compound should be discovered containing just half as much carbon in a molecule as any carbon compound now known, would this discovery change our present table of atomic weights of elements? Explain.

B

(5) Can you give a reason why the "grammar of chemistry" is not completely organized even now?

How Good Are You at Solving Problems?

(1) Calculate the percentage of each element in calcium carbide (CaC_2).

(2) Which compound has the greater percentage of chlorine, $SbCl_3$ or PCl_3? Prove your answer by computation.

(3) The mineral calcite is composed of calcium 40 per cent, carbon 12 per cent, and oxygen 48 per cent. Compute its simplest formula.

(4) Compute the simplest formula of a compound containing calcium 29.49%, sulfur 23.59%, and oxygen 46.92%.

(5) If the simplest formula of a substance is NO_2 and its molecular weight is found to be 92, what is its true formula?

(6) The gas acetylene contains 92.31% carbon and 7.69% hydrogen by weight. A liter of it weighs 1.161 grams. Calculate its true formula.

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(7) The weight of 250 ml of iodine vapor is 2.8348 g (standard conditions). Compute its molecular weight. How may the atomic weight of iodine be computed from the molecular weight?

(8) Compute the molecular weight of a gas if 368 ml at 20° C. and 735 mm pressure have a weight of 0.622 g. (Gas laws are given in appendix.)

Problem 21

WHAT ARE ATOMS MADE OF AND HOW ARE THEY CONSTRUCTED?

Up until the early part of this century the atom was considered the ultimate unit of matter. Today, as a result of many keen scientific investigations and experiments, it is known that atoms are composed of even smaller units of matter. A theory has been developed which tries to give a picture of how the atom is constructed and why some atoms easily enter into chemical combinations and others do not. This is known as the *electronic theory* of the structure of matter.

All atoms contain one or more electrons and one or more protons —these are "building blocks" of atoms. Scientists have succeeded in "breaking down" atoms and have found different kinds of particles, two of which are the proton and the electron. Each of these two particles has an electric charge.

The *proton* has a positive charge of electricity. In weight a proton is slightly lighter than a hydrogen atom. Recent research indicates that the weight of a proton is $^{1844}/_{1845}$ the weight of a hydrogen atom.

The *electron* has a negative charge of electricity. It also has a definite weight. Recent research indicates that the weight of an electron is only $^{1}/_{1845}$ the weight of a hydrogen atom.

Although the proton and the electron have very different weights, their charges are *equal* but *opposite*.

The number of protons and the number of electrons in an atom are equal. Under ordinary conditions atoms are neutral

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—they show neither a positive nor a negative charge of electricity. This means that an atom contains equal numbers of protons and electrons which neutralize each other since they have opposite charges of electricity. This fact enables us to begin a "picture" of an atom.

Neutrons are another type of "building block" of atoms. In "breaking down" atoms, scientists also have obtained the *neutron* which has *no* electric charge. Its weight is very nearly the same as that of a proton. A neutron may be a compact bundle of one proton and one electron. However, in this book the term *proton* refers to the *free* protons in the nucleus, and the term *electron* refers to the *planetary* electrons which are outside of the nucleus.

Positrons and mesotrons have been found in the wreckage of some atoms. Very little is known about either the *positron* or the *mesotron.* The mesotron has a negative charge and a speed nearly equal to that of light. The positron has a positive charge of electricity and has about the same weight as the electron. It is not known definitely that the positron exists as such in atoms. It may be formed when an atom is "smashed." It is thought that a proton may be a combination of a neutron and a positron. This of course would account for the positive charge of a proton.

An atom is composed of a nucleus and one or more electrons which are at a distance from the nucleus. The atom is wonderfully constructed. The nucleus of an atom contains all its protons and neutrons and is therefore very dense. The number of protons, as previously stated, equals the number of electrons. This accounts for the fact that atoms are neutral. Since the electrons are comparatively very light, the weight of an atom is generally regarded as equal to the sum of the weights of its neutrons and protons.

Compared with their extremely small size, the electrons are spaced far out from the nucleus. Indeed the electrons around the nucleus of an atom have been compared with our planets around the sun, in so far as "open space" is concerned.

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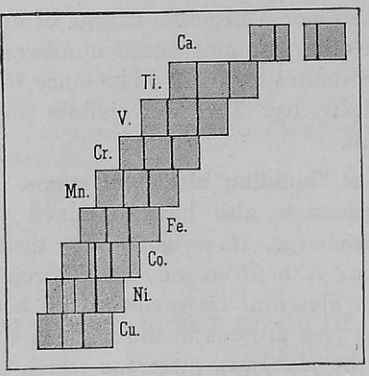

Moseley determined the X-ray spectra of the elements. He found there was a regular shift in the spectrum as the atomic weight increased. He arranged the elements in the order of their spectra, and numbered them from 1 (for hydrogen) to 92 (for uranium). These are the atomic numbers. The atomic number is equal to the number of positive charges on the nucleus.

56. X-RAY SPECTRA OF SOME ELEMENTS

What is the atomic number of an element? The atomic number represents the electric charge *of the nucleus* of an atom. This differs for each element. It has been found that the atomic number is the same as the number of free protons in the nucleus of the atom. Hence the atomic number represents the number of planetary electrons.

Perhaps the most important information concerning an atom is the number and arrangement of the electrons it contains. In particular it is the number of electrons in the *outer* shell of an atom that determines the chemical properties of the atom.

How the electrons are arranged in orbits or "shells." As you already have learned, the number of electrons in an atom equals the number of its protons. All of the electrons are located *outside* the nucleus. It is thought that the electrons are arranged about the nucleus in orbits or "shells." It is thought also that there are never more than 2 electrons in the first shell, never more than 8 electrons in the second shell, and no more than 8 electrons in the third shell (in case the atomic number of the element is not above 25).

How atoms are pictured. You may see by now that it is possible to "picture" the atoms of different elements and thus

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show what is thought to be the differences in their structures. In the "pictures" of atoms in this book the electrons are usually represented by black dots; protons are represented by the + sign; that is, 3 + in the center of a "picture" indicates that there are 3 protons in the nucleus; and 4 ± indicates that there are 4 neutrons in the nucleus.



57. HOW THREE KINDS OF ATOMS ARE PICTURED

The hydrogen atom has the simplest structure. Since its weight so closely agrees with the weight of the proton, scientists believe that it contains but one proton. One electron accompanies it to balance the positive charge and this makes the atom neutral. This electron is at a relatively great distance from the very small but very dense proton. It is pictured as revolving about the proton.

The helium atom has an atomic weight of 4 and its atomic number is 2. This means that its nucleus contains two neutrons and two protons. There are two electrons revolving about the nucleus. You have seen in Unit 2 that helium is an inactive element, forming no compounds. Hence it is believed that this arrangement of two electrons is an exceedingly stable condition. The two electrons seem to form a completed shell.

Lithium has an atomic weight of 7 and an atomic number of 3. Its nucleus contains four neutrons and three protons, and it has three electrons in its planetary system. This is one more than enough to make the very stable arrangement found in the helium atom. The third electron forms the beginning of a second electron shell. There seems to be a strong tendency to return to the stable condition, so the lithium atom very easily gives up this extra electron to some other element and thus becomes the positive portion of a compound.

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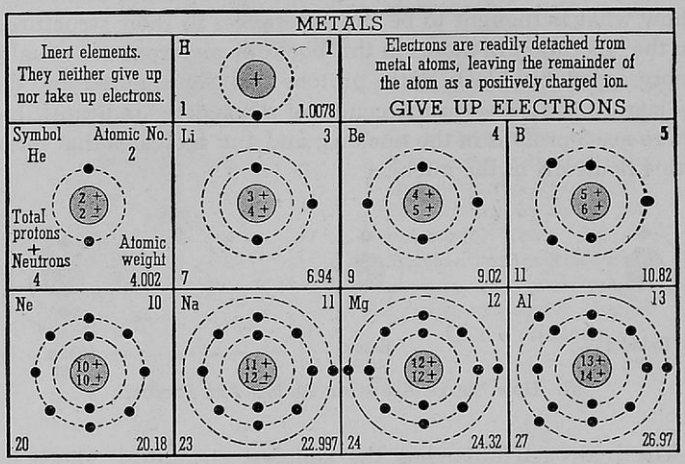

58a. ATOMIC STRUCTURE OF THE ELEMENTS

1. The nucleus of each atom is represented by the total number of neutrons and protons in it (center circle).

2. The number of protons in the nucleus is the *atomic number.* (See the upper right corner of each square.)

3. The number of planetary electrons also equals the atomic number.

4. The total number of protons and neutrons is equal to the *nearest whole number* of the atomic weight. Compare them.

5. Two electrons complete the first planetary shell as shown by the chemically inert nature of the helium atom. Note that this shell appears in all other atoms after helium.

6. Lithium gives up only one electron in chemical changes, so it is thought that this electron is located in a second planetary shell at a greater distance from the nucleus. Lithium is a very active metal.

7. With each following atom, beryllium to fluorine, the nucleus shows an additional proton with an additional electron in the second shell to balance it.

8. When the second planetary shell contains *eight* electrons, the element, represented as neon, is inert, so this second shell must be considered complete.

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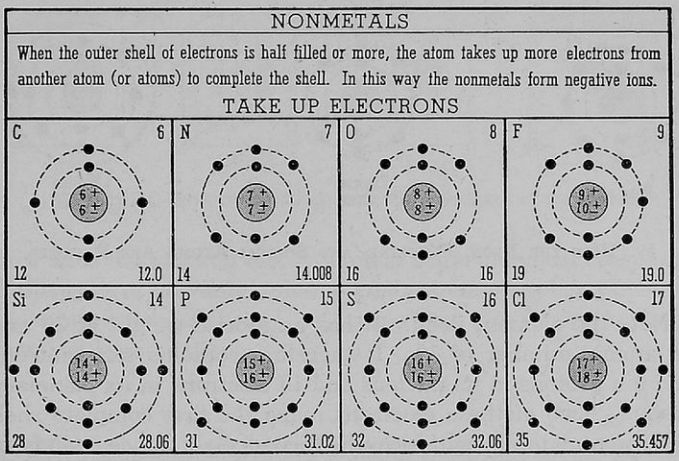

58b. ATOMIC STRUCTURE OF THE ELEMENTS

9. Another series of elements starts with the next atom which is sodium. A new planetary shell begins with one electron. Sodium is an active metal like lithium.

10. The elements following sodium continue to fill the third planetary shell with electrons until it is complete with the third inert element, argon, having eight electrons.

11. If the outer shell of electrons is less than half filled, such atoms are metals (except boron).

12. If the outer shell is half filled or more with electrons, such atoms are usually nonmetals.

13. The nonmetal elements take up electrons to complete their outer shells.

14. Active metals have few outer shell electrons and readily give them up to other atoms, thus becoming positively charged.

15. Active nonmetal elements lack a few electrons in their outer shell and eagerly take up more to complete the shell, becoming negatively charged.

16. The number of electrons given or taken up in its outer shell by an atom is an index of its combining value with other atoms. It is commonly called valence.

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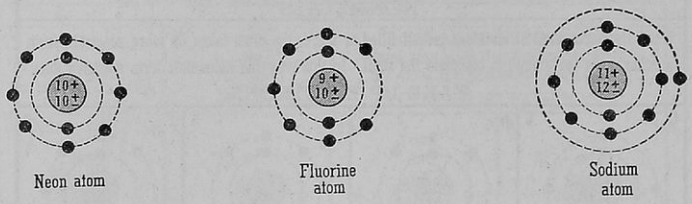

59. HOW THE NEON, FLUORINE, AND SODIUM ATOMS ARE PICTURED

Note the element neon. It has an atomic weight of 20 and an atomic number of 10. It therefore contains ten neutrons and ten protons in its nucleus and 10 electrons in its planetary system. Two of these electrons make the first complete shell and the remaining eight form the second shell. Since neon is an inactive element like helium, it also is thought to have a completed shell. Neon like helium forms no compounds. Its atomic structure is not capable of being altered in a chemical change.

Next, note the element fluorine. It has an atomic weight of 19 and an atomic number of 9. It has nine planetary electrons. Two are in the first shell and seven in the second. Fluorine, therefore, lacks only one electron of having enough to complete the second shell. The tendency to attain this stable condition is so great that fluorine readily takes on an electron from some other element to complete the shell. In this manner it becomes the negative portion of a compound.

The element with atomic number 11 is sodium. Its atomic weight is 23. It has eleven electrons, two of which are in the first shell, eight of which are in the second shell, and one starts the third shell. In this respect it is similar to lithium; it readily yields an electron to some "greedy" neighbor. A study of the tables on pages 160-161 will bring out some of these principles more clearly.

It is convenient to draw diagrams of the electrons in the atom as if they were all in one plane. In reality it is thought that the electrons are arranged about the nucleus in three dimensions, but this is difficult to show in diagrams.

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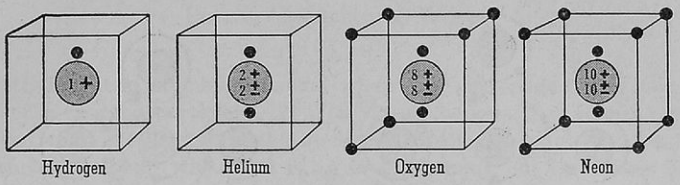
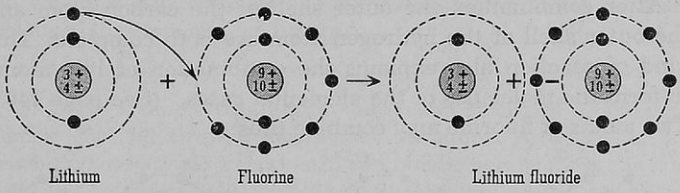


60. ATOMIC STRUCTURE IS SOMETIMES REPRESENTED BY CUBES

How does the electron theory explain some chemical reactions? A theory is of no value unless it enables us to explain phenomena when we meet them. Let us see how this theory explains chemical combination.

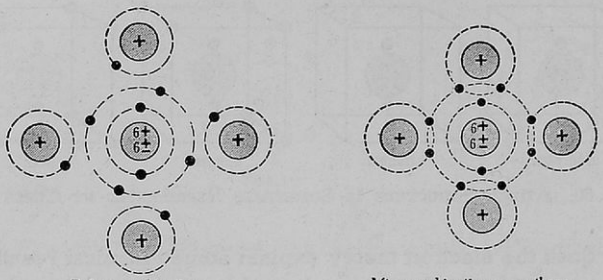


61. FORMATION OF LITHIUM FLUORIDE

If some lithium is brought in contact with some fluorine, they combine instantly. In the light of this theory let us see what may happen. A lithium atom contains one more electron than enough to make a complete shell, and fluorine lacks one of having enough to complete a shell. It seems reasonable to assume that the fluorine takes on the extra electron of the lithium and thus gains a negative charge, while the lithium acquires a positive charge because it has lost an electron.

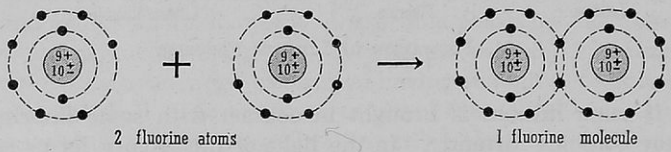
Another kind of combination may take place. Suppose an atom of carbon combines with hydrogen to form methane, CH_4. In this case there is no evidence of any change in the charge on the atom. In such cases it is believed that the atoms *share* electrons. Each hydrogen atom shares its electron with the carbon atom, and in turn one of the electrons of the carbon atom comes under the influence of the hydrogen nucleus.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



62a. COMBINATION OF ATOMS IN A NONPOLAR COMPOUND

After combination, the outer shell of the carbon atom and the outer shell of the hydrogen atom are both complete. This kind of reaction also explains the combination of like atoms to form the molecules of the elemental gases. (See page 146.) Two atoms of fluorine may combine thus:



62b. LIKE ATOMS MAY COMBINE BY SHARING ELECTRONS TO FORM MOLECULES

Likewise it can be shown how the oxygen molecule contains two atoms.

Readings for Pleasure and Profit

DAVIS, WATSON. *The Advance of Science.* Chap. IV, pp. 34-44, "Within the Atom"; Chap. V, pp. 45-61, "The Birth of Nuclear Chemistry."

KENDALL, JAMES. *At Home among the Atoms.* Chap. XIX, pp. 260-270, "Moving Out into the Country."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. XIV, pp. 168-186, "The Age of Electrons."

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Putting Chemistry to Work

A

(1) How can atoms be neutral when they are made up of electrically charged particles? (2) Why do we believe that all protons of an atom are located in the nucleus? (3) By means of its atomic structure explain why neon is an inert element. (4) By means of its atomic structure explain why chlorine is an active element. (5) How does the activity of sodium differ from that of fluorine? (6) You have noticed a chain dragging on the ground from a gasoline tank truck. Explain in terms of electrons, friction, and insulation how this safety device prevents a mischievous gang of electrons from gathering in numbers large enough to do some possible damage. (7) Write a paragraph explaining the relation of these four units: the molecule, the atom, the electron, the proton. (8) Try to find why the negative electrons are not attracted to the positive nucleus of the atom and held there.

B

(9) Draw a simple diagram of the atomic structure of element number 20. (10) Draw a diagram of the atomic structure of an element whose atomic weight is 28 and atomic number is 14. Is it a metal or a nonmetal? (11) Obtain any further data needed and make a drawing of an atom having 27 protons. What condition of its outer shell shows it to be a metal? (12) An atom has 15 planetary electrons. Determine its atomic number and its number of protons. How many electrons are there in the nucleus? (13) You most likely have not seen element number 21 or read about its properties, yet you may state its general properties from information gained in this lesson. Try it.

Problem 22

HOW DO THE ATOMS HOOK UP WITH EACH OTHER TO FORM COMPOUNDS?

The combining capacity of atoms is known as valence. When you experimentally determine the formulas of compounds by some of the methods given earlier in this unit, you find that atoms combine in various proportions. For example *one* atom

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of chlorine combines with one atom of sodium to form sodium chloride, while *two* atoms of chlorine combine with one atom of calcium and *three* atoms of chlorine combine with one atom of aluminum to form calcium chloride and aluminum chloride, respectively. The formulas of these compounds are NaCl, $CaCl_2$, and $AlCl_3$. This shows that the different metals have different abilities to hold chlorine in combination. This combining capacity of an element is known as the *valence* of the element.

How does the electron theory explain valence? You already have seen that certain electron structures seem to be very stable. When the outer shell or ring of electrons is complete (2 for the first ring, 8 for the second, etc.), the atoms seem satisfied. No electron exchanges are made, and the element forms no compounds. This condition is found in the atoms of helium, neon, argon, krypton, and xenon. These atoms have zero valences.

When the outer ring contains but a single electron, this electron is easily given up, and the atom acquires a positive valence of one. In this way atoms with less than four electrons in the outer shell easily give up their electrons and acquire positive valences. *Such elements are metals.* A metal may be defined as an element which readily gives up electrons and acquires a positive valence.

In a similar manner atoms whose electron rings are nearly complete can add electrons, borrowed from some metal, to complete the shell, and thus acquire a negative charge or valence. *Such elements are nonmetallic.*

In the diagrams on page 167, the electron exchanges that take place when sodium reacts with oxygen are shown.

Each sodium atom has one electron in its outer shell. The oxygen atom, having six electrons in its outer shell, needs two additional electrons to make a complete shell. Two atoms of sodium are therefore required to furnish the two electrons necessary to complete the oxygen shell. The transfer of the extra electrons from the sodium to the oxygen gives each of the sodium atoms an excess positive charge of one and the oxygen

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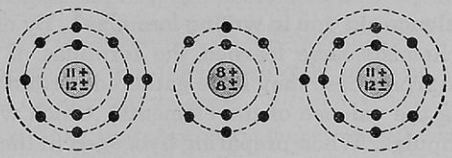
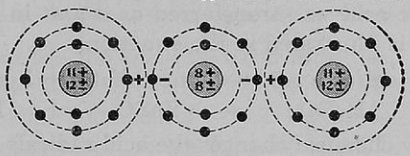
atom an excess negative charge of two. In this manner the valence of the sodium becomes +1 and the valence of the oxygen becomes —2.



Before combination—1 oxygen atom, 2 sodium atoms.



After combination—sodium oxide molecule

63. How Sodium Combines with Oxygen to Form Sodium Oxide

Elements which have from three to five electrons in the outer shell find it about as easy to lose electrons as to gain them to complete the shell. Sometimes these elements may give up electrons, acting as metals, and sometimes these same elements may take on electrons, acting as nonmetals. Such elements are *amphoteric*. Arsenic is such an element. It may give up three electrons to chlorine atoms forming $AsCl_3$, or it may take on electrons from a metal, as copper, forming a compound, such as Cu_3As_2.

In cases where electrons are shared, there is a union of neutral atoms. In this case there is no loss or gain of electrons, so we cannot say that either atom gets a positive or negative charge. In such cases the atoms are said to possess *covalence*, and their covalence is measured by the number of electron pairs they share with other atoms. (See Fig. 62a, page 164.)

Note that each hydrogen atom shares one electron pair with carbon while the carbon shares four electron pairs. Thus the valence of hydrogen is called 1, and the valence of carbon is called 4. In cases of this kind, it is customary to speak of the element which more nearly resembles a metal as positive and

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the less metallic element as negative. In this case, it is said that hydrogen has a positive valence of 1 and that carbon has a negative valence of 4.

How will valence aid you in writing formulas? By experimental processes chemists have learned the formulas of many compounds, and from these they have gathered certain information (concerning the valence of the elements) which will help you to write formulas. When preparing hydrogen in the laboratory, you found, no doubt, that the SO_4 group (the sulfate radical) of the sulfuric acid was transferred *as a unit* in the chemical change. This is illustrated in the equation:

zinc + sulfuric acid → zinc sulfate + hydrogen

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

Since in many chemical changes the acid radicals do not break up but are transferred as units, it is said that they too have valence. In your work in the laboratory it is convenient to know whether an element or radical has a positive or negative charge. The following table gives some valuable information.

COMMON VALENCES OF COMMON ELEMENTS AND RADICALS

+	++	+++	++++
H	Most other common metals not in columns I, III, and IV	Al	C
		Sb	Sn
Alkali (Li, Na, K) metals		Fe (ic)	S
Ag			
NH_4			
−	**−−**	**−−−**	**−−−−**
Halogen (F, Cl, Br, I) acid radicals	O	PO_4	SiO_4
	CO_3		
Nitrogen acid radicals	Sulfur acid radicals		
OH			

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This table is far from complete, but it will do to start with.[1] As you use it to write formulas, keep in mind the following:

> Principles for You to Remember
>
> 1. Combination will take place only between elements or radicals of opposite valence.
>
> 2. The sum of the positive valences must balance the sum of the negative valences.

Note how to use the table to write formulas. Suppose you wish to write the formula of silver chloride. Silver has a valence of +1 and chlorine a valence of −1. The valences are equal and will balance each other, so the formula is AgCl. The formula for silver nitrate is written $AgNO_3$ because the +1 valence of silver is balanced by the −1 valence of the nitrate radical, NO_3.

If you wish to write the formula of aluminum chloride, you find that aluminum has a valence of +3 and that chlorine has a valence of −1. It will take three negative chlorine atoms to balance the charge on the aluminum, so the formula is $AlCl_3$.

Suppose you wish to write the formula of aluminum oxide. Oxygen has a valence of −2, and aluminum has a valence of +3. These positive and negative charges must balance. In a case of this kind,

1. Write the symbols of the elements or the radicals with the valence charge, as: $Al^{+++}\ O^{--}$

2. Find a common multiple of the valences. In this case it is 6.

3. Divide this common multiple by the valences of the elements. Use the numbers so obtained as subscript figures in writing the formula, as:

$$\underset{6 \div 3 = 2}{Al} \qquad \underset{6 \div 2 = 3}{O}$$

$$Al_2O_3$$

[1] See the table of valences opposite the inside back cover. It will also be very helpful for you to learn the names and formulas of the acids given on page 789. Your instructor will tell you which ones to learn first.

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When radicals are used, care must be taken to inclose them in parentheses if they are used with subscript figures. For example, in writing the formula for ferric hydroxide, the valence of the ferric (iron) atom is +3, and the valence of the hydroxide (OH) radical is —1. You must, therefore, use 3 hydroxide (OH) radicals for each iron atom. The formula should be written $Fe(OH)_3$. The formula for calcium nitrate is $Ca(NO_3)_2$. Can you explain why? Also explain why the formula for ammonium sulfate is $(NH_4)_2SO_4$ and calcium phosphate is $Ca_3(PO_4)_2$.

Knowledge of a few valences enables you to learn others. When you know the valences of a few common elements and radicals, you can use them to find the valences of other elements and radicals with which they combine. For example, what is the valence of osmium in the compound osmium oxide, OsO_4? The valence of oxygen is —2. Four oxygen atoms will have a total valence of —8. Since OsO_4 is the correct formula, you can infer that the valence of osmium must be +8 because there must be a balance between the positive and negative charges. In a similar manner, explain why the valence of magnesium is +2 if the correct formula for magnesium chloride is $MgCl_2$.

Note how to determine the valence of the acid radical in the compound, Na_3AsO_4. Sodium has a valence of +1. The total valence of the sodium atoms in this formula is +3. The acid radical, AsO_4, then must have a valence of —3.

The formula of magnesium acetate is $Mg(C_2H_3O_2)_2$. What valence do you infer for the acetate radical? Explain.

A thorough understanding of valence and particularly the ability to use valence in the writing of formulas will be most important to you in future work. If you will learn your valence table and learn to use it automatically in writing formulas, you will find your chemistry work much easier.

Readings for Pleasure and Profit

KENDALL, JAMES. *At Home among the Atoms.* Chap. X, pp. 141-158, "Valencia."

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Applying in Life What You Have Learned in Chemistry

A study hint: You can study chemistry better after you have learned the meaning of formulas and have learned to represent substances with formulas.

Putting Chemistry to Work

A

(1) What objection would there be to having an atom of high combining value as a standard of valence? (2) When two atoms of the same valence combine, why are no subscripts written? (3) Explain how the subscripts in a correct formula make an equality between the total positive and negative units of valence. (4) Indicate the valence of the negative part of these compounds by the proper number of minus signs: HBr, HF, HI, H_2S, $HClO_3$, H_2CO_3, $HMnO_4$, H_4SiO_4. (5) By means of a diagram show the conditions of valence electrons for the molecule of chlorine (Cl_2). Also show by a simplified diagram the molecule of bromine (Br_2). (6) Make simplified diagrams of the compounds: $MgCl_2$, Ag_2O, LiOH, $Ca(OH)_2$, H_3P.

(7) Copy this form on a separate sheet and write the correct formulas in the spaces where the columns intersect.

Positive radical	*chloride* Cl	*oxide* O	*nitrate* NO_3	*hydroxide* OH	*sulfide* S	*sulfate* SO_4	*phosphate* PO_4	*silicate* SiO_4
H	HCl	H_2O	HNO_3	HOH	H_2S	H_2SO_4	H_3PO_4	H_4SiO_4
Na	NaCl	Na_2O	$NaNO_3$	NaOH	Na_2S			
Ca								
Bi								
Mg								
Al								
NH_4		(omit)						
Ag								

(8) Consider the number of valence electrons and give reasons why metals do not form two-atom molecules. (9) The atomic weight of a metal is 56. Twenty-eight grams of it replace one gram

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of hydrogen. What is the valence of the metal? (**10**) How does the outer shell of electrons determine the degree of activity of an element?

(**11**) Write the formulas for the following compounds: (a) Silver nitrate, (b) Ammonium hydroxide, (c) Barium nitrate, (d) Potassium carbonate, (e) Sodium phosphate, (f) Magnesium chlorate, (g) Calcium sulfate, (h) Aluminum hydroxide, (i) Zinc sulfide, (j) Ferric sulfate, (k) Calcium iodide, (l) Zinc oxide, (m) Hydrogen phosphate, (n) Potassium oxide, (o) Calcium chloride, (p) Nitrogen (tri) oxide, (q) Potassium sulfate, (r) Zinc sulfate, (s) Aluminum nitrate, (t) Ammonium sulfide, (u) Phosphorus (pent) oxide, (v) Hydrogen chloride, (w) Sodium carbonate, (x) Ammonium sulfate, (y) Potassium hydrogen sulfate.

(**12**) Write the formulas for the following compounds: (a) Ferrous carbonate, (b) Copper (ic) chloride, (c) Potassium chlorate, (d) Aluminum acetate, (e) Magnesium hydroxide, (f) Manganese dioxide, (g) Silver chloride, (h) Aluminum sulfide, (i) Magnesium nitride, (j) Aluminum carbonate, (k) Hydrosulfuric acid, (l) Hydrobromic acid, (m) Barium chlorite, (n) Ferrous chloride, (o) Mercuric oxide, (p) Cupric nitrate, (q) Sodium sulfite, (r) Carbon dioxide, (s) Calcium carbonate, (t) Ammonium carbonate, (u) Calcium nitride, (v) Sodium nitrite, (w) Chlorous acid.

B

(**13**) How does the electronic theory explain valence? (**14**) In terms of the electronic theory, what is a metal? What is a nonmetal? (**15**) Show how the electronic theory explains the fact that sulfur may have a valence of -2 and $+6$. (**16**) The electronic theory of atomic structure has been developed largely since 1905. Did we know anything about valence before then? Explain. (**17**) How is it possible for some elements to act sometimes as a metal and sometimes as a nonmetal? (**18**) Draw a diagram to show how electrons are paired in the compound CCl_4. (**19**) Explain how a knowledge of the valences of elements and radicals makes chemistry easier for you.

Research and Activities That You Will Enjoy

Langmuir; Lewis; Millikan: Irving Langmuir, Gilbert N. Lewis, and Robert Millikan are three American scientists whose work in the study of the atom is outstanding and authoritative. Investigate one of their achievements in the field of atomic structure.

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Looking Back into Unit 4

Be sure you know the purpose of this unit. Read again the material on page 138, "Looking Ahead into Unit 4." Then study the following Summary Test.

Summary Test

1. *Why do you believe that molecules are composed of atoms?*
   (a) Distinguish between a hypothesis, a theory, and a law. Illustrate each.
   (b) How does the electrolysis of water indicate that molecules are made up of particles smaller than molecules?
   (c) How does the Law of Definite Composition point toward atoms as units of matter?
   (d) How does the Law of Multiple Proportions give convincing evidence of the existence of atoms?
   (e) What are the main points in the atomic theory?
2. *What discoveries enable you to know about the molecular weights of substances?*
   (a) What two laws made possible the determination of molecular weights?
      (1) What is Gay-Lussac's law?
      (2) What is Avogadro's law?
   (b) How can you show that an oxygen molecule contains two atoms?
   (c) Why are the weights of units of matter expressed relatively?
      (1) What is the standard of reference for expressing the relative weights of atoms and molecules?
      (2) What is the gram-molecular weight (G.M.W.) of a substance?
      (3) What is the gram-molecular volume (G.M.V.) of a gas?
   (d) How can you determine molecular weights by using gram-molecular volume?
3. *How may you know about and use atomic weights?*
   (a) How are atomic weights determined?
   (b) How can you use formulas and atomic weights to compute the molecular weight of a substance?
   (c) How can you use formulas and atomic weights to compute the percentage composition of a compound?
   (d) How can you use atomic weights and the percentage composition of a compound to compute its formula?

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4. *What are atoms made of and how are they constructed?*
   (a) What are the "building blocks" of atoms?
      (1) Distinguish between a proton and an electron.
      (2) Why is an uncombined atom electrically neutral?
   (b) Where are the protons in an atom located? the electrons?
   (c) What is the atomic number of an element? What does it show you?
   (d) How are atoms "pictured"? Give several examples.
   (e) How can you use the electron theory to explain some chemical combinations?

5. *How do atoms hook up with each other to form compounds?*
   (a) What is valence?
      (1) How does the electron theory explain valence?
   (b) How do you use valence in writing formulas? Illustrate.
   (c) How can you infer valences from correct formulas? Show with examples.
   (d) What rules should you remember and use in writing formulas?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

It has been said that the *philosophers* of ancient *Greece* did a great deal of *thinking* but little *experimentation;* that the *alchemists* of the *middle* ages did a great deal of *experimenting* but gave little *thought* to what they did. However, a study of this unit shows that *modern chemists* are basing their *thinking* upon *experimental evidence.* You may not be able to understand all the fine points they bring out, but you can appreciate the fact that they are putting up a good argument and giving much concrete evidence by their findings.

It is evident that *order* can *come out* of *chaos* if the *scientific method* is applied. A *theory* or a supposition, set forth by some farseeing scientist, may eventually be *supported* by enough *proof* to become a *law.* Even such small and invisible particles as *molecules* and *atoms* yield their secrets to the scientists' measuring devices.

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Courtesy, General Electric Co.

SODIUM VAPOR LIGHTS. These lights are on the San Francisco-Oakland Bridge.

So you can talk glibly of *relative weights* of the *atoms* and *molecules* as though they were on the grocers' shelves or in the butchers' showcases waiting to be purchased for home consumption. Your excursion into the theoretical aspects of the study of chemistry should do a great deal to make you more respectful toward science and more appreciative of the scientist.

You find that *gases* are very uniform in their *behavior* and furnish one of the best means for obtaining information about the *chemical union of elements* to form *compounds*. This unit helps to bring in the chemical "architect," *valence*, to show you how the *92 "building blocks"* are put together in the formation of compounds. This "architect" does not use very many rules, but the rules that are used are exact and binding.

The *modern chemist and physicist* were not satisfied with the atom as it was. They wanted to know *why* atoms of various elements could combine with each other, so they started *"tearing the atom apart."* They used their imagination, some delicate instruments, and common sense; and they have worked out an *electron theory*.

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Looking Ahead into

Unit Five

Have you ever noticed how easy it is to find a book in a library? and how uncertain it frequently is even for the owner to locate a book in a second-hand book store?

Likewise have you ever stopped to consider what a large number of chemical compounds are known to chemists? On first thought it might appear that the task of learning about so many compounds would be a very difficult one indeed. And it most certainly would be difficult if it were not possible to group many of them into three general classes of compounds —acids, bases, and salts.

One of the aims of any science is to simplify by applying general statements to many individual cases. Often it is desirable to bring similar substances together and to represent them with a single typical example. Thus we say that hydrochloric acid is a typical acid, sodium hydroxide is a typical base, and sodium chloride (table salt) is a typical salt.

You will study more about these representative compounds in this unit. You will also explain by means of the ionic theory how these and other acids, bases, and salts react in solutions—why solutions of these compounds are different from the solutions of other compounds.

Problem 23. *Hydrochloric Acid Is a Typical Acid. How Is It Prepared and Used?*

Problem 24. *Sodium Hydroxide Is a Typical Base. How Is It Used and Produced?*

Problem 25. *What Are the Properties of Acids, Bases, and Salts; How Are They Prepared?*

Problem 26. *How Do Solutions of Acids, Bases, and Salts Differ from Other Solutions; How Are These Differences Explained by a Theory of Ions?*

Problem 27. *What Part Does Electricity Play in Your Chemical World?*

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Acids and Bases: How the Ionic Theory Explains the Action of Acids, Bases, and Salts

Problem 23

HYDROCHLORIC ACID IS A TYPICAL ACID. HOW IS IT PREPARED AND USED?

Hydrochloric acid is prepared from the gas, hydrogen chloride. Hydrochloric acid is formed when the gas hydrogen chloride dissolves in water. Hydrogen chloride in turn is made from table salt. You may not yet be familiar with hydrogen chloride but you most certainly are acquainted with table salt, or sodium chloride, which is produced in the United States at the rate of approximately eight million tons each year.

Common table salt is one of the chief materials used in obtaining hydrogen chloride. Every year a vast amount of salt is used. Only a small part of this amount comes from the evaporation of ocean water which contains only about three per cent of it. There are in the United States vast deposits of rock salt of varying degrees of purity. These beds of salt were deposited from ancient oceans by evaporation of water much as is now happening in the salt lakes of our western states. When it is not convenient to mine these deposits directly, the salt is removed as brine by pumping water down into the deposits. The salt solution is then evaporated by various means and the sodium chloride, along with other soluble minerals, is recovered and purified.

Salt is available in almost unlimited quantities. Since it is extremely abundant and cheap, one can easily see why sodium chloride is one of the chief materials used in obtaining not only hydrochloric acid and chlorine, but also sodium.

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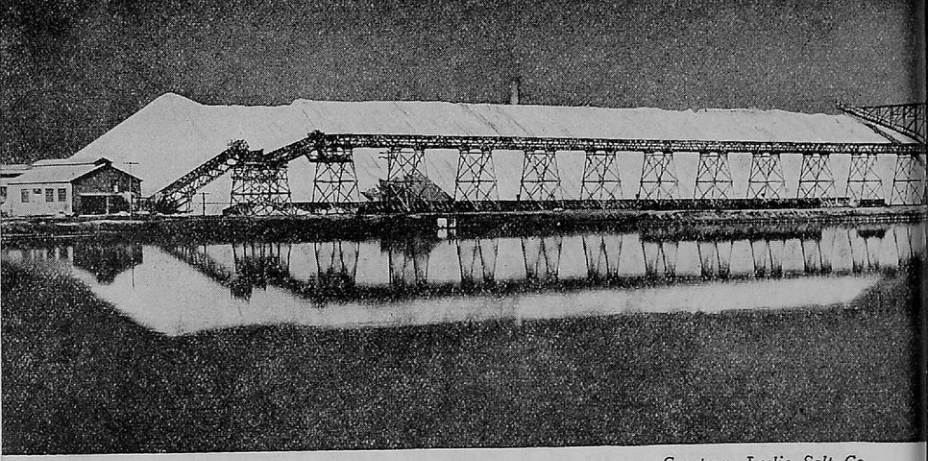

Courtesy, Leslie Salt Co.

64. Salt from the Ocean. This pile of NaCl contains about 320,000 tons reclaimed from sea water by solar evaporation. It has been further purified by recrystallization. About four million tons of salt are used annually in the United States.

Hydrogen chloride is prepared by heating table salt with sulfuric acid. When moderately concentrated sulfuric acid is gently heated with sodium chloride, there is formed a colorless gas with a sharp pungent odor. This gas is hydrogen chloride. The formula of hydrogen chloride is HCl and the equation for the reaction is:

$$\underset{\text{hydrogen sulfate}}{H_2SO_4} + \underset{\text{sodium chloride}}{NaCl} \longrightarrow \underset{\text{hydrogen chloride}}{HCl\uparrow} + \underset{\text{sodium hydrogen sulfate}}{NaHSO_4}$$

A glance at this equation shows that the sulfuric acid (H_2SO_4) supplies the hydrogen and that the sodium chloride furnishes the chlorine. Any soluble chloride *could* be used in the preparation of hydrogen chloride. Can you explain why sodium chloride is used in this preparation both in the laboratory and on a commercial scale?

You may be interested in seeing a diagram of the usual laboratory apparatus used in preparing hydrogen chloride since you will prepare this gas in your laboratory. (See Fig. 65.) The HCl gas may be dried by passing it through concentrated sulfuric acid.

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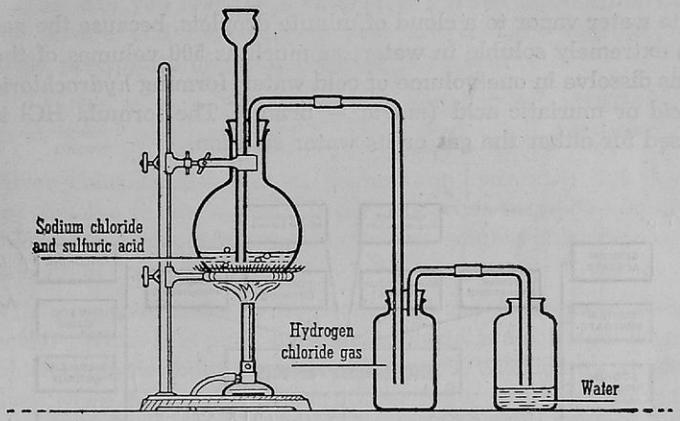

65. PREPARATION OF HYDROGEN CHLORIDE. Sulfuric acid and salt exchange radicals to make hydrogen chloride and sodium hydrogen sulfate. This drawing illustrates a general method for preparing acids.

How hydrogen chloride is prepared commercially. In the reaction on page 178 you will note that only one atom of the hydrogen in sulfuric acid was replaced by sodium. In the commercial preparation a mixture of sodium chloride and sulfuric acid is heated at a higher temperature than is used in the laboratory preparation. The high-temperature reaction with an excess of sodium chloride is:

$$H_2SO_4 + 2\ NaCl \longrightarrow 2\ HCl\uparrow + Na_2SO_4$$

hydrogen sulfate	sodium chloride	hydrogen chloride	sodium sulfate

Hydrogen chloride is also formed commercially by the direct union of hydrogen and chlorine when both of these gases are by-products obtained in the electrolysis of sodium chloride.

What are the properties of hydrogen chloride? This pungent, colorless gas is somewhat heavier than air ($36.5 \div 29 = 1.26$). One liter weighs 1.64 grams at standard conditions. It does not burn or support combustion. Hydrogen chloride unites with ammonia gas to form a white smoke of ammonium chloride. In moist air hydrogen chloride fumes by condensing

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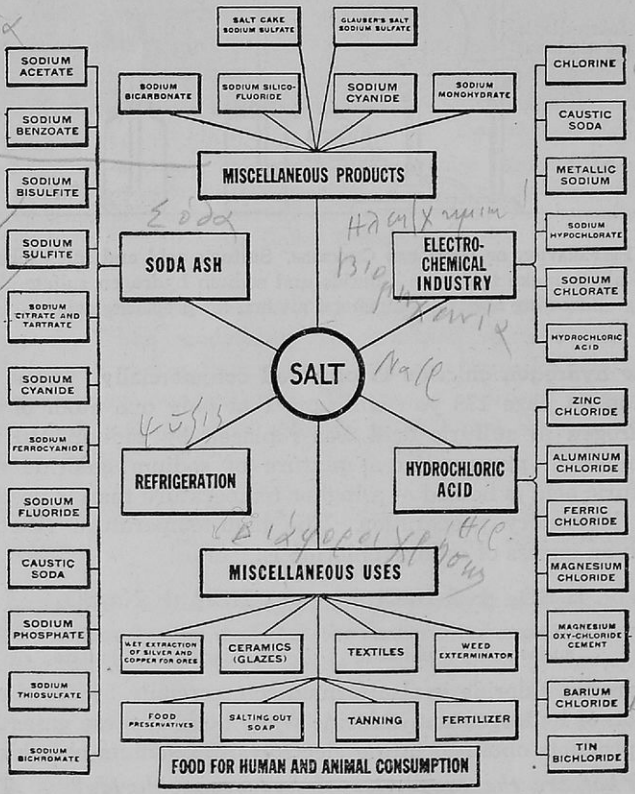
the water vapor to a cloud of minute droplets, because the gas is extremely soluble in water; as much as 500 volumes of the gas dissolve in one volume of cold water, forming *hydrochloric acid* or muriatic acid (*muria* = brine). The formula HCl is used for either the gas or its water solution.



Courtesy, International Salt Company

66. SALT IN THE CHEMICAL INDUSTRY. This diagram shows a wide variety of products obtained from ordinary salt. Can you name at least one use for each compound in the outside columns?

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How can you test for a chloride? When solutions of silver nitrate and hydrochloric acid are brought together, a white precipitate of silver chloride is formed:

$$\underset{\text{silver nitrate}}{AgNO_3} + \underset{\text{hydrogen chloride}}{HCl} \longrightarrow \underset{\text{silver chloride}}{AgCl\downarrow} + \underset{\text{hydrogen nitrate}}{HNO_3}$$

Silver chloride dissolves in ammonium hydroxide but does not dissolve in nitric acid. These properties serve to identify chlorine in hydrochloric acid or in any soluble chloride, such as sodium chloride.

What properties make hydrochloric acid one of the most useful acids? When it is pure, hydrochloric acid is a colorless liquid which contains about 38 per cent hydrogen chloride by weight. Even when dilute it has a sharp, sour taste. It is interesting to know that the gastric juice in the stomach may contain as much as 0.2 per cent hydrochloric acid. It is necessary in the digestion of proteins.

Hydrochloric acid reacts with active metals forming hydrogen and a chloride of the particular metal used. With magnesium the reaction is:

$$\underset{\text{magnesium}}{Mg} + \underset{\text{hydrogen chloride solution}}{2\,HCl} \longrightarrow \underset{\text{hydrogen}}{H_2\uparrow} + \underset{\text{magnesium chloride}}{MgCl_2}$$

Hydrochloric acid also reacts as a typical acid with carbonates, with oxides, and with hydroxides:

$$\underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{hydrochloric acid}}{2\,HCl} \longrightarrow \underset{\text{calcium chloride}}{CaCl_2} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2\uparrow}$$

$$\underset{\text{magnesium oxide}}{MgO} + \underset{\text{hydrochloric acid}}{2\,HCl} \longrightarrow \underset{\text{magnesium chloride}}{MgCl_2} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{aluminum hydroxide}}{Al(OH)_3} + \underset{\text{hydrochloric acid}}{3\,HCl} \longrightarrow \underset{\text{aluminum chloride}}{AlCl_3} + \underset{\text{water}}{3\,H_2O}$$

Hydrochloric acid is one of the most important acids; it serves many uses. The reactions shown above suggest several important uses for this typical acid. Much hydrochloric acid is used in removing the coating of oxide from iron which is to be

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covered with zinc or tin. In a similar reaction it is used in cleaning metals in preparation for soldering. Any one of the four reactions may be used in the preparation of various metallic chlorides. Great quantities of hydrochloric acid are used as a catalyst in the preparation of sirup from cornstarch (see page 512), in dissolving the calcium phosphate in animal charcoal, and in the manufacture of textiles, dyes, and also drugs.

Readings for Pleasure and Profit

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. VIII, pp. 117-118, "Hydrochloric Acid"; Chap. IX, pp. 129-132, "Acids."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. VI, pp. 200-204, "Hydrochloric Acid."

Applying in Life What You Have Learned in Chemistry

The chief purpose of any good bath salt is to soften water. Many cheap bath salts contain colored and cheaply perfumed rock salt which does not soften water. What test could you make to determine if a bath salt contains sodium chloride? Why not make the test on several samples?

"Can you let me have a little muriatic acid for soldering?"

"Sure, if we have any. Mr. Sharp stepped out for just a minute, but maybe I can get it for you. Though I don't believe I've seen any around—what kind of acid did you say?"

The chemistry student found all the usual concentrated acids but found none labeled "muriatic acid," so he stated that he did not have any.

What would you have done?

Putting Chemistry to Work

A

(1) Why does glassware frequently become cloudy in the laboratory? (2) How may table salt be kept from "caking"? (3) Why and how is hydrochloric acid used in soldering? (4) In the classroom a student stated, "When hydrochloric acid is electrolyzed, equal volumes of hydrogen and chlorine are evolved." When he tried the experiment in the laboratory, he was surprised to find a

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smaller volume of chlorine. Can you explain? (5) In the laboratory a bottle of gas is believed to be hydrogen chloride. How can you test it? Outline a plan. (You have at hand solutions of ammonium hydroxide, silver nitrate, nitric acid, magnesium ribbon, a splint, red litmus paper, and the usual laboratory apparatus.)

B

(6) Which has the lower freezing point, water from Great Salt Lake or water from the ocean? How do you know? (7) Give the names and formulas of five salts of hydrochloric acid. (8) In the laboratory preparation of hydrogen chloride, what four compounds aside from water are present in the flask? Why does only one of these compounds leave the flask while the others remain in it? (9) Show why common salt is one of the few most important minerals known. (10) Scheele prepared chlorine for the first time by heating a mixture of hydrochloric acid and manganese dioxide, but he thought chlorine was an oxide. Can you explain?

Research and Activities That You Will Enjoy

A demonstration: Devise and perform before the class an experiment to show the great solubility of hydrogen chloride. Use the hydrogen-chloride fountain method or the mercury-in-a-long-tube method. (These methods are described in Fowles, *Lecture Demonstrations in Chemistry,* pp. 140-141.)

A chart: Make and use a large chart to show what can be done with sodium chloride.

Problem 24

SODIUM HYDROXIDE IS A TYPICAL BASE. HOW IS IT USED AND PRODUCED?

What properties of sodium hydroxide make it useful? Another well-known and very useful compound which is obtained commercially from table salt is sodium hydroxide (NaOH). This substance is a white, crystalline solid. It is very soluble in water. It has a bitter taste, feels slippery between the fingers, and "burns" the skin. In the home sodium hydroxide is known as *lye.* It is useful as a strong cleaning agent because it acts

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67. IMPURE AND PURE SODIUM HYDROXIDE. "Lye" is crude sodium hydroxide. The highly purified product is known as chemically pure (C. P.) sodium hydroxide.

on grease and fats to form soluble compounds. Its use in cleaning drainpipes (*Drano*) of kitchen sinks depends on this action.

For laboratory use sodium hydroxide is usually purchased in slender sticks, in pellets, or in flakes. Since it rapidly absorbs moisture and carbon dioxide from the air, its containers should always be kept tightly closed. A solution of sodium hydroxide slowly acts on glass, and seals the stoppers of glass bottles. For this reason bottles of sodium hydroxide solution often have rubber stoppers.

In industry sodium hydroxide is extremely important as a raw material. Here it is usually known as *caustic soda* because it quickly disintegrates most vegetable and animal

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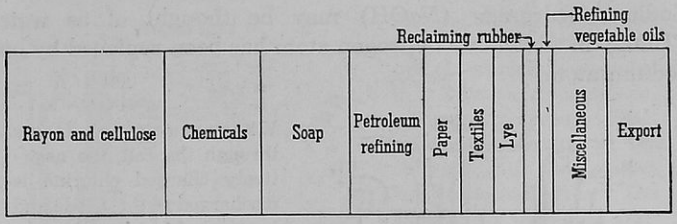

68. USES OF SODIUM HYDROXIDE

material. Caustic soda is used in the making of soap and in the refining of petroleum. Next to sulfuric acid, sodium hydroxide is probably the most widely used and important chemical. Sodium hydroxide, like all bases, contains the hydroxyl radical (OH). It turns red litmus blue and colorless phenolphthalein red. This base acts on fats to form soaps and glycerin. (See page 506.) Sodium hydroxide reacts with hydrochloric acid to form water and sodium chloride:

BASE	+	ACID	→	WATER	+	SALT
NaOH	+	HCl	→	HOH	+	NaCl
sodium hydroxide		hydrochloric acid		water		sodium chloride

Metallic sodium reacting with water produces sodium hydroxide. In the section on hydrogen you will recall that you obtained small amounts of this gas by the action of metallic sodium on water. The action was so vigorous that only a small piece of sodium was placed on water at a time. It was pointed out that one atom of sodium replaces one atom of hydrogen from a molecule of water. This action is expressed by the equation:

2 Na	+	2 HOH	⟶	2 NaOH	+	$H_2\uparrow$
sodium		water		sodium hydroxide		hydrogen

The remaining solution contains sodium hydroxide; it turns red litmus paper blue which is a test of its basic action.

The ease with which sodium replaces hydrogen shows that sodium is more active than hydrogen. From the standpoint of electrons this means that a sodium atom (Na: 2, 8, 1) is more eager than an atom of hydrogen to lose its outer electron.

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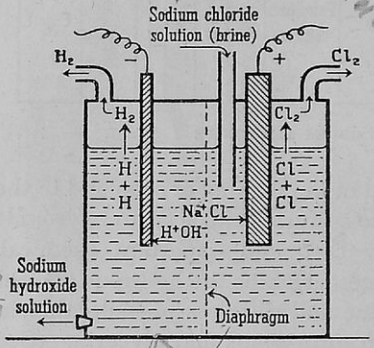
Sodium hydroxide (*Na*OH) may be thought of as water (*H*OH) in which one hydrogen atom has been replaced by one sodium atom.



When a current flows through the cell, the negatively charged chlorine is discharged at the anode and becomes chlorine molecules. The positively charged ions of sodium and hydrogen move to the cathode where hydrogen is liberated and sodium hydroxide remains in solution. A porous partition separates the two electrodes.

69. ELECTROLYSIS OF BRINE

Sodium hydroxide may be produced by electrolysis. With the preceding explanation in mind, you can more easily understand how sodium hydroxide is prepared directly from table salt and water by electrolysis. Electrolysis was mentioned on page 71 as a method of obtaining hydrogen from water. You are now concerned with obtaining the sodium hydroxide, the sodium coming from the table salt and the hydroxide (OH) coming from the water.

A diagram of the electrolysis of sodium chloride solution (brine) is shown in Fig. 69. The equation for the electrolysis of sodium chloride solution is:

$$\underset{\text{sodium chloride}}{2\,NaCl} + \underset{\text{water}}{2\,HOH} \xrightarrow{+\text{ electrical energy}} \underset{\text{hydrogen}}{H_2\uparrow} + \underset{\text{chlorine}}{Cl_2\uparrow} + \underset{\text{sodium hydroxide}}{2\,NaOH}$$

A diaphragm is used between the electrodes to keep the chlorine from reacting with the sodium hydroxide solution.

The apparatus which is most often employed in the commercial preparation of sodium hydroxide is the Nelson cell or the Vorce cell. (See Fig. 70.) The brine is contained in an

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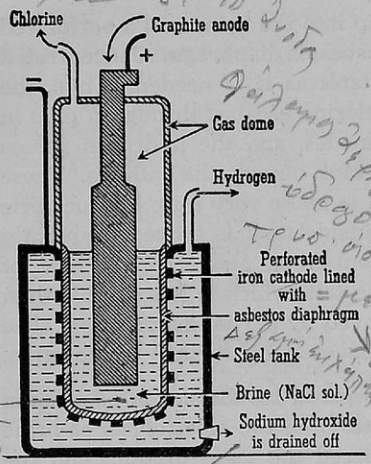
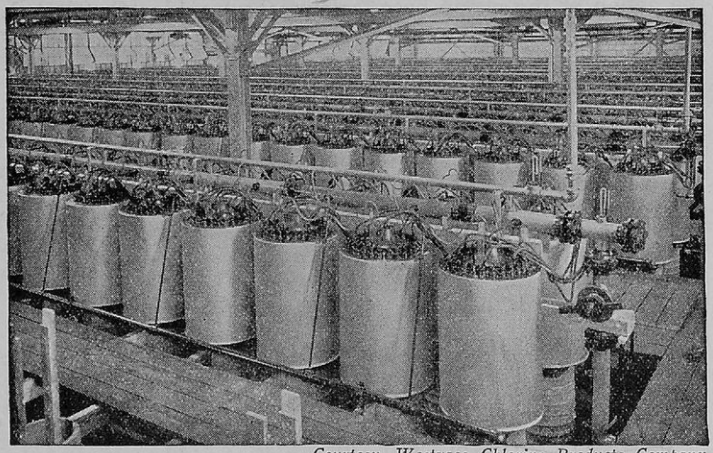


This cell consists of an iron tank. The anode is made up of graphite suspended in a solution of brine. An asbestos diaphragm prevents the diffusion of the chlorine into the sodium hydroxide solution. The cathode is a U-shaped sheet of perforated iron. The positively charged ions of sodium and hydrogen move to the cathode where hydrogen is liberated and sodium hydroxide remains in solution. The sodium hydroxide solution is drawn off at times and more brine is added.

70. DIAGRAM OF A NELSON CELL USED TO PRODUCE CHLORINE INDUSTRIALLY



Courtesy, Westvaco Chlorine Products Company

71. PRODUCING CHLORINE IN QUANTITY. Chlorine is obtained on a commercial scale by means of hundreds of cells connected in batteries. About 65% of this industrial chlorine is used in the paper industry, 22% in bleaching textiles, and 10% in sanitation including the sterilization of public water supplies.

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iron tank. Graphite anodes dip into the brine and a perforated steel cathode is lined with an asbestos diaphragm. Concentrated salt solution is fed into the tank as it is needed. Thus, the process is continuous. The chlorine escapes through a pipe in the dome which covers the anodes, and the hydrogen passes off through an opening in the tank outside the cathode. These by-products may be combined to make very pure hydrochloric acid. (See page 314.) The outside tank is tapped frequently to obtain the salt solution containing about 10 per cent of sodium hydroxide. Most of the salt, which is less soluble than the sodium hydroxide, is removed by partial evaporation. The sodium hydroxide is then recovered by further evaporation.

Sodium hydroxide may be prepared by the action of calcium hydroxide on sodium carbonate. In the electrolysis of brine the chlorine usually is considered the main product and the sodium hydroxide and the hydrogen, the by-products. If sodium hydroxide alone is desired, it is cheaper to prepare it by the action of the cheap base, calcium hydroxide [$Ca(OH)_2$], on sodium carbonate (Na_2CO_3). About one-third of the half million tons of sodium hydroxide prepared annually in this country is made by this older method. A solution of sodium carbonate is heated with a suspension of calcium hydroxide. Calcium carbonate is precipitated and removed by filtration. The reaction is:

$$\underset{\text{sodium carbonate}}{Na_2CO_3} + \underset{\text{calcium hydroxide}}{Ca(OH)_2} \longrightarrow \underset{\text{calcium carbonate}}{CaCO_3\downarrow} + \underset{\text{sodium hydroxide}}{2\,NaOH}$$

Readings for Pleasure and Profit

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. IX, pp. 132-136, "Alkalies."

Applying in Life What You Have Learned in Chemistry

You accidentally spill a little dilute sulfuric acid on your clothing. You remember that you should neutralize the acid, but you are uncertain what to use. One student suggests ammonium hydroxide. Another says that sodium hydroxide would be better because it is a stronger base and would neutralize the acid better.

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Which advice will you follow? What will probably happen if you use the wrong base?

Someone tells you that you can remove old paint from woodwork with a hot solution of sodium hydroxide. What precautions would you take in using such a solution?

You are the foreman in a chemical plant. One of your men accidentally spills hot caustic soda on his arm. What will you do?

Putting Chemistry to Work

A

(**1**) After recalling the properties of lye, suggest several uses for it in the home and in industry. Point out precautions in storing and using it. (**2**) Account for the large quantities of sodium hydroxide used in the United States each year. (**3**) A bottle of sodium hydroxide was carelessly left unstoppered for several weeks. Later when a solution of the substance was treated with hydrochloric acid, bubbles of a gas appeared. What was the gas and why was it formed? (**4**) Generally the cheapest compound is used as the raw material for the manufacture of an element. Is this so with sodium? (See what you can learn about the Downs process.)

B

(**5**) A stick of sodium hydroxide when exposed to the air first becomes a liquid. After being exposed for a long time, it dries up and changes to a white powder. Explain these changes. (**6**) Ask three questions whose correct answers will be *sodium hydroxide.* (**7**) From the standpoint of electrons, explain why sodium is a metal and why chlorine is a nonmetal. To what extent is sodium typical of metals? (**8**) Why was sodium not discovered earlier than 1807?

Research and Activities That You Will Enjoy

A model: Plan and devise a model of a cell to be used for the electrolytic production of sodium hydroxide. Take this occasion to point out the importance of by-products in industrial processes.

A demonstration: Examine the contents of a can of *Drano* before the class, testing its reaction to litmus. Note and try to identify the metallic-looking specks among the lumps of white substance. Add water to a small amount, observe, and explain how the action aids in clearing a clogged drainpipe. *Be careful.*

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A stage setting: See what interesting and useful information on naturally occurring acids, bases, and salts you can find for the class as a "stage setting" for the consideration of these topics in the next problem.

Problem 25

WHAT ARE THE PROPERTIES OF ACIDS, BASES, AND SALTS; HOW ARE THEY PREPARED?

There is no doubt that long before you started to study chemistry you knew that certain substances possess a sour taste. Vinegar, lemon juice, and sour milk are well known and often used for their property of sourness. Likewise, you may remember another group of substances, such as strong soap, baking soda, lye, and lime which show a characteristic bitter taste. It is easy to remember still another class of substances which are more or less salty like table salt.

The early chemists recognized all of these substances and named the sour ones *acids* (from *acidus,* Latin for *sour*). The second group of substances seemed to have the ability to destroy sourness of acids and to act as the foundation, or *base,* of still another class of substances which they called *salts.* These three classes of substances—acids, bases, and salts—are widely used in the home, in industry, and in the laboratory.

Some common acids that you need to know about. The compounds in this group are very numerous. You already are familiar with several of them. These are *hydrochloric acid, sulfuric acid,* and *nitric acid,* the three strong mineral acids common to the laboratory. Somewhat less familiar acids are *acetic acid* which is the acid in vinegar and *carbonic acid* which gives carbonated water (in soft drinks) its slightly sour, tingling taste. The usual phosphorus acid is *phosphoric acid. Citric acid* in lemons, *tartaric acid* in grapes, and *lactic acid* in sour milk are weak organic acids which are well known.

Hydrochloric acid (HCl). As you learned on page 180, this acid is a solution of hydrogen chloride gas in water.

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72. SOME COMMON ACIDS. The four common liquid acids and two solid acids used in the laboratory are shown here. What makes them acids?

Sulfuric acid (H_2SO_4). This acid is an oily, heavy liquid (oil of vitriol) whose formula indicates that it might more properly be called hydrogen sulfate. "Concentrated sulfuric acid" ordinarily is only about 2 per cent water. The dilute sulfuric acid is prepared by slowly adding the concentrated acid to water with stirring. Sulfuric acid is our most important acid.

Nitric acid (HNO_3) is another strong mineral acid whose chemical name is hydrogen nitrate. "Concentrated nitric acid" is nearly colorless and contains about 68 per cent HNO_3 by weight. Because of its very active properties the alchemists gave it the name *aqua fortis* ("strong water"). Nitric acid is a strong acid and a powerful oxidizing agent.

Acetic acid ($HC_2H_3O_2$) is common in the home in the form of vinegar which is a dilute solution of it (about 4 to 6 per cent). Glacial acetic acid is pure anhydrous hydrogen acetate, a solid which melts at about 16° C. Acetic acid has a pungent odor and a sour taste. It mixes with water in all proportions forming a solution which has weak acidic properties.

What is an acid? Acids are generally used in water solutions where they are thought of as the solute. Sometimes the solute

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is a compound of hydrogen and a nonmetal, as for example hydrochloric acid (HCl). In the case of sulfuric acid (H_2SO_4), the solute may be thought of as being formed by the union of the oxide of a nonmetal with water, thus $SO_3 \cdot H_2O$. All acids contain hydrogen and in solution they yield hydrogen ions, H^+, which are formed when hydrogen atoms lose their electrons. The hydrogen ions give the properties which are characteristic of every acid.

How do you know when you have an acid? Although acids show their characteristic properties best when they are dissolved in water, for most purposes it is not necessary to make a distinction between the compound and its water solution. The following properties are shown by water solutions of all acids.

1. *Taste.* Acids have a sour taste.

2. *Affect indicators.* Acids affect the color of certain organic substances which are called indicators. Litmus is such a dyestuff obtained from a lower form of plant life. Acids turn blue litmus a red or pink color. Phenolphthalein is red in the presence of bases but becomes colorless in acid solutions.

3. *React with metals.* When dilute acids are in contact with certain metals (such as Mg, Zn, and Fe), the hydrogen of the acid is evolved as a gas and a soluble compound of the metal is formed. You have seen that this is a common method of preparing small amounts of hydrogen in the laboratory:

$$\underset{\text{zinc}}{Zn} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{2\,HCl} \longrightarrow \underset{\substack{\text{zinc}\\\text{chloride}}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

4. *React with metallic oxides.* Acids react with metallic oxides in a similar manner except water is formed instead of hydrogen:

$$\underset{\substack{\text{magnesium}\\\text{oxide}}}{MgO} + \underset{\substack{\text{nitric}\\\text{acid}}}{2\,HNO_3} \longrightarrow \underset{\substack{\text{magnesium}\\\text{nitrate}}}{Mg(NO_3)_2} + \underset{\text{water}}{H_2O}$$

5. *Acids neutralize bases.* Acids react with bases to destroy their properties. The properties of the acids likewise are lost. The reaction which depends on this important behavior

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of acids and bases is discussed more in detail on page 196. Hydroxides, like oxides, react with acids, but larger quantities of water are produced, as shown by the following equation:

$$\underset{\substack{\text{magnesium}\\\text{hydroxide}}}{Mg(OH)_2} + \underset{\substack{\text{sulfuric}\\\text{acid}}}{H_2SO_4} \longrightarrow \underset{\substack{\text{magnesium}\\\text{sulfate}}}{MgSO_4} + \underset{\text{water}}{2\,H_2O}$$

How to prepare acids. One of two general methods may be used to prepare an acid, depending on whether the acid is volatile (easily vaporized) or nonvolatile (difficult to vaporize). The most usual method of preparing a volatile acid, however, is by heating the most common salt of the acid with sulfuric acid. The sulfuric acid furnishes the hydrogen and the salt supplies its nonmetallic radical. You will recall that this method was employed in preparing hydrochloric acid. Sulfuric acid is a nonvolatile acid which is prepared by the direct action of water on the nonmetallic oxide, sulfur trioxide (SO_3):

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

The relation of sulfur trioxide to sulfuric acid is shown by calling this nonmetallic oxide the *acidic anhydride* of sulfuric acid. Volatile acids containing oxygen may also be prepared in a similar manner by adding water to their corresponding acidic anhydrides.

How acids are named. You have seen that acids contain the element hydrogen. The name of the acid depends on whether it contains two or three elements. If the acid contains only *two* elements, it is a *binary* acid, and its name is derived from part of the names of both elements which compose it. Thus HCl is hydrochloric acid, the *hydro-* coming from the hydrogen and the *chlor-* coming from the chlorine. Binary acids therefore are known as *hydro-* (stem) *-ic acids,* and the stem always is a significant part from the name of the nonmetal. The binary acid of sulfur is hydrosulfuric acid (H_2S). HBr is hydrobromic acid.

If the acid contains three elements, it is known as a *ternary* acid and the *hydro- is not used in its name.* For the most

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common ternary acids the *-ic* is added to the stem derived from the nonmetal as above. Thus the most common acid of sulfur is sulfuric acid (H_2SO_4). The most common acid of nitrogen is nitric acid (HNO_3). Chloric acid, $HClO_3$, is the most common *oxygen* acid of chlorine.

The names of the acids which contain one atom less of oxygen than the common (-ic) acids are formed by adding *-ous* to the stem. Thus H_2SO_3 which contains one atom less of oxygen than H_2SO_4 is sulfur*ous* acid. HNO_2 is nitr*ous* acid and $HClO_2$ is chlor*ous* acid.

Some common bases you will use. While bases are probably not so familiar to you as acids, they are equally important and fully as useful. The following bases are common in the laboratory, in the home, and in industry.

Sodium hydroxide (NaOH). This is a typical base which already has been discussed. You will remember it also as lye or caustic soda.

Potassium hydroxide (KOH). This is known as caustic potash and is similar to sodium hydroxide. Potassium compounds are usually more expensive than the corresponding sodium compounds so they are not used when the sodium compounds will do.

Calcium hydroxide [$Ca(OH)_2$]. This base is commonly known as *slaked,* or hydrated, *lime.* It is sparingly soluble in water and its solution is not so strongly basic as are solutions of sodium and potassium hydroxides. It is a very cheap base, however, since it can be made by adding water to quicklime (calcium oxide, CaO). A solution of calcium hydroxide is *limewater.*

Ammonium hydroxide (NH_4OH) is an important, though weak and unstable base which is known only in solution. It decomposes easily, especially when heated. For this reason, ammonium hydroxide is often called the volatile base. "Concentrated ammonium hydroxide" is about a 28 per cent solution. More dilute solutions of ammonium hydroxide are used under the name of *household ammonia,* ammonia water, or simply ammonia.

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With the exception of ammonium hydroxide, hydroxides are not volatile when heated. The term *base* (meaning foundation) depends on the fact that the nonvolatile part of a salt comes from a metallic hydroxide while the other part of the salt comes from an acid which often is volatile.

What is a base? Bases contain the hydroxyl (OH) group combined with a metal or a metal-like radical — for example, (NH_4). In solution a base always yields hydroxyl ions (OH^-) which carry a negative electric charge. The hydroxyl ions are responsible for the characteristics of bases.

What are the properties of soluble bases? The following characteristic properties are shown by all bases in solution.

1. *Physical properties.* Although the taste of soluble bases may vary somewhat, they all possess a bitter, biting, or metallic taste. The stronger bases like sodium hydroxide are very caustic and "burn" the skin. They usually give a soapy or slippery feeling between the fingers.

2. *Bases turn litmus blue.* Other indicators are affected also although they do not necessarily show the same color change. Thus phenolphthalein is an indicator which turns red in basic solutions, while it is colorless in acidic and neutral solutions.

3. *Bases act on fats* forming a class of compounds known as soaps. The ability of lye and household ammonia to "cut" grease is due in part to this property.

4. *Bases neutralize acids* by destroying their acidic properties. The properties of the base likewise are lost. This type of reaction is discussed more fully on page 196.

How to prepare bases. A base may be formed by the action of an active metal on water. Such a reaction involving sodium hydroxide was given on page 68. A more common method of obtaining a base is by the direct union of water with a metallic oxide. Vast quantities of calcium hydroxide (slaked lime) are prepared in this simple manner.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

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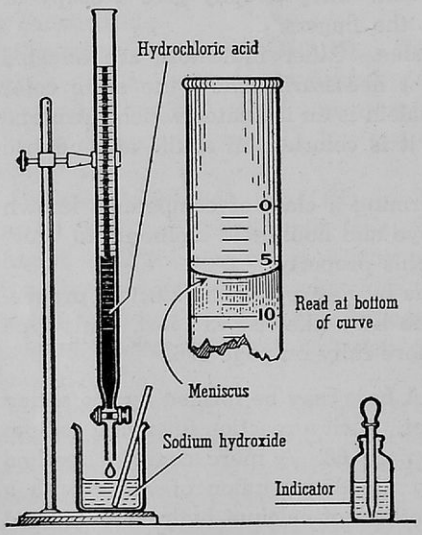
From this reaction you see that calcium oxide is the *basic anhydride* of calcium hydroxide. Ammonium hydroxide is formed when ammonia gas (NH_3) dissolves in and unites with water. Ammonium hydroxide is unstable so the reaction is reversible:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Is ammonia a basic anhydride? See the glossary for the definition of basic anhydride before you answer.

How bases are named. The method of naming bases is simpler than the system of naming acids. A base is named by adding hydroxide to the name of the metal or metal-like radical (NH_4) which the base contains. Thus NaOH is sodium hydroxide, $Ca(OH)_2$ is calcium hydroxide, and NH_4OH is ammonium hydroxide.

How salts are produced by neutralization. When an acid solution and a base solution are mixed in the proper amounts, the acid loses its sour taste and its ability to turn blue litmus paper red. The properties of the base also are changed and the mixed solution no longer is slippery between the fingers or has the ability to turn litmus paper blue. These significant changes in the properties of the acid and of the base indicate that a new compound has been formed by the reaction between them. This new compound is water (hydrogen hydroxide, HOH) formed by the combination of the hydrogen (H) from the acid and the hydroxide group (OH) from the base. Such a reaction is



73. AN ACCURATE NEUTRALIZATION

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known as *neutralization,* and the acid and the base are said to have neutralized each other. The solution thus obtained is a neutral solution.

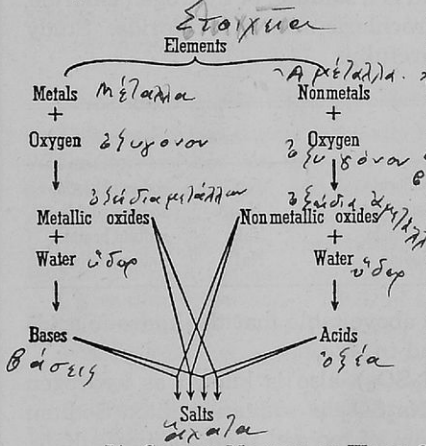
When solutions of sodium hydroxide and hydrochloric acid are mixed, the reaction which takes place is:

NaOH	+	HCl	⟶	HOH	+	NaCl
sodium hydroxide, a typical base		hydrochloric acid		water		sodium chloride, a typical salt

Upon evaporation, solid sodium chloride is formed. This compound illustrates a typical salt. All salts contain a metal (or ammonium radical) from a base combined with a nonmetallic element (or radical) derived from an acid. The general word equation for any neutralization reaction usually is written:

A BASE + AN ACID ⟶ WATER + A SALT

It should be remembered that the main point in any neutralization reaction is the formation of water. Upon evaporation, it is possible also to obtain a salt.



acid + base → salt + water

acid + basic oxide → salt + water

base + acid oxide → salt + water

basic oxide + acid oxide → salt

Show how $CaCO_3$ can be prepared by each of these reactions. Which one of these methods must be used to prepare NaCl? By what other method may NaCl be prepared?

74. SEVERAL METHODS BY WHICH SALTS MAY BE PRODUCED

How salts are named. In naming a salt it is convenient to think always of the acid from which it may be formed, because the "last" name of the salt depends on the name of the acid.

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You already have called sulfuric acid (H_2SO_4) hydrogen sulfate. If the hydrogen in the acid is replaced by the metal sodium, you have Na_2SO_4, a salt whose name is sodium sulfate. Study the following table carefully *until you master it.*

Name and formula of acid			*Name and formula of salt*	
Sulfuric acid,	H_2SO_4	hydrogen sulfate	Na_2SO_4	sodium sulfate
Nitric acid,	HNO_3	hydrogen nitrate	$NaNO_3$	sodium nitrate
Carbonic acid,	H_2CO_3	hydrogen carbonate	Na_2CO_3	sodium carbonate
Chloric acid,	$HClO_3$	hydrogen chlorate	$NaClO_3$	sodium chlorate
Phosphoric acid,	H_3PO_4	hydrogen phosphate	Na_3PO_4	sodium phosphate
Acetic acid,	$HC_2H_3O_2$	hydrogen acetate	$NaC_2H_3O_2$	sodium acetate

It is seen from the preceding table that a ternary *-ic* acid forms a salt whose name ends always in *-ate.*

Since the binary [hydro- (stem) -ic] acids contain only two elements, the salts derived from them contain only two elements. Hydrochloric acid is a solution of hydrogen chloride, so a salt formed from hydrochloric acid is a chloride. Study the following table very carefully.

Name and formula of acid			*Name and formula of salt*	
Hydrochloric acid,	HCl	hydrogen chloride	NaCl	sodium chloride
Hydrosulfuric acid,	H_2S	hydrogen sulfide	Na_2S	sodium sulfide
Hydrobromic acid,	HBr	hydrogen bromide	NaBr	sodium bromide
Hydriodic acid,	HI	hydrogen iodide	NaI	sodium iodide

It is likewise seen from the above table that the *hydro-ic* acids form salts whose names end in *-ide.*

Since sulfurous acid (H_2SO_3) also is known as hydrogen sulfite, you will see that Na_2SO_3 is sodium sulfite. Sodium sulfite contains one less atom of oxygen than sodium sulfate. The sodium salt of nitr*ous* acid (HNO_2) is sodium nitr*ite* ($NaNO_2$). You see that the *-ous* acids form salts whose names end in *-ite.* This is shown for several acids in the table at the top of the next page.

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Name and formula of acid			*Name and formula of salt*	
Sulfurous acid,	H_2SO_3	hydrogen sulfite	Na_2SO_3	sodium sulfite
Nitrous acid,	HNO_2	hydrogen nitrite	$NaNO_2$	sodium nitrite
Chlorous acid,	$HClO_2$	hydrogen chlorite	$NaClO_2$	sodium chlorite
Phosphorous acid,	H_3PO_3	hydrogen phosphite	Na_2HPO_3	sodium phosphite

Do not fail to master the following rules for naming acids and their salts. This will make your future work a great deal easier.

Endings of names of acids and salts	*Examples*
-ic acids form *-ate* salts	Sulfur*ic* acid forms sulf*ates*
-ous acids form *-ite* salts	Sulfur*ous* acid forms sulf*ites*
hydro-ic acids form *-ide* salts	*Hydro*sulfur*ic* acid forms sulf*ides*

Readings for Pleasure and Profit

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. IX, pp. 129-144, "Acids and Alkalies."

Applying in Life What You Have Learned in Chemistry

The Arnold family was especially fond of cream of tomato soup. While their mother was away, the three Arnold sisters were acting as chief cook and first and second assistants. Cream of tomato soup was on the dinner menu. Everything went along nicely until the second assistant, who was preparing the soup, added the tomatoes to the milk too quickly. Then the milk curdled.

"Why didn't you add a pinch of soda to the tomatoes?" asked the first assistant. "I've seen Mother do that."

What reason can you give for the suggestion?

A friend says that you cannot prepare table salt in the laboratory. How can you prove that he is wrong?

What would you do to determine which of three samples of vinegar contains the most acetic acid? Could you determine the percentage of acetic acid in each sample? Outline a plan.

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Putting Chemistry to Work

A

(1) What typical properties of bases are you making use of when: (a) you use household ammonia to clean greasy windows and woodwork; (b) you take milk of magnesia to relieve indigestion; (c) you use lye to clean out a clogged drainpipe; (d) slaked lime is used to remove hair from hides; (e) you put a little ammonium hydroxide on a garment spotted with sulfuric acid; (f) you add a little limewater to babies' milk? (2) Criticize this statement of a careless student: "All hydrogen compounds are acids." (3) How many practical uses can you suggest for your knowledge of neutralization? List them and write a concise explanatory statement about each.

(4) A salt reacts with another salt to make two new salts. Why will one acid reacting with another acid, or a base reacting with another base, not make two new acids or bases? (5) Remembering that carbon dioxide is an acidic anhydride, show that the reaction between limewater and carbon dioxide may be considered as neutralization.

B

(6) How do you recognize acids, bases, and salts by their formulas? Illustrate with the following: $Al(OH)_3$; H_3PO_4; LiOH; Na_2CO_3; $Ba(OH)_2$; H_2S; $Cu(NO_3)_2$; HI; $Pb(C_2H_3O_2)_2$. (7) What factors help to determine the uses of acids and bases? (8) Why is it not possible to have an acid salt of nitric acid? (9) Name two elements which are found in ternary acids. Why is one of them more easily released than the other? (Consider electronic connections.)

Research and Activities That You Will Enjoy

A display chart: Make a color chart showing the colors of various indicators in acidic solutions and in basic solutions.

A historical sketch: See what unusual and interesting things you can tell your class about the discovery and property-uses of the common acids. (Refer to Lowry, *Historical Introduction to Chemistry.)*

A panel discussion: Organize a small discussion group to bring before the class the results of outside reading on the importance of neutralization in industrial processes. Interesting results may be obtained if each student chooses and "sponsors" the most important application he can find.

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Problem 26

HOW DO SOLUTIONS OF ACIDS, BASES, AND SALTS DIFFER FROM OTHER SOLUTIONS; HOW ARE THESE DIFFERENCES EXPLAINED BY A THEORY OF IONS?

You already have studied some of the reasons for believing that matter is composed of molecules and that molecules are in turn composed of atoms. You learned also that atoms are composed of electrons and protons. The peculiar behavior of acids, bases, and salts in solution, which you will study in this problem, leads scientists to believe in another type of tiny particle—the *ion*.

What facts need explaining? You will remember that in the electrolysis of water (see page 71) you found that it was necessary to add a little sulfuric acid to the water to make it a better conductor of an electric current. In your more recent study of solutions (page 116) you learned also that the addition of solutes to water lowers its freezing point, but that certain classes of solutes (acids, bases, and salts) behave abnormally in this respect. Again, you have just found that all acids have a sour taste and affect indicators in a similar manner. Are these interesting facts accidental and unrelated or is it possible to suggest reasons for them? Let us think a little more about the conductivity of solutions and about the lowering of their freezing points, hoping that we may find a suitable explanation for these processes.

Why do solutions of acids, bases, and salts conduct an electric current? It is not difficult to determine whether, or not, a solution will conduct an electric current or to determine roughly the extent of conductivity. An apparatus similar to the one shown in Fig. 75 is usually used. When the plates (*electrodes*) are out of the solution, the light does not glow because the circuit is broken. When the electrodes are immersed in the solution, however, the light does glow if the solution conducts the current. The dimness or brightness of

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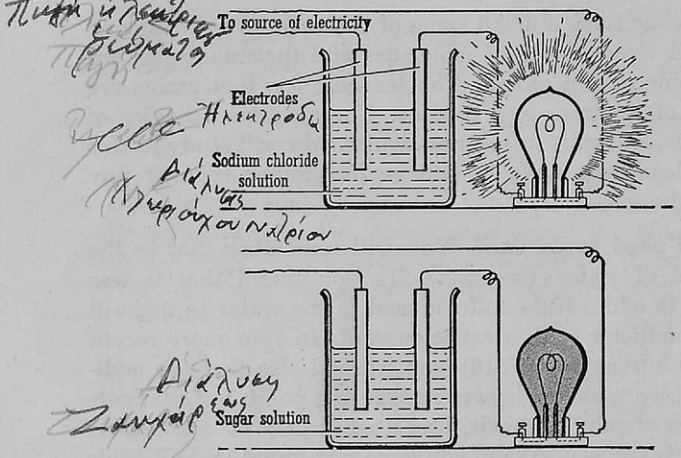
the light is a rough indication of the extent of the conductivity.

By testing solutions, as you may do in the laboratory, of such substances as table salt, sugar, alcohol, sulfuric acid, glycerin, and the like, it is possible to make two lists of substances on the basis of their conductivity. Those substances whose solutions conduct the current are known as *electrolytes,*



75. ELECTRICAL CONDUCTIVITY OF SOLUTIONS. Solutions of electrolytes conduct an electric current, while solutions of nonelectrolytes do not.

while those substances whose solutions do not conduct are *non*electrolytes. It is further interesting to note that soluble acids, bases, and salts form conducting solutions, although the degree of conductance may vary considerably. Solutions of sugar, alcohol, and glycerin are nonconductors, so these substances are nonelectrolytes. Dry solid table salt is a nonconductor; so is pure water. But table salt dissolved in water forms an excellent conducting solution.

Why do the freezing points of solutions of acids, bases, and salts differ from the freezing points of other solutions? The practice of placing substances like alcohol, glycerin, and *Prestone* in auto radiators in the winter to keep the water from freezing

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is well known. In order to compare the effectiveness of these three different antifreeze substances, it is necessary to use equivalent (but not equal) amounts, which in this case means using the same number of molecules in the same volume of solvent. Suppose then that you use a gram-molecular weight of each substance separately in one liter of water. The first solution contains 46 grams of alcohol ($C_2H_5OH = 46$) in one liter of water. The second solution contains 92 grams of glycerin [$C_3H_5(OH)_3 = 92$]. The third solution contains 62 grams of Prestone [$C_2H_4(OH)_2 = 62$]. When these solutions are cooled, they do not freeze at 0° C. as pure water would do. Instead they all freeze at —1.86° C.

If the freezing point of these solutions of nonelectrolytes is compared with the freezing point of a solution of the electrolyte, table salt, containing one gram-molecular weight ($NaCl = 58.5$) per liter of water, a very interesting and perhaps unexpected observation can be made. The solution of sodium chloride freezes at approximately —3.49° C. In other words, the freezing point of a solution of sodium chloride is lowered nearly *twice* as much as the freezing point of the solutions of nonelectrolytes (alcohol, glycerin, sugar, etc.). Furthermore, the freezing point of a similar solution of calcium chloride ($CaCl_2$) is lowered almost three times as much. Thus, we say that electrolytes (acids, bases, and salts) behave abnormally in lowering the freezing point of solutions. Notice that the substances whose solutions have abnormal freezing points are the very ones whose solutions conduct electricity.

Summary of facts to be explained. (1) Why do some solutions conduct an electric current, while others do not? (2) Why do acids have similar properties, and why do bases possess similar properties? The reasons for these facts puzzled chemists for a long time until Arrhenius, a Swedish chemist, in 1887 proposed an explanation—the ionic theory.

What the ionic theory is.[1] When you studied the kinetic-molecular theory, you learned that matter, regardless of its physical state (a gas, liquid, or solid), is composed of particles

[1]For information concerning the Brönsted theory, see Appendix Page 782.

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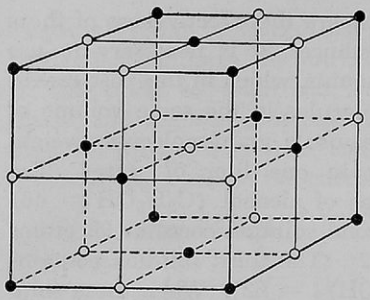


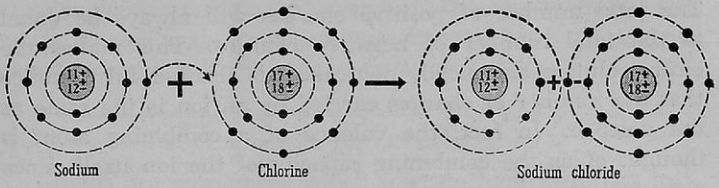
X-ray pictures prove that salt crystals are made with a lattice-like structure of sodium ions and chloride ions. These are not arranged in pairs, but each ion is equally distant from many surrounding ions of opposite charge. The total number of sodium ions and chloride ions is equal.

76. DIAGRAM OF SODIUM CHLORIDE CRYSTAL

which are in motion. In a gas the particles move about freely and tend to fly away from each other; in a liquid the particles move over each other freely but tend to cling together; and in a solid the motion of the particles is greatly restricted so they do not change positions. Furthermore, you learned in Unit 3 (page 114) that when a solid such as table salt or sugar dissolves in water, the particles of the solid are freed from the forces which hold them in position. They are free to move about through the solvent and as a result distribute themselves uniformly. In the ways mentioned above, electrolytes and nonelectrolytes behave in a similar manner. But when an electric current is applied to the solutions of these two types of materials, a difference in behavior is noted.

It has been learned from X-ray studies that a crystal of sodium chloride is composed of ions of sodium and chlorine and that these ions are held in position by forces which permit only slight motion. When such a crystal dissolves in water, the ions are set free and can move about. When charged electrodes are put into such a solution, the ions begin to move toward the electrode of opposite charge and away from the one of like charge. This behavior suggested the name *ion,* which means "wanderer" or "traveler." The process of setting the ions free so they can move freely under the influence of an electric current is known as *ionization,* or dissociation. It should be remembered, however, that an electric current is not necessary for ionization to occur.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



77. FORMATION OF NaCl. When sodium combines with chlorine, the sodium atom gives up an electron thus acquiring a positive charge; the chlorine atom gains an electron and acquires a negative charge.

How do you know that ions are electrically charged? Metallic conductors, such as a copper wire, are not permanently changed when a current passes through them. But when an electric current passes through a solution of an electrolyte such as table salt, a different element collects at each electrode. Chloride ions (Cl^-) are discharged at the anode (positive terminal) and sodium ions (Na^+) gather around the cathode (negative terminal). This shows that each ion of an electrolyte carries one or more positive or negative charges of electricity.

How ions and atoms are different. It should be noted carefully that these electric charges which the ions carry make a great deal of difference in the properties which the ions possess. An ion of sodium (Na^+) differs greatly from an atom of sodium (Na) as shown by the fact that ions of sodium do not react with water while atoms of sodium do. Chlorine is poisonous; chloride ions (Cl^-) are nonpoisonous. Cupric ions (Cu^{++}) are blue in color; copper itself is a reddish metal.

How the ionic theory explains valence. The ionization of calcium hydroxide is shown by the equation:

$$Ca(OH)_2 \text{ (in water)} \rightleftarrows Ca^{++} + 2\ OH^-$$

How many ions are formed by each molecule of calcium hydroxide here? It should be noted that the calcium ion (Ca^{++}) carries *two positive* charges and that there are two hydroxyl ions (OH^-). Each has a single negative charge.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

The total number of positive charges will always be equal to the total number of negative charges. This makes the entire solution electrically neutral. It is also helpful to notice that the number of charges carried by an ion is the same as the valence. In fact, the valence of a combining atom is thought of as the combining capacity of the ion itself, since a neutral atom has no valence.

How the ionic theory explains the freezing points of solutions of acids, bases, and salts. The lowering effect on the freezing point of a solution depends on the number of particles of solute present in the solution. A greater number of particles lowers the freezing point more. On the basis of the ionic theory it is not difficult to see why the freezing point of a solution of sodium chloride (an electrolyte) is lower than the freezing point of a solution of sugar (a nonelectrolyte) of the same concentration. This is because the electrolyte when dissolved furnishes ions while the nonelectrolyte furnishes undissociated molecules. The ions are nearly twice as abundant as the molecules. Or, with sodium sulfate ($Na_2SO_4 \rightleftarrows 2\ Na^+ + SO_4^{--}$) the lowering of the freezing point is almost three times as great as with a sugar solution. You should note, however, that the lowering effect of salt solutions is not *exactly* twice or exactly three times as great as with the sugar solution. This shows that the ionization of the salts is not complete.

How the ionic theory explains the properties of acids and bases. The ionic theory offers a suitable explanation for the similar properties of all acids and for the similar properties of all soluble bases. The ionic equations for the four acids listed on pages 190 and 191 are:

$$HCl \rightleftarrows H^+ + Cl^-$$
$$H_2SO_4 \rightleftarrows 2\ H^+ + SO_4^{--}$$
$$HNO_3 \rightleftarrows H^+ + NO_3^-$$
$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

A glance at these ionic equations shows that the solutions of these acids all contain the hydrogen ion (H^+). Since this is the only ion common to all of the acids, the similar properties

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of acids depend on this hydrogen ion. It is the hydrogen ions which give all acids their sour taste, cause them to turn litmus paper red, and to show other similar properties.

A Principle for You to Remember

Acids are substances which liberate hydrogen ions in solution.

A similar explanation is given for the common properties of all soluble bases. The ionic equations for a few common bases are:

$$NaOH \rightleftarrows Na^+ + OH^-$$
$$Ca(OH)_2 \rightleftarrows Ca^{++} + 2\,OH^-$$
$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$
$$KOH \rightleftarrows K^+ + OH^-$$
$$Mg(OH)_2 \rightleftarrows Mg^{++} + 2\,OH^-$$

It is readily seen that solutions of the above bases all contain the hydroxyl ion (OH^-) which gives to these solutions their characteristic taste, their ability to turn litmus paper blue, and other similar properties.

A Principle for You to Remember

Bases are substances which liberate hydroxyl ions in solution.

How neutralization of acids and bases takes place. The process of neutralization also is readily explained by the ionic theory. Solutions of all acids contain hydrogen ions (H^+). Likewise, solutions of all bases contain hydroxide ions (OH^-). When solutions of an acid and of a base are mixed in the proper amounts, the acid and the base lose their properties because the hydrogen ions unite with the hydroxyl ions to form water which ionizes only slightly. In neutralization the formation of water removes the characteristic ion of the acid as well as

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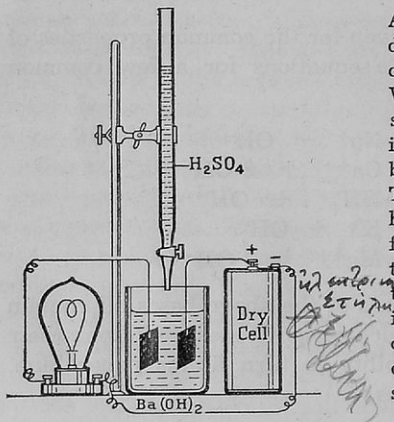
the characteristic ion of the base. Study carefully the ionic equation below.

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$(Na^+ + OH^-) + (H^+ + Cl^-) \rightarrow (Na^+ + Cl^-) + HOH$$

The sodium ions and the chloride ions which remain in the solution account for the properties shown by the product (NaCl).



A solution of barium hydroxide is a fairly good conductor of electricity. When it is neutralized by sulfuric acid, the barium ions and sulfate ions combine to form a precipitate. The hydrogen ions and the hydroxyl ions combine to form water, which is practically un-ionized. After the ions have been removed in this manner, the conductivity becomes zero, because the conductivity of a solution is due to the ions.

78. TESTING FOR NEUTRALIZATION BY CONDUCTIVITY

A Principle for You to Remember

Neutralization is the union of the hydrogen ion of an acid and the hydroxyl ion of a base to form water.

Why acids and bases are strong or weak. In the conductivity experiment you noted that some acids like hydrochloric acid (HCl) are excellent conductors, while others like acetic acid ($HC_2H_3O_2$) are poor conductors. Also some bases (NaOH) conduct an electric current well, while others (NH_4OH) are poor conductors. You have often been referred to the *strong*, or active, *acids* like hydrochloric acid and to the *weak*, or less active, *acids* like acetic acid. The ionic theory offers an ex-

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planation for this difference in strength on the assumption that strong acids ionize almost completely, while weak acids ionize but slightly. A dilute solution of hydrochloric acid is a strong acid because it contains a large proportion of hydrogen ions. A dilute solution of acetic acid is weak because it contains a relatively small proportion of hydrogen ions.

How the ionic theory explains conductivity of solutions. The story of the ionization of an electrolyte is told briefly by using an ionic equation. From your study of freezing points (page 203) you learned that the effect of sodium chloride in lowering the freezing point of a solution is nearly twice as great as that of a nonelectrolyte because each ion that is set free has the same effect as a whole molecule. If all the ions of sodium chloride were set free, the lowering of the freezing point of such a solution would be twice as great as that of a nonelectrolyte. You found the freezing point of the nonelectrolyte to be —1.86° C. and of the sodium chloride solution to be —3.49° C., but if the ionization were complete the freezing point would be —3.72° C. This indicates that most of the ions of the sodium chloride crystals are set free and affect the freezing point.

$$NaCl \text{ (in water)} \rightleftarrows Na^+ + Cl^-$$

In this equation NaCl represents the ion-pairs which are not free (inactive) while Na^+ and Cl^- represent the ions which are free to carry the current and enter actively into chemical reactions. So the ability of a solution of sodium chloride to carry the electric current depends upon the fact that the sodium atom (Na: 2, 8, 1) readily loses an electron forming Na^+ and the chlorine atom (Cl: 2, 8, 7) gains an electron to form Cl^-. (See Fig. 77.) You can conclude that electrolytes are polar compounds, formed by the exchange of electrons. Polar compounds dissociate in water and liberate the ions so they are free to travel through the solvent.

The fact that sugar does not form a conducting solution is explained by stating that sugar is a nonpolar compound. In a crystal of sugar all the molecules are formed by the sharing

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of electrons. As a result there are no ions and when sugar dissolves in water there can be no ionization. There are no charged particles (ions) in solution to conduct the electric current or to enter into chemical reactions in which there is an exchange of ions.

How the ionic theory explains electrolysis. When an electric current is applied to a solution like sodium chloride, the ions begin to travel or migrate. Because of its negative charge the chloride ion (Cl^-) is repelled by the cathode (negative terminal) and attracted by the anode (positive terminal). On the other hand, the sodium ion (Na^+) is attracted by the cathode and repelled by the anode. As a result of these forces the two varieties of ions travel in opposite directions. When a chloride ion (Cl^-) reaches the anode, it gives up the extra electron which it was carrying and becomes a chlorine atom; two of the atoms combine to form a molecule (Cl_2) and many molecules collect to form a bubble of gaseous chlorine. So you see that chlorine gas is set free at the anode. In a similar manner you find that sodium ions (Na^+) gather around the cathode, but metallic sodium is not set free; if it were, it would immediately react with the water which is serving as the solvent. Hydrogen ions from the water, being less active than sodium ions, are discharged at the cathode and hydrogen gas is set free. The sodium ions and the hydroxyl ions from the water remain in solution until the solvent water is evaporated. Then sodium hydroxide is formed. (Carefully study again this explanation by referring to Fig. 69 on page 186.)

SUMMARY OF THE IONIC THEORY

Facts Observed	*How the Facts Are Explained*
1. The lowering of freezing point and the raising of boiling point of molecular solutions of organic substances like sugar have normal values, 1.86° and 0.52°C.	1. The lowering of freezing point and the raising of boiling point are due to the *number of dissolved molecules.*

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2. The lowering of freezing point and the raising of boiling point of solutions of acids, bases, and salts are greater than can be accounted for by the number of dissolved molecules.	2. Such solutions contain more particles due to the ionization of molecules. The abnormality of freezing and boiling points is proportional to the number of ions formed.
3. Solutions with normal freezing and boiling points do not conduct an electric current, while those with abnormal values do.	3. Ions and not molecules cause solutions to conduct.
4. Conductivity and abnormality of freezing and boiling points are proportional.	4. The degree of electrical conductivity is determined by the number of ions.
5. During electrolysis, hydrogen and metals collect at the cathode; nonmetals collect at the anode.	5. Hydrogen and metal ions are charged positively; nonmetal ions, negatively.
6. Solutions of all acids have similar properties.	6. All acid solutions contain the hydrogen ion (H^+).
7. Solutions of all bases have similar properties.	7. All basic solutions contain the hydroxyl ion (OH^-).
8. Solutions of acids, bases, and salts are more active chemically.	8. Ions are the reacting particles in most solutions.

Solutions of all salts are not neutral to litmus—hydrolysis. When sodium carbonate is dissolved in water and its solution tested with litmus, the litmus paper turns blue. This indicates the presence of hydroxyl ions. The hydroxyl ions cannot come from the sodium carbonate, so they must come from the water.

When copper sulfate is dissolved in water, the litmus paper turns red, showing the presence of hydrogen ions. Since these cannot come from the copper sulfate, they must come from the water. Water is neutral to litmus, so some reaction must take place between the water and the sodium carbonate in one case and the copper sulfate in the other to produce the ions which affect the litmus paper.

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How the ionic theory explains why some salt solutions are not neutral. Let us consider what happens when sodium carbonate dissolves in water. As soon as solution takes place, the sodium carbonate ionizes to give sodium ions and carbonate ions. The water also shows a very slight tendency to ionize giving hydrogen ions and hydroxyl ions. With these two sets of ions free in solution, combination may take place between any pair of positive and negative ions producing sodium hydroxide and carbonic acid:

$$\begin{array}{ccccc} Na_2CO_3 & \rightleftarrows & 2\,Na^+ & + & CO_3^{--} \\ & & + & & + \\ 2\,H_2O & \rightleftarrows & 2\,OH^- & + & 2\,H^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & 2\,NaOH & & H_2CO_3 \end{array}$$

Sodium hydroxide is a strong base and most of it stays in the ionic form, while carbonic acid is a weak acid and only slightly ionizes. In this manner most of the hydrogen ions and the carbonate ions are removed from the solution, leaving an excess of hydroxyl ions in the solution to turn the litmus blue:

$$(2\,Na^+ + CO_3^{--}) + (2\,H^+ + 2\,OH^-) \rightleftarrows (2\,Na^+ + 2\,OH^-) + H_2CO_3$$

In a similar manner, copper sulfate in solution reacts with water to form copper hydroxide and sulfuric acid. One heavy arrow indicates that the main tendency is towards the formation of molecules, while the other points to ions.

$$\begin{array}{ccccc} CuSO_4 & \rightleftarrows & Cu^{++} & + & SO_4^{--} \\ & & + & & + \\ 2\,HOH & \rightleftarrows & 2\,OH^- & + & 2\,H^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & Cu(OH)_2 & & H_2SO_4 \end{array}$$

In this case sulfuric acid is a strong acid remaining largely in the ionic form, and copper hydroxide is a very weak base furnishing but few ions to the solution. This gives a large excess of hydrogen ions to turn the litmus red.

$$(Cu^{++} + SO_4^{--}) + (2H^+ + 2OH^-) \rightleftarrows (2H^+ + SO_4^{--}) + Cu(OH)_2$$

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If you have some sodium chloride in solution, the reaction to litmus is neutral. The reaction of the salt and water in the solution is somewhat similar to the cases just explained.

$$\begin{array}{ccccc} NaCl & \rightleftarrows & Na^+ & + & Cl^- \\ & & + & & + \\ H_2O & \rightleftarrows & OH^- & + & H^+ \\ & & \uparrow\downarrow & & \uparrow\downarrow \\ & & NaOH & & HCl \end{array}$$

Here the products of the reaction—sodium hydroxide and hydrochloric acid—are both highly ionized to about the same extent. This gives no excess of either hydrogen or hydroxyl ions, so the reaction to litmus is neutral.

$$(Na^+ + Cl^-) + (H^+ + OH^-) \rightleftarrows (Na^+ + OH^-) + (H^+ + Cl^-)$$

If you have a salt made by the reaction between a weak acid and a weak base, the ionic reaction with water causes the decomposition of the compound. When aluminum sulfide is put into solution, hydrogen sulfide is liberated, and a gelatinous precipitate of aluminum hydroxide forms.

$$\begin{array}{ccccc} Al_2S_3 & \rightarrow & 2\,Al^{+++} & + & 3\,S^{--} \\ & & + & & + \\ 6\,H_2O & \rightarrow & 6\,OH^- & + & 6\,H^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & 2\,Al(OH)_3 & & 3\,H_2S \end{array}$$

Here the products of the reaction—aluminum hydroxide and hydrogen sulfide—are both only very slightly ionized, and both tend to leave the solution:

$$(2\,Al^{+++} + 3\,S^{--}) + (6\,H^+ + 6\,OH^-) \rightarrow 2\,Al(OH)_3\downarrow + 3\,H_2S\uparrow$$

These facts may be summarized as follows:

1. A double-decomposition reaction in which water is one of the reacting substances is called *hydrolysis.*

2. A salt formed by the reaction between a strong acid and a weak base gives an acid reaction in solution.

3. A salt formed by the reaction between a weak acid and a strong base gives a basic reaction in solution.

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4. A salt formed by the reaction between a strong acid and a strong base is neutral in solution.

5. A salt formed by the reaction between a weak base and a weak acid, decomposes in water to form the weak base and weak acid.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. VII, pp. 89-109, "Solutions and Physical Chemistry."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. X, pp. 145-160, "The Ionic Theory."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. VIII, pp. 90-98, "When Will It Freeze?"

JAFFE, BERNARD. *Crucibles.* Chap. XII, pp. 219-241, "Svante Arrhenius."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. IX, pp. 176-183, "Solutions"; Chap. X, 183-191, "Electrolysis."

Applying in Life What You Have Learned in Chemistry

"This farm life's the thing!" agreed the Roberts twins as they prepared to make a large freezer of "honest-to-goodness, home-made" ice cream.

To their dismay they found that they had no salt to sprinkle on the crushed ice for the freezing mixture.

Recalling that the addition of sugar also lowers the freezing point of water, they decided to substitute sugar for salt.

Do you think that they were successful? Point out advantages or disadvantages in the substitution.

Many persons have been seriously injured or even killed by adjusting electrical devices while bathing. Does this agree with the statement: "Water is a nonconductor"? Explain. Make a list of all the electrical devices in your home which might be considered most dangerous in this connection.

To prepare some aluminum carbonate, Tom dissolved some aluminum sulfate in water. He added some sodium carbonate solution. He got aluminum hydroxide instead of aluminum carbonate. Why?

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Putting Chemistry to Work

A

(1) Why do not hydrogen chloride and hydrochloric acid have the same properties although the formula HCl is used for both? (2) When solutions of potassium hydroxide and nitric acid are mixed, how can you tell when the resulting solution is neutral? Which two kinds of ions are most abundant in the mixed neutral solution? What happened to the other ions? (3) Distinguish between a weak base and an unstable base. Name and give the formula for one of each to illustrate your points. Do the same for acids. (4) Give two reasons why 10 grams of table salt in a liter of water lowers its freezing point more than 10 grams of sugar ($C_{12}H_{22}O_{11}$) in the same volume of water. (5) In testing for the sulfate ion, either barium chloride or barium nitrate may be used. Explain. Would barium phosphate do?

B

(6) Show how a solution of barium chloride differs from a solution of sugar with respect to three physical properties. (7) In terms of the ionic theory, why is a reaction between an acid and a base always the same? (8) Explain clearly the difference between a weak base and a dilute base. Illustrate your points. (9) Contrast the chemical action between the molecules of two dry compounds with that of the same substances in solution. (10) Why do the solutions of all chlorides give the same precipitate with soluble silver compounds? (11) Distinguish between a strong acid and a concentrated one. (12) Why will chloroform ($CHCl_3$) and potassium chlorate ($KClO_3$) not respond to the test for a chloride ion? (13) Reactions of substances in the dry state are complex, while in solution the reactions of acids, bases, and salts are simple and uniform. Why is this?

How Good Are You at Solving Problems?

(1) What freezing point would you expect for a solution formed when 23 grams of alcohol (C_2H_5OH) are dissolved in 500 ml of water?

(2) How many grams of *Prestone* [$C_2H_4(OH)_2$] should be added to 4 liters (about a gallon) of water to depress the freezing point 5° C.?

(3) A solution containing 0.49 gram of sulfuric acid is being tested in a conductivity apparatus. As barium hydroxide is slowly

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added the light gets dimmer. Why? How many grams of barium hydroxide will have been added when the light ceases to glow? Explain.

(4) Calculate the volume of alcohol (C_2H_5OH, density 0.8) you should use in your 3½-gallon auto radiator to protect it against 10° F. weather. Then compare your figures with the chart used by filling stations to determine what margin of safety the chart allows.

Research and Activities That You Will Enjoy

An advanced topic: After outside reading and careful thought and organization of your topic, explain to the class as simply as you can the meaning and application of pH values. (See Appendix, pages 785-788, or "The Application of pH Control," *J. Chem. Ed.*, *6*, 36-43.

A report: Modern ideas regarding the dissociation of electrolytes. See Appendix, pages 782-784.

Arrhenius. Humiliation may sometimes be the price for explaining a new theory in science to superiors. Read the story of Svante Arrhenius, a chemist whose ideas about ionization helped to clarify chemical action.

Problem 27

WHAT PART DOES ELECTRICITY PLAY IN YOUR CHEMICAL WORLD?

In a preceding problem you learned that hydrogen, sodium hydroxide, and chlorine may be prepared by the electrolysis of a solution of sodium chloride. In this case electricity produces chemical change. It is possible also to have a chemical change liberate energy in the form of electricity.

You can produce a small current of electricity by connecting strips of zinc and copper in a dilute solution of sulfuric acid. When you prepared hydrogen by placing zinc in dilute sulfuric acid, a great deal of heat was given off. The zinc atoms disappeared in the solution as zinc ions and the hydrogen ions came out of solution as hydrogen atoms.

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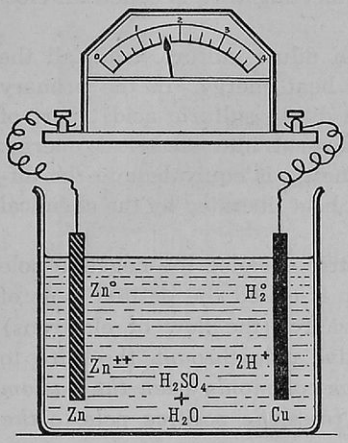
$$Zn^0 + (2\,H^+ + SO_4^{--}) \rightarrow (Zn^{++} + SO_4^{--}) + 2\,H^0$$

ionized sulfuric acid — ionized zinc sulfate

$$2\,H^0 \rightarrow H_2\uparrow \text{ (molecule)}$$



In a simple primary cell, two metals of different activity are immersed in a solution of an electrolyte. In this case the metals are zinc and copper. The chemical action of the acid on the zinc liberates energy—most of which appears as electricity in the external circuit. When the circuit is closed, bubbles of hydrogen rise from the copper. Can you account for this? What other metals can be used? You can easily make a simple cell.

79. SIMPLE PRIMARY CELL

If you place a zinc strip in a solution of dilute sulfuric acid, bubbles of hydrogen are given off and heat is generated. If you also put a strip of copper (platinum or carbon will serve just as well) in the same solution of sulfuric acid, no action takes place on the surface of the copper strip. When you connect the zinc and copper strips by a wire, you find (1) that hydrogen bubbles come from the copper strip instead of the zinc strip and (2) that there is not so much heat given off as before.

By connecting the zinc and copper strips to an ammeter, Fig. 79, you find that electricity is flowing through the wire. This electricity was produced from what is known as a simple or primary cell.

As explained above, the zinc is slowly "eaten" and disappears, because each zinc atom loses two electrons and goes into solution as a zinc ion. The electrons from the zinc atom pass along the zinc strip, then along the connecting wire,

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through the ammeter, and to the surface of the copper strip. Here each hydrogen ion from the acid adds to itself one of these electrons and becomes a hydrogen atom. The movement of the electrons through the connecting wire is called an electric current.

When zinc alone is placed in dilute sulfuric acid, all the chemical energy is released as heat energy. In the primary cell (zinc and copper strips in dilute sulfuric acid), part of this chemical energy is transformed into electrical energy. The amount of this electrical energy is equivalent to the difference between the amounts of heat liberated by the chemical action in these two cases.

In the primary cell the zinc strip is called the negative pole of the cell, and the copper strip is called the positive pole of the cell. The current of electricity (the flow of electrons) actually moves from the negative pole through the wire to the positive pole, *although it has commonly been the custom to say that the current moves from the positive pole to the negative pole.*

The dry cell is a convenient primary cell. In the dry cell, chemical energy is converted into electrical energy in a manner similar to the primary cell just described. The zinc vessel, Fig. 80, contains a moist paste of ammonium chloride, manganese dioxide, and other chemicals with a fairly large carbon rod in the center. A paper liner keeps the ammonium chloride from direct contact with the zinc. When the negative zinc electrode is connected to the positive carbon electrode, chemical action takes place; the zinc atoms become zinc ions and the electrons thus liberated move through the connecting wire to the carbon rod. Here ammonium ions (NH_4^+) (from the ammonium chloride paste) add on these electrons to form neutral ammonium radicals, which release ammonia gas and hydrogen gas.

$$2\ NH_4^+ + 2\ \text{electrons} \rightarrow 2\ NH_3\uparrow + H_2\uparrow$$

Manganese dioxide in the ammonium chloride mixture oxidizes the hydrogen which tends to collect on the carbon electrode. The ammonia dissolves in the moisture of the cell. The

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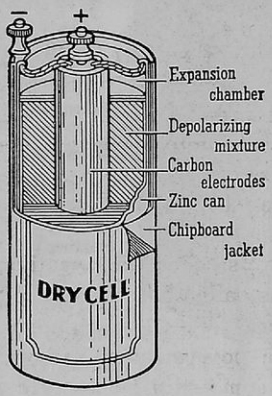
dry cell is convenient and is useful where small currents of electricity are necessary for short times as laboratory work, flashlights, and doorbells.



The common dry cell is similar to the simple primary cell. It has a carbon electrode surrounded by a paste containing ammonium chloride which is the electrolyte. The zinc container is the other electrode.

80. DRY CELL SUCH AS YOU USE IN YOUR FLASHLIGHT

The storage battery converts chemical energy into electricity. When one of the major materials in a primary cell is exhausted, the cell cannot be "recharged," so it is usually discarded. It is not strange that someone should try to reverse the reaction and thus regenerate the materials for further use. This has really been done and such cells are known as storage batteries or *secondary cells.*

How to make a simple lead storage cell. When two lead plates are used as electrodes and a dilute sulfuric acid solution is used as the electrolyte, the reactions which take place when an electric current is passed through the cell are similar to those which take place during the electrolysis of water. The negatively charged plate attracts the hydrogen ions to it and discharges them, forming free hydrogen gas. The sulfate ions migrate toward the positive plate where oxygen is liberated. Since the sulfuric acid is not consumed in the reaction it is obvious that the oxygen must come from the water. Not all of the oxygen escapes as free gas. Some of

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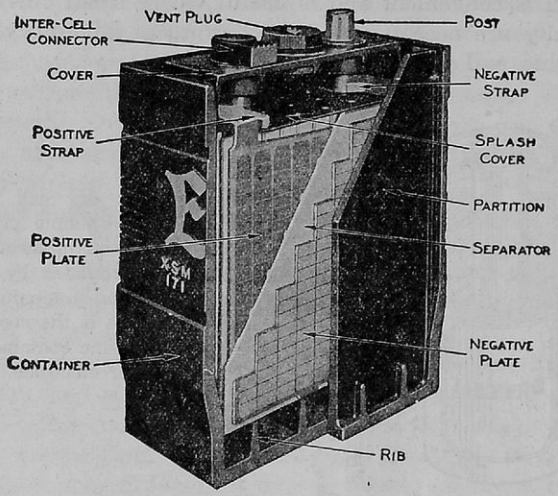

Courtesy, The Electric Storage Battery Company

81. A STORAGE BATTERY. Plates of spongy lead and lead dioxide are immersed in dilute sulfuric acid. The chemical change produces electrical energy in the external circuit. When the chemical change is nearly complete, electricity is passed into the cell to reverse the reaction.

it reacts with the lead of the positive plate forming a coating of brown lead dioxide.

When the current that has been passing through the electrolyte is cut off, one lead plate is coated with lead dioxide, the other, with spongy lead. If these two electrodes are connected by a wire that is outside the electrolyte, a weak current flows through them. This current flows in the direction that is opposite to the direction of the current used in charging. A cell of this kind (with only two comparatively small lead plates) discharges so quickly that it has little use.

In order to have more plate surface and a greater amount of active material in contact with the electrolyte, modern plates are made up of lead grids, and the open spaces of the grids are filled with porous pastes of PbO_2 and of Pb. Such material has less strength than the all-metal plate and also has a tendency to crumble and disintegrate in use. These "pasted

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plates" also have a greater resistance to the current flow than solid metal plates, but the greater surface obtained from the porous material more than compensates for this. In order to decrease internal resistance and to prevent warping of the plates when a cell is being rapidly discharged, the positive plates are mounted as closely as possible between the negative plates.

What chemical changes take place in a storage cell? When a current is passed through a cell containing electrodes made up of these pasted plates, the lead oxide in the paste on the negative plate is reduced to spongy metallic lead by the hydrogen, and any lead sulfate on the positive plate is changed to lead dioxide by the oxygen. This reaction increases the concentration of the sulfuric acid in the electrolyte until its density is 1.300 when the cell is fully charged.

In the discharge of the cell, the following reactions take place.

At the positive plate:

$$PbO_2 + (4\,H^+ + 2\,SO_4^{--}) \rightarrow SO_4^{--} + 2\,H_2O + PbSO_4$$

At the negative plate:

$$Pb^0 + SO_4^{--} \rightarrow PbSO_4 + \text{electrons}$$

By adding these two equations to make one general reaction, all the chemical changes may be shown. The reverse reaction shows the changes during the charging of the cells.

$$\underset{\text{pos. plate}}{PbO_2} + 2\,H_2SO_4 + \underset{\text{neg. plate}}{Pb} \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftarrows}} PbSO_4 + 2\,H_2O + PbSO_4$$

Since both plates become lead sulfate by the discharge, the process is called sulfation. If a cell is completely discharged, much of the acid is removed from the solution. Thus a test of the density of the acid gives a fair indication of the condition of the charge. At a density of 1.220 a cell is about half charged; a density below 1.140 shows the battery is practically discharged or "dead."

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How to take care of a storage cell. It is best to recharge a battery about once a month, when it is not in use, for it slowly loses its charge on standing. The acid acts slowly on the materials of the plates to form lead sulfate.

When freshly formed, the lead sulfate is finely divided and is readily converted back to free lead and lead dioxide by the charging current. On standing, the sulfate becomes coarsely granular. In this condition it is difficult to convert it back to the charged condition.

Water must be added to the cell from time to time to replace the water lost through chemical action while charging and the water lost through evaporation. The tops of the plates must be kept covered, for sulfation increases if the plates are exposed. A cell should never be completely discharged, and it should never be charged or discharged too rapidly. This causes distortion of the plates and shortens the life of the battery.

The Edison cell is a storage cell that has an alkaline electrolyte. Thomas A. Edison devised a storage cell with the intention of having it free from the fragile and short-lived limitations of the "lead cell." He succeeded in doing this, but certain less desirable qualities have somewhat limited the use of the Edison cell.

The positive plate of this cell is made of nickelic oxide and the negative plate is iron. The solution used is a 21 per cent solution of potassium hydroxide containing some lithium hydroxide. The chemical action in the Edison cell is shown by this general equation:

$$\underset{\text{positive plate}}{Ni_2O_3} + \underset{\text{21\% solution}}{2\,KOH} + \underset{\text{negative plate}}{Fe} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftarrows}} \underset{\text{positive plate}}{2\,NiO} + \underset{\text{21\% solution}}{2\,KOH} + \underset{\text{negative plate}}{FeO}$$

The liquid does not change in density during operation and the active materials do not deteriorate when the cell is left in an uncharged condition. Since it is constructed of lighter materials, its capacity per pound of battery is about twice as great as that of the lead cell. Mainly for this reason the

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Edison cell finds use on airplanes. This cell is also used as motive power in electric cars and trucks. Battery-operated locomotives are particularly suited for short hauls in railway stations and for underground railways in mines.

An electric current is used to deposit suitable metallic surfaces on various substances. It is often desirable to improve the appearance or the chemical nature of a substance by a thin coating of a more desirable metal. In electroplating, the object to be plated is placed in a solution of a salt of the metal to be deposited. The postive ions from the salt solution are attracted to the object to be plated, which is made the cathode. These positive ions on reaching the cathode receive electrons and are thus changed into atoms of the element. Much of the silverware with which you are familiar is covered with a layer of silver atoms. The plates used in the printing of this book were plated with a thin coat of copper. Since the copper plating is harder than lead type, these plates give more service than lead type.

Electrical energy can be converted into heat. Heat is generated by the resistance of a wire or an electrode which is a poor conductor of electricity. A poor conductor resists the flow of electrons through it. This produces friction, and therefore heat. The electrical energy carried by the current has thus been changed to heat energy. This principle is used in electric irons, toasters, and percolators. Much higher temperatures are produced in a similar way in industrial electric furnaces in which temperatures of 3500° C. and above can be obtained.

Readings for Pleasure and Profit

Findley, Alexander. *The Spirit of Chemistry.* Chap. XII, pp. 242-263, "Electricity and Chemistry."

Foster, William. *The Romance of Chemistry.* Chap. X, pp. 145-160, "Electricity in the Service of Chemistry."

Rogers, Allen. *Manual of Industrial Chemistry.* Vol. I, Chap. XI, pp. 315-351, "Electrochemical Industries."

Slosson, Edwin E. *Creative Chemistry.* Chap. XIII, pp. 238-264, "Products of the Electric Furnace."

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HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. VI, pp. 85-94, "Chemistry in Electrical Industry"; Vol. I, Chap. VII, pp. 95-102, "Applications of Electrochemistry"; Vol. II, Chap. VII, pp. 110-130, "Chemistry Behind Electric Batteries"; Vol. II, Chap. VIII, pp. 131-150, "Electroplating."

Applying in Life What You Have Learned in Chemistry

Why is smoking dangerous around batteries that have been "on charge" for some time?

If your family car is to be put in storage for six months or so, suggest what should be done with the battery.

Would you be interested in how two farm boys not only solved the problem of keeping their radio battery charged but also built a business for themselves? Read "Going with the Wind" in *Popular Science Monthly* (May, 1938) or in *The Reader's Digest* (June, 1938).

Putting Chemistry to Work

A

(1) Give definite reasons why the most active metals are not used in primary cells. (2) Why are two different metals or poles needed in a cell to produce a flow of electrons? (3) Which of the metals used in a cell is always the positive one? (4) Which of the metals used is always the one that needs replacing? (5) Are all the metals above hydrogen in the electrochemical (activity) series always negative and those below always positive when used in cells? (6) What is the particular purpose of the substance in solution (the electrolyte) in a cell? (7) When carbon is used as the positive pole in a cell, what is the advantage of having it large in size?

(8) What particular advantage has a secondary cell over a primary cell? (9) Why is a primary cell unsuited for starting the engine of an automobile? (10) After considering the reaction in a storage cell, state why it is unnecessary to supply more acid while the cell is in use. (11) Why does the liquid in a lead storage cell decrease when the cell is in use? What is added to keep the level of the liquid above the plates? (12) Which is in greater danger of freezing during cold winter weather, a charged battery or one that is nearly run down? Explain.

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B

(13) If a dry cell is left unused in a warm place, it may become useless by drying out. Why is this? (14) When zinc reacts chemically in acid, why is energy evolved as heat and not as electricity? (15) Why does the voltage of a dry cell in continued use fall rapidly? (16) Iron guard rails are frequently fastened into holes in stone by molten lead. Why does the iron usually rust away just beyond the edge of the lead? (17) What is stored in a storage battery? Explain. (18) Why do pure metals resist rusting better than most unrefined metals? (19) For electroplating in the laboratory, why is a storage battery often used instead of the regular "electric-light" current?

Research and Activities That You Will Enjoy

A demonstration: Arrange to demonstrate a primary cell before the class. See if you can learn the meanings of *polarization* and *local action.* Explain these terms to the class; show the effect of these processes and how the effects may be decreased.

A report: After outside study, tell the class more about the different types of electric furnaces: resistance furnace, arc furnace, and induction furnace. How is electricity changed to heat in each?

A paper: After outside preparation, write a short account of the development of the electric furnace. Present your ideas to the class for their consideration.

An advanced topic: See if you can learn more about the preparation of sodium hypochlorite (NaClO), sodium chlorate, and sodium perchlorate ($NaClO_4$) by the electrolysis of common salt solution. Present this in the form of a brief report to the class.

Looking Back into Unit 5

Be sure you know the purpose of this unit. Read again the material on page 176, "Looking Ahead into Unit 5." Then study the following Summary Test.

Summary Test

1. *How is hydrochloric acid prepared and used?*
   (a) How is hydrochloric acid produced—
      (1) In the laboratory?
      (2) On a commercial scale?
   (b) What properties make hydrochloric acid useful?
   (c) How is hydrochloric acid used?

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2. *Sodium hydroxide is a typical base. How is it used and produced?*
   (a) What properties of sodium hydroxide make it useful?
   (b) How is sodium hydroxide used?
   (c) How is sodium hydroxide produced?

3. *What are the properties of acids, bases, and salts? How are they prepared?*
   (a) What common acids are used most frequently?
   (b) How do you know when you have an acid?
   (c) What is an acid?
   (d) How are acids prepared?
   (e) What is a base?
   (f) What common bases are used most frequently?
   (g) How do you know when you have a base?
   (h) How are bases prepared?
   (i) What is neutralization?

4. *How are the properties of solutions of acids, bases, and salts explained with a theory of ions?*
   (a) What does the conductivity of solutions of electrolytes suggest about their molecules?
   (b) What does the abnormal freezing point of solutions of acids, bases, and salts indicate?
   (c) How can you explain the similar properties of acids and of bases with a theory of ions?
   (d) What are the main points in the ionic theory?
   (e) How can electrolysis be explained by means of the ionic theory?
   (f) How can neutralization be explained by means of the ionic theory?

5. *What part does electricity play in your chemical world?*
   (a) How can you produce a small current of electricity?
      (1) What is the source of the electrical current in a primary cell?
      (2) How can a primary cell be renewed?
   (b) In what ways does a secondary cell differ from a primary cell? How are they alike?
      (1) What chemical action occurs in a secondary cell?
      (2) How can a storage cell be renewed?

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(c) What main points should you remember in the care of a storage battery?
(d) How is an electric current used to deposit metals?
(e) How can electricity be changed to heat? How is this change useful in chemistry?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

In this unit the *scientific method* scores another victory. The chemist was not satisfied until he could explain why certain *reactions* take place in *solution.* It seems that *acids* and *bases* and *salts* that dissolve in water break apart into particles called *ions.*[1] These *ions* are free to act in *solution* and in a *chemical reaction* for themselves.

The ions are real friends of industry because by uniting to form an insoluble compound, or a gas, or any substance that does not ionize, they cause a reaction to go to completion. A typical illustration is *in neutralization* where the *hydrogen ion* of an acid and the *hydroxyl ion* of a base react to form water which ionizes very little but which can be evaporated and from which the desired salt can be recovered.

You find that it is the common *hydrogen ion* that makes all *acids sour* and the *hydroxyl ion* that gives *bases* those properties that make them so helpful in cleaning solutions. To illustrate, washing soda hydrolyzes (reacts with water) to form an excess of hydroxyl ions which readily attack grease.

It is interesting to see that the *electron theory* strengthens the *ionic theory.* Ions have the ability to move through *solutions.* Electrons have the ability to move along certain *metallic* (and a few nonmetallic) *plates* and *wires,* forming a "flow of *electricity.*" It is even possible by the use of proper *chemical actions* to "*store*" *energy* for later use as *electricity.*

Have you noticed that as this chemical story develops, chemical ideas, theories, or laws, interweave and form a continuous picture? Nothing, once studied, must be abandoned; all your chemical information fits in together to give a logical, rational explanation of matter.

[1] A suggestion for the modification of the ionic theory has recently been made. But, from a practical standpoint the information given on the ionic theory holds.

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Looking Ahead into

Unit Six

The Long Way . . .	The Short Way . . .
The layman writes:	The chemist writes:
Carbon burns by uniting with oxygen. Carbon dioxide, a gas, is formed. In order to burn 12 pounds of carbon, 32 pounds of oxygen are needed; 44 pounds of carbon dioxide are formed by the combustion.	$C + O_2 \rightarrow CO_2\uparrow$ . . . and tells the same story! Simplicity, accuracy, conciseness—all in one.

Try to get a clear picture of the struggles of early chemists:

Lavoisier—overthrowing the incorrect idea of burning and giving the correct explanation that started modern chemistry;

Dalton—explaining the laws of definite composition and of multiple proportions with his now famous atomic theory;

Gay-Lussac—showing that volumes of combining gases are always in the ratio of small whole numbers;

Avogadro—making a bold, but correct, guess about the number of particles in equal volumes of gases—a guess that was almost ignored by chemists for fifty years until . . .

Cannizzaro—reviving Avogadro's guess, dispelled the confusion between atoms and molecules;

Berzelius—discarding the old, very cumbersome symbols and inventing the simple symbols we now use; and determining atomic weights.

Problem 28. *How Can You Use Equations as the Shorthand of Chemistry?*

Problem 29. *How Much Will You Get?*

Problem 30. *What Is Going to Happen?—An Inquiry into Equilibrium*

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Equations in Use: Interesting Shorthand Stories of Chemical Changes

Problem 28

HOW CAN YOU USE EQUATIONS AS THE SHORTHAND OF CHEMISTRY?

Why equations are used in chemistry. Equations have been used from the very beginning of this book. At first "word" equations were used in which chemical reactions were expressed in words. Chemical reactions are more often expressed in formula equations in which the weight of the substances used in a reaction *equals* the weight of the substances produced. Such equations are much more useful than word equations because they give a more complete picture of the chemical reactions that take place. For example, the chemist has learned how to convert tasteless starch into sweet sugar. At first this seems almost as mysterious as the old alchemist's dream of changing copper into gold, but when you see the simplest formula of starch ($C_6H_{10}O_5$) and of the sugar formed from it ($C_6H_{12}O_6$), the reaction is not so mysterious after all. The formulas show that when each starch molecule unites with a water molecule, sugar is produced.

$C_6H_{10}O_5$ (simple starch molecule)
H_2O (water molecule)

$C_6H_{12}O_6$ (resulting sugar molecule)

This reaction is shown by the following equation:

$$\underset{\text{starch}}{C_6H_{10}O_5} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{sugar}}{C_6H_{12}O_6}$$

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In a similar manner the reaction between sulfuric acid and zinc has been expressed in the word equation:

zinc + sulfuric acid → zinc sulfate + hydrogen

But this word equation does not show as much about the nature of the reaction as the same statement expressed in a formula equation:

$$\underset{\text{zinc}}{Zn} + \underset{\text{sulfuric acid}}{H_2SO_4} \rightarrow \underset{\text{zinc sulfate}}{ZnSO_4} + \underset{\text{hydrogen}}{H_2\uparrow}$$

The formula equation shows you that the more active zinc changes places with the less active combined hydrogen; and the arrow (↑) indicates that the hydrogen thus displaced comes off as a free gas. This expression also gives definite information concerning the quantities of materials involved in the chemical change.

What you must know in order to write an equation. In writing an equation you must know (1) that a reaction takes place. An equation is a statement of fact, not a prediction. You must also know (2) the names and formulas of the substances that enter into the reaction and (3) the formulas of the substances that are formed.

Since matter is neither lost nor gained in a reaction (Law of Conservation of Matter), an equation must show that *the sum of the weights of the substances used equals the sum of the weights of the products formed.* To show this, an equation must be *balanced;* that is, each side of the equation must show the same kind and number of atoms. If there are 2 atoms of oxygen on the left hand side of an equation, there must also be 2 atoms of oxygen on the right hand side although they can be in different chemical combinations.

Writing equations need not be difficult for you. It is a mechanical process that you can easily master by giving it careful attention.

How to write equations for double-decomposition reactions. Perhaps the easiest equations to write are those representing double-decomposition reactions, which consist of an exchange

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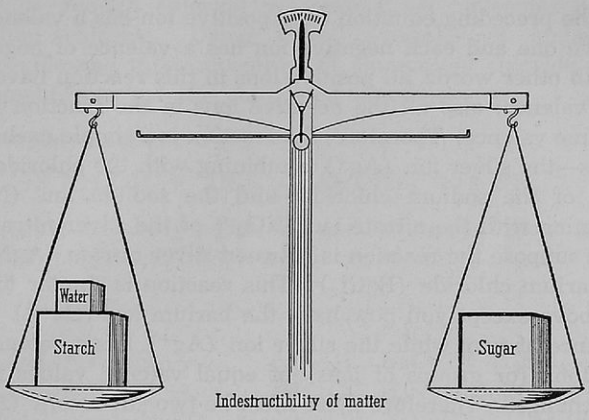

82. INDESTRUCTIBILITY OF MATTER. Each side of an equation must show the same amount of material. Matter cannot be created or destroyed in any chemical reaction. The process of making an equation show this fact is called "balancing the equation."

of ions in solution. In these reactions ions of equal valence values are transferred. For example, the reaction between solutions of silver nitrate and sodium chloride yields silver chloride and sodium nitrate. Expressed in an equation, the statement becomes:

$$\underset{\text{silver nitrate}}{(Ag^+ + NO_3^-)} + \underset{\text{sodium chloride}}{(Na^+ + Cl^-)} \rightarrow \underset{\text{silver chloride}}{AgCl\downarrow} + \underset{\text{sodium nitrate}}{(Na^+ + NO_3^-)}$$

When you write chemical equations, use a horizontal arrow to indicate the direction in which the reaction proceeds. When you read an equation, remember that the horizontal arrow means "produces," or "yields." For example, read the preceding equation as follows: "Silver nitrate reacting with sodium chloride yields (produces) silver chloride and sodium nitrate." If the reaction goes in either direction, depending upon the conditions of the experiment, double arrows ($\rightleftarrows$) are used. The arrow pointing downward shows that silver chloride is insoluble, so it is not written in ionic form.

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In the preceding equation each positive ion has a valence of positive one and each negative ion has a valence of negative one. In other words, all positive ions in this reaction have the same valence; also all the negative ions in the reaction have the same valence. Therefore, the reaction is a simple exchange of ions—the silver ion (Ag^+) combining with the chloride ion (Cl^-) of the sodium chloride—and the sodium ion (Na^+) combining with the nitrate ion (NO_3^-) of the silver nitrate.

But suppose the reaction is between silver nitrate ($AgNO_3$) and barium chloride ($BaCl_2$). This reaction is similar to the one above except you now have the barium ion (Ba^{++}) with a valence of two, while the silver ion (Ag^+) has a valence of one. Ions (or groups of ions) of equal valence values must be exchanged. Therefore there must be two silver ions (Ag^+) to exchange for one barium ion (Ba^{++}). (See the valence table on page 168.) This forms two molecules of silver chloride, so the ionic equation becomes:

$$(Ba^{++} + 2\ Cl^-) + (2\ Ag^+ + 2\ NO_3^-) \rightarrow 2\ AgCl\downarrow + (Ba^{++} + 2\ NO_3^-)$$

And the molecular equation is:

$$BaCl_2 + 2\ AgNO_3 \rightarrow 2\ AgCl\downarrow + Ba(NO_3)_2$$

This procedure will always give products whose formulas satisfy the valences of the radicals. In forming such equations, you may also work from the formulas of the products if you desire. For example, the reaction between ammonium hydroxide and aluminum chloride yields aluminum hydroxide and ammonium chloride. Remembering the valences of the radicals, you can write the statement as a *trial* equation.

Trial equation:

$$?\ NH_4OH + ?\ AlCl_3 \rightarrow ?\ Al(OH)_3 + ?\ NH_4Cl$$

Inspection shows that this is *not* a completed equation. Each molecule of ammonium hydroxide contains but one hydroxyl radical, while each molecule of aluminum hydroxide contains three. Also note that each molecule of aluminum chloride

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contains enough chlorine to make three molecules of ammonium chloride. Using three molecules of ammonium hydroxide and three molecules of ammonium chloride in the statement, you get the completed equation.

Completed equation:

$$3\ NH_4OH + AlCl_3 \rightarrow Al(OH)_3 + 3\ NH_4Cl$$

Keeping the above points in mind, write the following on a separate paper and complete the equations.

Drill Exercise

1. $KOH + H_2SO_4 \rightarrow$
2. $KOH + HNO_3 \rightarrow$
3. $Fe(OH)_3 + H_3PO_4 \rightarrow$
4. $KI + Pb(NO_3)_2 \rightarrow$
5. $Na_2CO_3 + Ca(OH)_2 \rightarrow$
6. $NaCl + H_2SO_4 \rightarrow$
7. $BaCl_2 + H_2SO_4 \rightarrow$
8. $H_2S + CuSO_4 \rightarrow$
9. $Al(OH)_3 + H_3PO_4 \rightarrow$
10. $MgCl_2 + Na_2CO_3 \rightarrow$
11. $FeCl_3 + NH_4OH \rightarrow$
12. $CuO + HNO_3 \rightarrow$

How to write equations for displacement reactions. In equations for simple displacement reactions there must also be a balance between the formulas of the reacting substances and the products. When magnesium and hydrochloric acid react, you have seen that hydrogen is liberated and that the magnesium replaces the hydrogen to form magnesium chloride. The word equation for this reaction is:

$$\text{magnesium} + \text{hydrochloric acid} \rightarrow \text{hydrogen} + \text{magnesium chloride}$$

The next step is to write the formulas instead of the names. The trial equation then becomes:

$$?\ Mg + ?\ HCl \rightarrow ?\ H_2\uparrow + ?\ MgCl_2$$

But this is not a completed equation. Each molecule of hydrochloric acid contains but one chlorine atom and one hydrogen atom, while the magnesium chloride molecule contains two chlorine atoms and the hydrogen molecule contains two hydrogen atoms. (See page 146.) To make a completed equation you

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must use two molecules of hydrochloric acid.

$$Mg + 2\ HCl \rightarrow H_2\uparrow + MgCl_2$$

A strip of copper immersed in a fairly concentrated solution of silver nitrate becomes coated with crystals of silver, while the solution takes on the blue color of the copper ion. The copper has displaced the silver.

$$?\ AgNO_3 + ?\ Cu \rightarrow ?\ Cu(NO_3)_2 + ?\ Ag$$

This is not yet a completed equation for the silver nitrate contains but one nitrate ion while the copper nitrate contains two. To complete the equation you must use two molecules of silver nitrate. The equation then becomes:

$$2\ AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2\ Ag$$

Write the following on a separate paper and complete the equations.

Drill Exercises

1. $Zn + AgNO_3 \rightarrow$
2. $Al + HCl \rightarrow$
3. $Zn + HCl \rightarrow$
4. $Fe + CuSO_4 \rightarrow$
5. $Al + Fe_2O_3 \rightarrow$
6. $Na + H_2SO_4 \rightarrow$

How to write equations for decomposition and combination reactions. You have also had experience with two other types of chemical reactions. These are decomposition (analysis) and combination (synthesis). Equations for these types of reactions are written in a manner similar to those already described. When magnesium burns in oxygen, the product is magnesium oxide. Placing formulas for these substances in an equation, we have:

$$?\ Mg + ?\ O_2 \rightarrow ?\ MgO$$

Each molecule of oxygen contains enough oxygen to form two molecules of magnesium oxide. To obtain two molecules of magnesium oxide, we must use two molecules of magnesium. The completed equation then becomes:

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

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A common laboratory method for preparing oxygen is to heat potassium chlorate. Manganese dioxide is added as a catalyst. Since no change in the catalyst is noted, it need not appear in the equation. The potassium chlorate decomposes, yielding oxygen and potassium chloride. The word equation becomes:

potassium chlorate → oxygen + potassium chloride

Substituting formulas:

$$? \ KClO_3 \rightarrow ? \ O_2\uparrow + ? \ KCl$$

It is quite evident that this is not yet a completed equation; you must have the same number of oxygen atoms on each side of the arrow. To get this number, find the least common multiple of the number of oxygen atoms on each side. In this case the number is six. There are six oxygen atoms in two molecules of potassium chlorate and six atoms in three molecules of oxygen. The equation then becomes:

$$2 \ KClO_3 \rightarrow 3 \ O_2\uparrow + 2 \ KCl$$

Write the following on a separate paper and complete the equations.

Drill Exercises

1. $Sb + Cl_2 \rightarrow$
2. $Na + Cl_2 \rightarrow$
3. $P + O_2 \rightarrow$
4. HgO (heated) $\rightarrow$
5. $C + O_2 \rightarrow$
6. $Cu + O_2 \rightarrow$
7. $NaClO_3$ (heated) $\rightarrow$
8. $H_2 + O_2 \rightarrow$

Summary. All equations are balanced by processes similar to these. Here are a few points to keep in mind.

1. The reaction must really take place.
2. Be sure that you have the correct formulas for the substances entering into the reaction and for the products.
3. In completing the equation never change a subscript figure in a formula. The balancing must be done entirely by changing the coefficients (the number of formula or molecular weights used), and not by any change in the formula itself.

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4. When you have finished, check the result. Count the number of each kind of atom to be sure that there is the same number of them on each side of the equation.

Applying in Life What You Have Learned in Chemistry

Three young students were having a heated argument; they all could not agree on how much oxygen is required to burn magnesium.

The first boy insisted, "It's as plain as anything to me that in order to burn magnesium you have to use an equal amount of oxygen. You see, the formula of magnesium oxide is MgO, that is one part of magnesium and one part of oxygen. So if I burn 6 grams of magnesium I'll need 6 grams of oxygen, won't I?"

"Aw, you don't know what you're talking about," declared the second student. "The equation here shows that one molecule of oxygen will combine with *two* molecules of magnesium, so of course it will take twice as much oxygen. Can't you see that 12 grams of oxygen must be used to burn 6 grams of magnesium? Isn't that so, Tom?"

But Tom wasn't so sure. "Couldn't we try it?" he suggested.

They heated a carefully weighed amount of magnesium in a weighed covered crucible. After letting it cool, they again weighed the covered crucible and its contents. They listed their data like this:

(a) Covered crucible weighed	27.46 g
(b) Covered crucible and magnesium	27.94 g
(c) Covered crucible and contents after heating	28.26 g
(d) Weight of magnesium	?
(e) Weight of oxygen	?

Who won the argument? Finish their simple calculation and then answer the question, "How many grams of oxygen are required to burn 6 grams of magnesium?"

The weight of an element which combines with 8 grams of oxygen is called the *equivalent,* or combining, *weight* of the element. What is the equivalent weight of magnesium? of hydrogen?

Putting Chemistry to Work

A

(1) What facts must you know before you can write a chemical equation? (2) What physical and chemical law requires that an

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equation be balanced? (3) Someone has said that "the four main types of chemical change correspond to marriage, divorce, highway robbery, and fair exchange." What type fits each description? (4) What important facts about a chemical reaction are not expressed in its equation as ordinarily written? (5) Tell briefly the nature and value of (a) a scientific fact, (b) a scientific law, (c) a hypothesis, and (d) a theory. How are these terms related?

B

(6) As a general rule, what happens to a radical during a chemical change? Can you think of any exceptions to this rule? (See how many you can find as you study the next unit.) (7) Show how the atomic theory accounts for the law of conservation of matter by applying it to the reaction, $NaOH + HBr \rightarrow HOH + NaBr$. (Assume the weights of the "atoms" in the reaction to be Na = 23, OH = 17, H = 1, Br = 80.)

Equations to Write and Balance Correctly

(1) $Fe_2O_3 + C \rightarrow Fe + CO$
(2) $P + O_2 \rightarrow P_2O_5$
(3) $HCl + MnO_2 \rightarrow MnCl_2 + H_2O + Cl_2 \uparrow$
(4) $H_2 + Cl_2 \rightarrow HCl$
(5) $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$
(6) $Pb(C_2H_3O_2)_2 + Na_2CO_3 \rightarrow PbCO_3 \downarrow + NaC_2H_3O_2$
(7) $Al(OH)_3 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2O$
(8) $PbS + O_2 \rightarrow PbO + SO_2$
(9) Aluminum sulfate and calcium hydroxide
(10) $AgNO_3 + AlCl_3 \rightarrow AgCl + Al(NO_3)_3$
(11) $BaCl_2 + Al_2(SO_4)_3 \rightarrow BaSO_4 + AlCl_3$
(12) $Fe(OH)_3 + HNO_3 \rightarrow$
(13) Magnesium and hydrochloric acid
(14) $BaCO_3 + HCl \rightarrow$
(15) $CS_2 + O_2$ (excess) $\rightarrow$
(16) Calcium nitrate and sulfuric acid
(17) Oxidation of aluminum in air
(18) Action of sodium on water
(19) Sulfur dioxide and sodium hydroxide
(20) Ferric chloride and ammonium hydroxide
(21) Reduction of copper oxide with hydrogen
(22) Sulfur burning in air
(23) Complete burning of acetylene (C_2H_2) in air

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(24) Ethyl alcohol (C_2H_5OH) burning completely in air
(25) Complete oxidation (roasting) of zinc sulfide (ZnS)

Research and Activities That You Will Enjoy

A pictorial summary: By means of a diagram show how an equation illustrates the law of conservation of matter.

A report: Chemical investigation by analysis and synthesis.

An interview: Ask a chemist what kinds of errors are most frequently made in analyzing compounds. Ask him to explain to you how he uses in his work the ideas you have been studying in this unit. Report fully to the class what you learn from the interview.

Problem 29

HOW MUCH WILL YOU GET?

An equation shows the amounts of materials involved in a reaction. Every formula stands for a definite amount of a substance (molecular weight). By substituting molecular weights in the place of formulas, an equation becomes a quantitative (weight) statement of a reaction. An equation shows that the sum of the weights of the substances used equals the sum of the weights of the products formed. The equation for the oxidation of magnesium is:

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

When you substitute the proper molecular weights in the place of the formulas, you get the quantitative statement of what occurs:

$$2\ Mg + O_2 \rightarrow 2\ MgO$$
$$2(24) + 2(16) = 2(24 + 16)$$
$$48 + 32 = 80$$

This equation tells you that 48 parts by weight of magnesium combine with 32 parts by weight of oxygen to form 80 parts by weight of magnesium oxide. Notice that the sum of the weights on both sides of the equation is the same.

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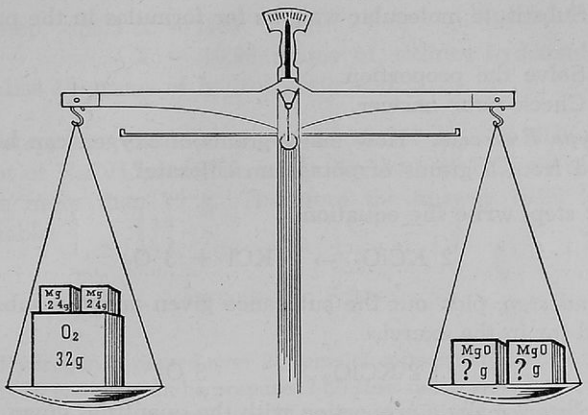

83. HOW MUCH MAGNESIUM OXIDE MUST BE FORMED?

How to determine what weight of material you get. Suppose you have 10 grams of magnesium and you want to know how much magnesium oxide can be made from it. You see from the previous page that 48 parts by weight of magnesium make 80 parts by weight of magnesium oxide. Since this is true, it is easy to see that 10 grams will make a proportional amount, or—

$$\frac{48}{10} = \frac{80}{X}$$

Solving this proportion:

$$48\ X = 800$$
$$X = 16.66 \text{ grams of MgO}$$

Numerical exercises like this constantly arise in chemistry. In solving them, you can follow this procedure:

1. Be sure that you have the correct completed equation for the reaction.

2. From the equation, pick out and write (a) the formula of the substance whose weight is given and (b) the formula of the substance whose weight is asked for in the exercise.

3. Make a proportion with these formulas and with the weights of the substances given and asked for in the exercise.

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4. Substitute molecular weights for formulas in the proportion.
5. Solve the proportion.
6. Check your answer.

Type Exercise. How many grams of oxygen can be produced from 5 grams of potassium chlorate?

First step, write the equation.

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$

Second step, pick out the substance given and the substance asked for in the exercise.

$$2\ KClO_3 \qquad\qquad 3\ O_2$$

Third step, make a proportion with the quantities given in the exercise.

$$\frac{2\ KClO_3}{5} = \frac{3\ O_2}{X}$$

Fourth step, substitute weights for formulas.

$$\frac{2[39 + 35.5 + 3(16)]}{5} = \frac{6(16)}{X} \text{ or } \frac{245}{5} = \frac{96}{X}$$

Fifth step, solve the proportion.

$$245\ X = 480$$
$$X = 1.95 \text{ grams of oxygen}$$

Sixth step, check your answer.

Another Example. Suppose you wish to know how much sodium hydroxide will be needed to neutralize 10 grams of hydrochloric acid. You would proceed as before.

First step, $NaOH + HCl \rightarrow NaCl + H_2O$

Second step, $NaOH \qquad HCl$

Third step, $\frac{NaOH}{X} = \frac{HCl}{10}$

Fourth step, $\frac{23 + 16 + 1}{X} = \frac{1 + 35.5}{10}$, or $\frac{40}{X} = \frac{36.5}{10}$

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Fifth step, $36.5\ X = 400$

$X = 10.96$ grams of sodium hydroxide to neutralize 10 grams of hydrochloric acid.

Sixth step, The equation shows 40 NaOH to 36.5 HCl. The amount of NaOH needed to neutralize 10 g of HCl should be a little more than 10 g. Therefore the answer 10.96 looks reasonable.

Exercises to Solve

(1) Hydrogen is passed over 2 grams of copper oxide. How much copper (by weight) can be prepared? (2) How much salt (by weight) can be prepared by neutralizing 10 grams of sodium hydroxide with hydrochloric acid? (3) How many grams of silver chloride can be prepared by adding a solution containing 2 grams of sodium chloride to a solution of silver nitrate? (4) In preparing hydrogen, 10 grams of zinc were used with sulfuric acid. What weight of zinc sulfate was prepared as a by-product? (5) How many grams of ferric oxide (Fe_2O_3) must be reduced by carbon to yield 7 grams of iron?

How to determine the volume of gas produced when you know the weights of the reagents. Sometimes you may need to know the volume of a gaseous product instead of its weight. Of course, if you know the weight of one liter of the gas, this volume can be determined easily. In the exercise on page 240 you found that 5 grams of potassium chlorate can produce 1.95 grams of oxygen. The *volume* of oxygen may be determined by dividing 1.95 by 1.43 (the weight of one liter of oxygen).

$$\frac{1.95}{1.43} = 1.37 \text{ liters of oxygen from 5 grams of } KClO_3$$

This same value may be determined in one operation. In a previous unit (page 148) you found that one gram-molecular weight of any gas at standard conditions occupies 22.4 liters.

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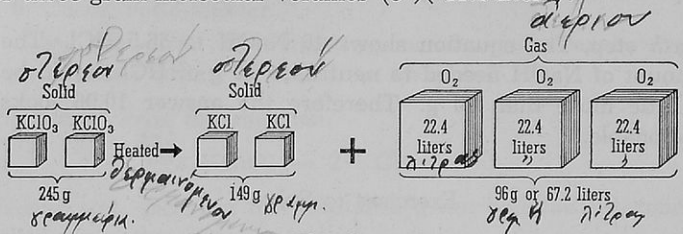
Note the following equation: $2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$ In this equation $3\ O_2$ represents three gram-molecular weights or three gram-molecular volumes (3×22.4 liters).



84. GAS VOLUMES IN REACTION. This illustration represents relative quantities in this reaction. In an equation the formula for a gas stands for a gram-molecular volume because the molecular weight of a gas occupies 22.4 l at standard conditions. This fact can be used in determining the volumes of gases in reaction.

If you want to determine the volume of oxygen that can be obtained by heating 5 grams of potassium chlorate, you can use the gram-molecular volume in the proportion instead of the gram-molecular weight which was used in the exercise on page 240. The exercise then becomes:

First step, showing the completed equation,

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$$

Second step, picking out the substances used and asked for in exercise,

$$2\ KClO_3 \qquad 3\ O_2$$

Third step, forming the proportion,

$$\frac{2\ KClO_3}{5} = \frac{3\ O_2}{X}$$

Fourth step, substituting values for formulas,

$$\frac{245}{5} = \frac{3\,(22.4)}{X}$$

(Here the gram-molecular volume is used instead of the gram-molecular weight.)

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Fifth step, solving the proportion,

$$245\ X = 336$$

$$X = 1.36 \text{ liters of oxygen}$$

Thus by one operation the volume of the gas may be obtained.

Sixth step, check with page 240. Does the answer seem reasonable?

Another Type Exercise. Suppose that you want to prepare 4 liters of hydrogen. How much zinc must you use with sulfuric acid? You must first have the completed equation:

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

You are concerned only with the zinc and the hydrogen. The formula H_2 represents the gram-molecular volume of hydrogen (22.4 liters). Using this in the proportion you have:

$$\frac{Zn}{X} = \frac{H_2}{4}, \text{ or } \frac{65}{X} = \frac{22.4}{4}$$

$$22.4\ X = 260, \text{ or } X = 11.6 \text{ grams of zinc}$$

You must remember that the gram-molecular volume (22.4 liters) can be used *only with gases* and only with the metric units of weight.

Here are a few exercises dealing with the volumes of gases. Solve them, using the method just explained.

Exercises to Solve

(1) What weight of salt must be used with sulfuric acid to give 1.12 liters of hydrogen chloride? (2) What volume of chlorine is needed to combine with 2.3 grams of sodium? (3) What volume of hydrogen is needed to reduce 2 grams of copper oxide? (4) What volume of sulfur dioxide can be formed by burning 10 grams of sulfur? (5) One-tenth of a gram of magnesium was treated with hydrochloric acid. What volume of hydrogen was produced?

How to determine volume relations in gaseous reactions. If all the reacting substances are gaseous, the number of formula weights used in the equation shows the relative volumes of

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the gases interacting. When methane is burned, the equation for the reaction is as follows:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

Since the reacting substances and the products are all gases, each formula stands for a gram-molecular volume (G.M.V.). This equation tells you that 1 G.M.V. of methane combines with 2 G.M.V. of oxygen forming 1 G.M.V. of carbon dioxide and 2 G.M.V. of water vapor.

These volume relations may be used to solve exercises. If you have 4 liters of carbon monoxide, how many liters of oxygen are needed to combine with it? First, you must have the completed equation:

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

In this exercise you are interested only in the carbon monoxide and the oxygen. The formulas of these two substances are taken from the equation and made into a proportion, using the quantities given and asked for in the exercise:

$$\frac{2\ CO}{4} = \frac{O_2}{X}$$

Since each formula stands for a gram-molecular volume (22.4 liters), you can substitute this value for each gram-molecular volume:

$$\frac{2\,(22.4)}{4} = \frac{22.4}{X}$$

Solving the proportion:

$$2\ X = 4$$
$$X = 2 \text{ liters of oxygen needed}$$

Since each formula stands for the same gaseous volume, the coefficients used represent the relative number of volumes. This makes it possible to solve exercises of this type by inspection after you have the completed equation. Write the equations for the reactions in the exercises at the top of the next page and solve them by inspection ("mentally").

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Inspection Exercises to Solve

(1) One hundred ml of nitrogen are combined with hydrogen to form ammonia (NH_3). What volume of hydrogen is needed and what volume of ammonia is produced? (2) How many liters of oxygen are needed to combine with 6 liters of hydrogen? (3) Acetylene (C_2H_2) burns to form carbon dioxide and water vapor. How many liters of oxygen are needed to combine with 10 liters of acetylene? (4) One hundred ml of chlorine are combined with hydrogen. What volume of hydrogen chloride is produced?

Applying in Life What You Have Learned in Chemistry

Of all the keepsakes which Esther Bowman found in her grandmother's old box in the attic, she probably prized the old book of recipes most of all. Esther tried many of the recipes for old dishes and most of them were more satisfactory than she even dared to hope.

She was especially interested in the recipe for homemade baking powders: "Sift thoroughly together three parts of soda, six parts of cream of tartar, and one part of flour or cornstarch. Keep the mixture in an airtight can." Esther prepared a small amount of the baking powder and used it in her baking, but the results were disappointing. She believed that the amounts of materials were not correct.

She remembered from her chemistry work that the carbon dioxide was liberated by the action of the cream of tartar on the baking soda. She found this equation in her chemistry book:

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow$$

and set about to calculate the correct amounts of the reacting materials.

Can you complete Esther's problem?

Putting Chemistry to Work

A

(1) On what fundamental chemical law and on what fundamental chemical theory do all equations depend? State each of them. (2) A chemical equation must be correct from what three standpoints? (3) Why does a given weight of sodium hydroxide "go farther" in neutralizing an acid than the same weight of potassium hydroxide? (4) "A knowledge of chemical equivalents is as

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important to the chemist as exchange rates are to a traveler in foreign countries." Justify this statement. (5) Does an equation tell you anything that someone did not have to find out by experiments before the equation could be written? *Think most carefully about this.*

B

(6) Point out clearly how an equation expresses quality; how it expresses quantity. (7) Show how volume relations are expressed by equations. What limitations are there? (8) Which would precipitate more barium sulfate from a solution of sodium sulfate, 10 grams of barium chloride or 10 grams of barium nitrate? Explain your reasoning.

How Good Are You at Solving Problems?

(1) Calculate the cost of enough potassium chlorate at 60 cents a kilogram to prepare 250 grams of oxygen; to prepare 250 liters of oxygen.

(2) Which substance is in excess when aluminum is burned in its own weight of oxygen?

(3) A 24-gram sample of carbon burned to form carbon monoxide, and another 24-gram sample burned to form carbon dioxide. What volumes of the gases were formed?

(4) Aluminum costs 20 cents per pound and zinc costs 8 cents per pound. Which is cheaper to use in displacing hydrogen from hydrochloric acid? (Show this by determining the amount of hydrogen produced in each case.)

(5) The equation for one method of preparing chlorine is:

$$MnO_2 + 4\ HCl \rightarrow MnCl_2 + 2\ H_2O + Cl_2 \uparrow$$

How many grams of chlorine would you expect to obtain from 100 grams of MnO_2 and 100 grams of HCl? (See which material is in excess; then use the weight of the other one.) How many liters of chlorine could you obtain?

(6) What weight of barium sulfate could be precipitated from a solution containing 22 grams of ammonium sulfate? from 22 grams of a 5 per cent solution of ammonium sulfate?

(7) When 15 liters of gasoline vapor (use C_8H_{18}) burns completely, how many liters of carbon dioxide are formed? How many liters of air would be required to supply the oxygen to burn the gasoline?

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(8) Silver nitrate is prepared from silver by the following reaction:

$$3\,Ag + 4\,HNO_3 \rightarrow 3\,AgNO_3 + NO\uparrow + 2\,H_2O$$

A silver dollar weighs 26.5 grams. It contains 90 per cent silver. How many grams of silver nitrate could be prepared from this coin? How many liters of nitric oxide will be formed? (Assume that the metal comprising the 10 per cent does not react with nitric acid.)

(9) How many grams of photographic silver bromide can be precipitated from the silver nitrate prepared in item 8?

Research and Activities That You Will Enjoy

A helpful summary: Make a list of all the *types* of numerical chemical problems you have learned to solve in your work thus far. Make, solve, and explain to the class an example of each of these types.

Profiting by an "accident": In this book the statement was made that "the gram-molecular volume (22.4 liters) can be used only with the metric units of weight." Now it is claimed that G.M.V. can be used to obtain volumes of gases *in cubic feet* when the weight is given *in ounces.* Prove to the class that this claim is or is not true.

A forum: By means of several brief, well-chosen reports and a general class discussion bring out the importance and applications of chemical arithmetic both in the home and in industry.

Problem 30

WHAT IS GOING TO HAPPEN? — AN INQUIRY INTO EQUILIBRIUM

It is very convenient to be able to predict whether or not a chemical reaction will occur—without actually performing the experiment. There are ways for you to foretell, with a reasonable degree of accuracy, which reactions will take place. Look at a few reactions to see if you can determine what factors control them. A study of these factors may aid you in predicting what reactions may occur.

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What is a reversible reaction? You have found (page 68) that when steam is passed over red-hot iron, iron oxide and hydrogen are produced:

$$4\ H_2O + 3\ Fe \rightarrow Fe_3O_4 + 4\ H_2\uparrow$$

You also have learned that hydrogen is a good reducing agent. If hydrogen is passed over a heated metallic oxide, the oxide is reduced and steam forms. When hydrogen is passed over the heated iron oxide, formed in the above experiment, iron is liberated and steam passes off:

$$Fe_3O_4 + 4\ H_2 \rightarrow 4\ H_2O\uparrow + 3\ Fe$$

You can easily see that these two reactions are the reverse of each other. A double arrow is used to show that the equation may be read in either direction:

$$Fe_3O_4 + 4\ H_2 \rightleftarrows 4\ H_2O + 3\ Fe$$

In the first reaction a continuous supply of steam is poured over the iron, and the hydrogen is swept away from the scene of the reaction. In the second reaction a continuous supply of hydrogen is passed over the heated oxide, and the steam is removed as fast as it is formed.

In a reversible reaction, what happens when the two opposite reactions attain the same velocity? Suppose you heat some iron and water in a sealed tube. At first, there is neither iron oxide nor hydrogen present, so the reaction can proceed only in one direction. But as soon as any iron oxide and hydrogen form, the reverse reaction may start since none of the products can escape from the tube. The speed of the reverse reaction increases as the amounts of iron oxide and hydrogen increase. Finally, a point is reached at which the speed of the reaction of iron oxide with hydrogen just balances the speed with which steam reacts with iron. When this condition is reached, *the reactions are in equilibrium,* or balance. This does not mean that the reactions cease. There is continual chemical change going on in the tube, but the two reactions just balance each other. It is not an equilibrium of rest, but an equilib-

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rium of motion, or a kinetic equilibrium. This state of balance between reacting substances is an example of *chemical equilibrium.*

If the tube is opened and the hydrogen is allowed to escape, the possibility of having a reverse reaction is destroyed. The removal of one of the reacting substances from either of the reactions will change the conditions that are necessary for the equilibrium. Let us apply this principle to some other reversible reactions.

When sodium chloride is dissolved in water, the ions become free to move. This is indicated by the ionic equation.

$$NaCl \rightarrow Na^+ + Cl^-$$

If the water is evaporated from the solution, the ions become inactive in solid form.

$$Na^+ + Cl^- \rightarrow NaCl$$

These two reactions may be expressed in one equation with the double arrow.

$$NaCl \rightleftarrows Na^+ + Cl^-$$

Silver nitrate in solution ionizes in a similar manner.

$$AgNO_3 \rightleftarrows Ag^+ + NO_3^-$$

When a precipitate is formed, you know that a double-decomposition reaction has gone to completion. Suppose you now mix the solution of sodium chloride with a solution of silver nitrate. There are two sets of positive and negative ions in the field of action. Since combination is possible between any pair of positive and negative ions, silver ions may react with chloride ions to form silver chloride. Likewise, sodium ions may react with nitrate ions to form sodium nitrate. Sodium nitrate is soluble, so it remains largely in the active ionic form; while the silver chloride is insoluble and comes out of the solution as a precipitate. The formation of the precipitate removes the silver and chloride ions from the solution, and this destroys any possibility of a reverse reaction.

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Study the following ionic equation until you are certain that you see why the reaction is not reversible.

$$\begin{array}{ccccc} NaCl & \rightleftarrows & Na^+ & + & Cl^- \\ & & + & & + \\ AgNO_3 & \rightleftarrows & NO_3^- & + & Ag^+ \\ & & \downarrow\uparrow & & \downarrow \\ & & NaNO_3 & & AgCl\downarrow \end{array}$$

The formation of silver chloride will go on as long as there are silver ions and chloride ions in the solution. Since this reaction can move only in one direction, it is said to go to completion; it is a *completion reaction.*

When a chemical reaction produces a gas, you know that a double-decomposition reaction has gone to completion. For a similar reason, reactions which result in the formation of gases also tend to go to completion. Let us take the case of the reaction between solutions of sodium sulfide and sulfuric acid. The sodium sulfide supplies sodium ions and sulfide ions to the solution. The acid furnishes hydrogen ions and sulfate ions. When these solutions are mixed, combination takes place between any positive and negative ions.

$$\begin{array}{ccccc} Na_2S & \rightleftarrows & 2\,Na^+ & + & S^{--} \\ & & + & & + \\ H_2SO_4 & \rightleftarrows & SO_4^{--} & + & 2\,H^+ \\ & & \downarrow\uparrow & & \downarrow \\ & & Na_2SO_4 & & H_2S\uparrow \end{array}$$

When hydrogen ions combine with sulfide ions, hydrogen sulfide gas is formed which leaves the solution. The removal of these ions from the field of activity prevents a reverse reaction taking place. Hence the reaction tends to go to completion.

Reactions behave in a similar manner when unstable compounds are formed, especially when these unstable compounds decompose to form gases. This behavior is nicely illustrated by the reaction between hydrochloric acid and sodium carbonate. This reaction in which carbonic acid is formed proceeds toward completion due to the escape of carbon dioxide.

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$$\begin{array}{rcccc} Na_2CO_3 & \rightleftarrows & 2\ Na^+ & + & CO_3^{--} \\ & & + & & + \\ 2\ HCl & \rightleftarrows & 2\ Cl^- & + & 2\ H^+ \\ & & \downarrow\uparrow & & \downarrow \\ & & 2\ NaCl & & H_2CO_3 \\ & & & & \hookrightarrow H_2O + CO_2\uparrow \end{array}$$

When a chemical reaction produces an un-ionized substance, you know that a double-decomposition reaction has gone to completion. In some reactions ions may combine to form an un-ionized compound such as water. This occurs in the reaction between acids and bases (neutralization). Suppose that a solution of hydrochloric acid (which contains hydrogen ions and chloride ions) is mixed with a solution of sodium hydroxide (which contains sodium ions and hydroxyl ions). Combination is possible between any positive and negative ions. When hydrogen and hydroxyl ions unite, they form water which does not ionize. The formation of this un-ionized water removes hydrogen ions and hydroxyl ions from the solution, so the reaction goes to completion.

$$\begin{array}{rcccc} NaOH & \rightleftarrows & Na^+ & + & OH^- \\ & & + & & + \\ HCl & \rightleftarrows & Cl^- & + & H^+ \\ & & \downarrow\uparrow & & \downarrow \\ & & NaCl & & HOH \end{array}$$

Reactions that form soluble ionized products remain in equilibrium. Suppose you mix a solution of sodium nitrate (containing sodium ions and nitrate ions) with a solution of potassium chloride (containing potassium ions and chloride ions).

$$\begin{array}{rcccc} NaNO_3 & \rightleftarrows & Na^+ & + & NO_3^- \\ & & + & & + \\ KCl & \rightleftarrows & Cl^- & + & K^+ \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & NaCl & & KNO_3 \end{array}$$

Here any possible combination of positive and negative ions can result only in the formation of a highly ionized soluble salt.

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Since no ions are removed from the field of action, the reaction cannot go to completion. It remains in equilibrium.

A Principle for You to Remember

Summary. Any double-decomposition reaction will go to completion when one kind of positive ions and one kind of negative ions have been removed from solution. This may happen through—

1. the formation of a precipitate (insoluble substance);
2. the formation of a gas;
3. the formation of an un-ionized product.

In order to predict which ionic reactions will go to completion, you must know which substances are insoluble (see the solubility chart, page 781), and which substances are ionized (see the table, page 789), as well as what products are gaseous or decompose to form gases. P(775)

Complete the following equations on a separate paper. Refer to the tables mentioned above, and tell which reactions go to an end, and why.

Drill Exercise

1. $NaCl + H_2SO_4 \rightarrow$
2. $NH_4Cl + NaNO_3 \rightarrow$
3. $BaCl_2 + H_2SO_4 \rightarrow$
4. $Pb(NO_3)_2 + K_2CrO_4 \rightarrow$
5. $CuSO_4 + HCl \rightarrow$
6. $KOH + HNO_3 \rightarrow$
7. $FeS + H_2SO_4 \rightarrow$
8. $HgNO_3 + NaCl \rightarrow$
9. $NH_4Cl + AgNO_3 \rightarrow$
10. $Ca(OH)_2 + HCl \rightarrow$

What other types of reactions occur? The reactions you have been studying in this problem so far are double-decomposition reactions. Other types of chemical changes you have studied are:

1. *Combination,* or synthesis, in which two or more substances combine to form a single substance;

2. *Decomposition,* or analysis, in which a substance decomposes into two or more products;

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3. *Displacement,* in which an element enters a compound, and takes the place of another element in the compound, thus setting the other element free.

In the combination type of reaction there is a definite heat of formation. In all chemical changes there are accompanying energy changes. In combination reactions, energy is usually liberated in the form of heat. The amount of energy (expressed in calories) which is given off during the formation of one gram-molecular weight of a compound is called its *heat of formation.* (See page 780 for the heat of formation of several compounds.) When 12 grams of carbon burn to form 44 grams of carbon dioxide (one gram-molecular weight), 97,000 calories of heat are set free. Similarly, during the formation of one gram-molecular weight of magnesium oxide, 143,000 calories are liberated; and during the formation of one gram-molecular weight of mercuric oxide, 21,500 calories are set free. These facts are shown in *thermal* (heat) *equations.* (The second and third equations are not molecular equations because it is convenient to show the calories of heat produced by the formation of only one gram-molecular weight of the product.)

$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ calories}$$

$$Mg + [O] \rightarrow MgO + 143{,}000 \text{ calories}$$

$$Hg + [O] \rightarrow HgO + 21{,}500 \text{ calories}$$

Note that the heats of formation are a measure of the ease with which the chemical combinations take place.

In general the higher the heat of formation of a compound, the more readily the reaction forming that compound takes place. In the activity series of metals (see page 72) the metals are arranged in the order of their activity. Those metals near the top of the list show more chemical activity and enter into combination more easily than those following. This means that compounds formed from elements high in the list have higher heats of formation than similar compounds formed from elements lower in the list.

The production of energy from chemical action is our most common method of obtaining heat. You do not burn coal or

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oil under a boiler or in a furnace to obtain the carbon dioxide and water vapor formed by the reaction; you want the heat that is set free by the reaction. Similarly, when you burn gasoline in an engine cylinder, you want the energy that is liberated, not the products of the combustion.

In the formation of certain compounds, it is necessary to apply energy to the combining elements. Compounds of this type have a negative heat of formation. Such combinations do not liberate heat but absorb it. Compounds with negative heats of formation are difficult to form.

Many decomposition reactions require the addition of energy. Decomposition reactions are the reverse of combinations. If you are going to reverse a reaction, you must put everything into it that came out of it. For example, if you wish to reverse the reactions shown by the equations on page 253, you must put energy equivalent to 97,000 calories of heat into each mole of carbon dioxide; 143,000 calories into each mole of magnesium oxide; and 21,500 calories into each mole of mercuric oxide. So you see that much less heat is needed to decompose mercuric oxide than is needed to decompose carbon dioxide. In general the lower the heat of formation of a compound, the easier it is to decompose. Compounds with a negative heat of formation are very unstable, since they liberate heat in their decomposition, which in turn increases the speed of the reaction.

A Principle for You to Remember

Compounds with high heats of formation form easily and decompose with difficulty. Compounds with low heats of formation are difficult to form but easy to decompose.

Displacement reactions are also accompanied by energy changes. Zinc in hydrochloric acid solution goes into solution as zinc chloride, and hydrogen is set free. Considerable heat is given off. Similarly, when fine iron filings react with a

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solution of copper sulfate, the iron goes into solution as iron sulfate and the copper is set free. Here, also, heat is liberated. This means that in these cases the new compounds formed have higher heats of formation than the compounds entering the reaction. That is, zinc chloride has a higher heat of formation than hydrochloric acid, and iron sulfate has a higher heat of formation than copper sulfate. Consequently, these new compounds are more stable than the old ones.

A Principle for You to Remember

In displacement reactions, *the reaction moves in the direction of greatest stability.*

In displacement reactions the most stable substance tends to form. Consider the direction in which each of the following reactions goes.

$$\underset{94{,}030 \text{ cal.}}{2\ KBr} + Cl_2 \rightarrow \underset{104{,}300 \text{ cal.}}{2\ KCl} + Br_2$$

$$\underset{94{,}030 \text{ cal.}}{2\ KBr} + I_2 \leftarrow \underset{71{,}920 \text{ cal.}}{2\ KI} + Br_2$$

In the first reaction the potassium chloride has a higher heat of formation than the potassium bromide so the reaction, moving in the direction of greater stability, moves to the right. In the second reaction the potassium iodide has a lower heat of formation than the potassium bromide and is therefore a less stable compound. The reaction, moving in the direction of greater stability, moves to the left.

In the activity series (page 72) metals are arranged in the order of their chemical activity. This means that they are arranged in the order of the stability of their oxides or of their chlorides. Since displacements move in the direction of greatest stability, those elements towards the top of the series will displace those below. Displacement reactions ordinarily are not reversible and always tend to go to completion.

You will find that these general principles will be much used further on in the study of chemistry.

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Consult the activity series and complete on a separate paper the equations for those reactions which will take place.

Drill Exercises

1. $Al + Fe_2O_3 \rightarrow$
2. $Cu + FeSO_4 \rightarrow$
3. $Pb + Al_2O_3 \rightarrow$
4. $Cu + AgNO_3 \rightarrow$
5. $Cu + HgCl_2 \rightarrow$
6. $KBr + I_2 \rightarrow$
7. $H_2S + I_2 \rightarrow$
8. $KI + Cl_2 \rightarrow$

How can you alter the speed of chemical changes? You already are familiar with a few methods of speeding up chemical changes. The different methods in summary form are as follows.

Temperature alters the speed of chemical changes. While copper will slowly oxidize at ordinary room temperature, at red heat the action is quite rapid and in only a few minutes a sheet of copper is completely covered with a layer of dark-colored copper oxide. At ordinary room temperature potassium chlorate gives off no oxygen. But when the potassium chlorate is heated, oxygen is easily liberated. For many reactions a rise of 10° C. in temperature about doubles the speed of the reaction. If you wish to retard the rate of a reaction, you can cool the reacting substances. When you put food in a refrigerator, you slow up the chemical changes that help cause the food to spoil.

Catalysts alter the speeds of chemical changes. When preparing oxygen from potassium chlorate, you found that the addition of manganese dioxide greatly speeded up the rate at which oxygen was liberated although the manganese dioxide took no active part in the reaction. The manganese dioxide is a catalyst. Many reactions are made practical by the presence of catalysts. These substances are not themselves permanently altered in the change, but reactions take place more readily in their presence. There also are negative catalysts which slow up the rate of chemical changes. When you buy a bottle of hydrogen peroxide, you may find a statement that it contains a small fraction of one per cent of acetanilide. This is put in

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as a "preservative" to slow up the rate of decomposition of the hydrogen peroxide.

The concentration of a reactant may affect the speed of a chemical change. The effect of changes in concentration are quite strikingly shown by burning various substances in oxygen. A splinter glows in air, but it bursts into flame in pure oxygen. Air is only about 21 per cent oxygen, while the pure oxygen in the bottle has a 100 per cent concentration. This difference in concentration causes the difference in the speed of the reactions.

A change in pressure may affect the speed of a chemical change. Pressure is of great importance in reactions between gases. At ordinary pressure, nitrogen and hydrogen show little tendency to combine even in the presence of a catalyst. With the gases under pressure, the speed of the reaction is increased. At the present time, pressures up to 15,000 pounds to the square inch are used to cause these gases to combine. As you can easily see, an increase in pressure on a gas means an increase in the concentration of the reacting molecules.

The amount of surface exposed affects the speed of a chemical change. You cannot start a fire by lighting a log of wood with a match. But if the log is shredded into excelsior, it is quite easily ignited. If the log is converted into very fine sawdust and blown into the air, a match may ignite it with explosive violence. Since many chemical changes depend upon surface contacts, the more surface that is exposed, the more rapid will be the rate of chemical action.

Applying in Life What You Have Learned in Chemistry

In the industrial laboratory where you work you are assigned the task of determining accurately the percentage of silver in a silver-copper alloy. You dissolve a carefully weighed piece of the alloy in nitric acid; you then wish to precipitate the silver so you can weigh it. How will you precipitate the silver ions from the solution? Why does the director advise you to add an excess of the reagent which causes the precipitation of the silver?

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211-214

A salesman is trying to interest you in buying stock in a concern which plans to obtain aluminum cheaply by reducing aluminum oxide with carbon. Will you or will you not listen to the plans of the process? Give a chemical reason for your decision.

In your next unit you will find that the essential reaction in the manufacture of sulfuric acid is $2\,SO_2 + O_2 \leftrightarrows 2\,SO_3 + 45{,}200$ calories. You find the following statement in a handbook for chemical engineers: "The following percentages of SO_2 are oxidized to SO_3 at equilibrium: at 400°, 98; at 645°, 60; and at 900°, practically none." Why must the oxidation of SO_2 be controlled carefully? At about what temperature would you favor running the process? As the oxidation proceeds, must the mixture be heated or cooled? You are the foreman in a sulfuric acid plant. Try to explain these conditions to the president of the company.

Putting Chemistry to Work

A

(1) How would you remove barium ions from a solution? Explain your answer. (2) Barium sulfate is not completely insoluble. Will the procedure employed in the answer to the last item remove *all* the barium ions? What would be the effect of the addition of an excess of the reagent? (3) In the reaction, $CaCO_3 \leftrightarrows CaO + CO_2$, how is the formation of lime dependent upon the removal of carbon dioxide during the heating of the limestone? Would this reaction go well in a closed retort? Why? (4) What relation will you expect to find between the displacement series and the ease or difficulty of winning metals from their ores?

B

(5) What is a completion reaction? a reversible reaction? Give an example of each and show clearly how the example illustrates the type of reaction. (6) Give your interpretation of chemical equilibrium. (7) Explain how a reaction goes to completion due to the formation of a precipitate.

Research and Activities That You Will Enjoy

A reported interview: Ask an industrial chemist how large-scale reactions are controlled so as to produce the maximum yield. Ask for a few good examples and report to the class everything you learn from the interview.

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A co-operative report: Organize a small group of students to present individual discussions of the factors which influence chemical equilibrium and how it is changed. These difficult topics *can* be made very enlightening with appropriate demonstrations and well-prepared discussions. (A good reference is: Foster, *Elements of Chemistry,* Chap. 19.)

Looking Back into Unit 6

Be sure you know the purpose of this unit. Read again the material on page 228, "Looking Ahead into Unit 6." Then study the following Summary Test.

Summary Test

1. *How can you use equations as the shorthand of chemistry?*
   (a) Why do you use equations in chemistry?
   (b) What must you know in order to write an equation?
   (c) How do you write and complete equations for—
      (1) Double decomposition reactions? Show with an example.
      (2) Displacement reactions? Write one to illustrate.
      (3) Decomposition and combination reactions? Give examples.
2. *How much will you get?*
   (a) What does an equation show you about the weights of the reactants and of the products?
   (b) How can you use equations to solve weight problems? Show with an example.
   (c) How can you use equations to determine volumes of gases produced? Illustrate.
   (d) What does an equation show you about the volumes of gases involved in a reaction?
3. *How can you use equilibrium ideas to predict what will happen in a reaction?*
   (a) What is a reversible reaction?
   (b) What do you mean by chemical equilibrium?
   (c) How is a reaction completed by the formation of—
      (1) A precipitate? Give an example.
      (2) A gas? Illustrate.
      (3) An un-ionized substance? Show with an example.
   (d) How can you use heats of formation to predict reactions?
   (e) How can you alter the speed of chemical changes?

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Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

Matter and *energy* cannot be *created,* neither can they be *destroyed,* but in this unit you see excellent proof that changes in the *chemical* make-up of *matter* and *changes* in *energy* are going on *constantly* about you. You can balance *equations mechanically,* but the final test as to whether a *reaction* will *work* according to the *equation* you have written must be gained by *experimental evidence* obtained in the *laboratory.*

By the use of *balanced equations* you can *determine accurately* on paper how much you need to use or how much you will get in a *chemical reaction;* every time you write and balance an equation you make it agree with the *law of conservation of matter*—if you do accurate work.

In the case of the *burning* or *oxidation* of substances, you have learned how much *heat energy* is *released* in the formation of one *gram-molecular weight* of the *oxide.* This is useful in determining the heat value of fuels.

You are now equipped with most of the *theories, fundamental principles, laws,* and *methods* for solving problems which you need for an *understanding* of the more practical side of *chemistry.* It will be well at this point for you to *cross-examine* yourself to see how well you have *mastered* the big ideas thus far presented.

If you can *honestly* answer the following *questions* in the *affirmative,* you are ready to go ahead. If your answer is *"no"* or if there is some *doubt* in your mind about the answer, review now the proper materials.

(1) Do you know the meaning of these laws: definite composition, conservation of matter and energy, Henry's law, Avogadro's law, and Gay-Lussac's law of volumes?

(2) Can you give the outstanding points in the kinetic-molecular theory, the atomic theory, the electron theory, and the ionic theory?

(3) Do you know the four types of chemical reactions? Give a balanced equation that illustrates each type.

(4) Do you understand the relationship which exists between oxidation and reduction in so far as hydrogen and oxygen are concerned?

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(5) Although you may not yet be proficient in the writing of formulas, do you know how to "construct" the formulas of simple inorganic compounds?

(6) Do you know the properties, the general rules, and the nomenclature for acids, bases, and salts?

(7) Do you know what neutralization really is? Can you recognize salts that will hydrolyze?

(8) Can you explain the general principles involved in the electrolysis of a substance such as sodium chloride?

(9) Do you know how to apply the rules for balancing molecular equations to the four types of chemical reactions and make them agree with the law of conservation of matter?

(10) Do you know how to work and to use the following types of problems? (a) getting the molecular weight of a compound from its formula? (b) using G.M.V. (22.4 liters) to obtain the molecular weight of a gas or the weight of one liter of that gas? (c) determining the percentage composition of a compound? (d) solving problems, based on equations, when weight only is involved? (e) solving problems, based on equations, when the weight of one substance and the volume of another is involved? (f) solving problems, based on equations, when volume only is involved?

(11) Can you use the appendix and the index of your book to find information that you need?

(12) Do you have a fair understanding of those terms which have been used thus far in this book? (See the glossary.)

(13) Have you gained a knowledge and appreciation of how scientific knowledge is obtained? of the scientific method? of the development of a scientific law? of significant historical achievements?

(14) Has your study of the chemical interpretation of matter given you a new concept of the world in which you live?

(15) Has your progress and work in the study of chemistry thus far given you the thrill of mastery that makes you want to learn more of this fascinating science?

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Looking Ahead into

Unit Seven

Sulfur is a cornerstone of industry. When the chemist rates the chemical industries, he usually places the manufacture of sulfuric acid first. And although sulfur compounds are indispensable, the free element has important uses.

Sulfur aptly illustrates allotropic forms of elements. It is a solid, a typically nonmetallic element, whose chemistry is orderly and complete. The element unites with hydrogen to form hydrogen sulfide, with oxygen to form oxides, and with metals to form a wide and useful variety of sulfides many of which are minerals found in nature.

Sulfur compounds are useful in the laboratory as reagents; in the home as refrigerants, bleaching agents, medicines, and paints; in agriculture as insecticides and fertilizers; in industry in making explosives, dyes, and rayon; in refining petroleum; in paper making; and in metallurgy.

Sulfur, free or combined in its compounds, touches practically every article and material you use daily. Note the story of sulfur in the following problems.

Problem 31. *Approximately Two Million Tons of Sulfur Are Used in the United States During an Average Year. How Is Sulfur Obtained and Used?*

Problem 32. *What Is Hydrogen Sulfide; How Can You Use It?*

Problem 33. *How Is Sulfur Dioxide a Useful Servant; How Can You Make It?*

Problem 34. *Millions of Tons of Sulfuric Acid Are Used Each Year. How Is It Used; How Is It Manufactured?*

Problem 35. *How Can a Study of Sulfuric Acid Enlarge Your Idea of Oxidation-reduction Reactions?*

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Sulfur in Use: An Important Element That Forms Many Compounds

Problem 31

OVER TWO AND A HALF MILLION TONS OF SULFUR ARE USED IN THE UNITED STATES DURING AN AVERAGE YEAR. HOW IS SULFUR OBTAINED AND USED?

Sulfur has been known since ancient times. Early man, cradled in the volcanic regions of the Mediterranean, knew sulfur because it was deposited with rock and pumice at the foot of many volcanoes. Long ago the Chinese learned to use it in making gunpowder, and early literature has many references to sulfur as brimstone ("a stone that burns"). Acids formed from it were used many centuries before the properties of these acids were understood.

How the great demand for sulfur was at one time supplied from deposits in other countries. Up to 1903 Sicily supplied about 95% of the sulfur used in the world. In Sicily and in some volcanic regions, including Japan and Mexico, sulfur is in the free state, mixed with rock and dirt. The earliest methods of purifying this sulfur were very wasteful. Cone-shaped piles of the sulfur mixture, covered with earth, were ignited; and openings were made at the base and top for the circulation of air (Fig. 85). Heat from the burning of some of the sulfur melted the rest, and it ran down from the pile into trenches from which it was collected. A later and better method of purifying the sulfur consisted of heating the mixture in brick retorts (furnaces) and collecting the melted sulfur. The sulfur vapor was sometimes passed from the heated retort into a large chamber where it cooled to form a very fine powder known as "flowers of sulfur."

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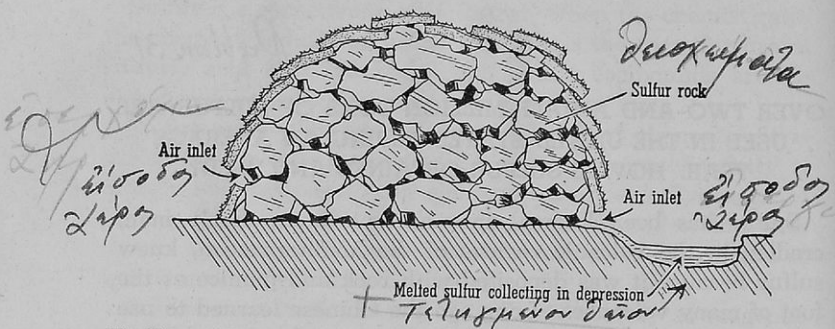
The American supply of sulfur is over 450 feet below the surface with a layer of quicksand above it! How do we get it? About 1860 the search for oil led to the discovery of sulfur in Louisiana and Texas, where deposits 100 feet thick were found at a depth of about 450 feet. However an overlying layer of quicksand made it impractical to sink shafts for shaft mining.



85. EARLY METHOD OF PURIFYING SULFUR IN SICILY. Sulfur is used as a fuel to separate sulfur from a rock mixture by the difference in melting points.

For thirty years American interests tried to find a way of tapping this sulfur "gold" mine. Many impractical schemes were suggested and attempted. One of the most laughed at and apparently impractical plans was that of an American chemist, Herman Frasch. One jeering engineer offered to eat all of the sulfur that Frasch could obtain by his method. But Frasch persisted and after almost ten years of experimenting was successful. Let us see how he did it.

How Frasch did an engineering job that experts said could not be done. The secret of the Frasch process lies in melting the sulfur with very hot water and then raising it to the surface by means of compressed air. Sulfur is insoluble in water and melts at 114° C. Under pressure, water can be heated to a much higher temperature than its boiling point; the water for this purpose is heated to about 160° C. This hot water, under pressure, is forced down directly into the beds of sulfur through the outer one of three concentric pipes (Fig. 86).

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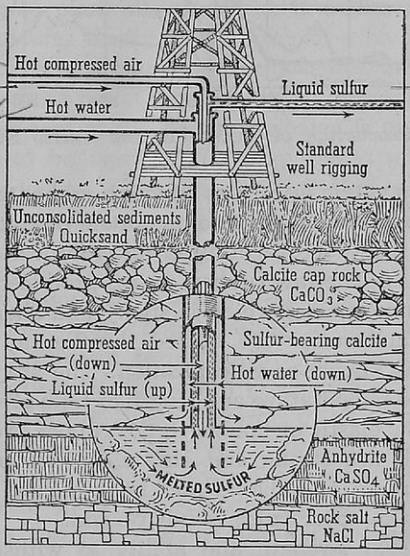
The sulfur melts. At the same time a stream of hot compressed air is forced down through the small central pipe. This hot compressed air mixes with the melted sulfur to make a light, foamy mass which is forced to the surface through the middle pipe by the strong pressure and the added volume of water.



86. THE FRASCH PROCESS OF MINING SULFUR. Sulfur is melted and made lighter by adhering air bubbles. The flowing water then carries the sulfur to the storage tank.

The molten sulfur is piped to bins where it solidifies in "blocks" which sometimes are 160 feet wide by 1200 feet long and 65 feet high—a 500,000-ton mountain of sulfur. Later the sulfur in these huge blocks is blasted and then loaded into freight cars by large power hoists. Frasch's "dream" has thus made available each year more than 2 million tons of American sulfur, which is more than 99 per cent pure. Much of this sulfur is shipped by boat to the northeastern sections of the United States for industrial purposes, three-fourths of it going into the manufacture of sulfuric acid.

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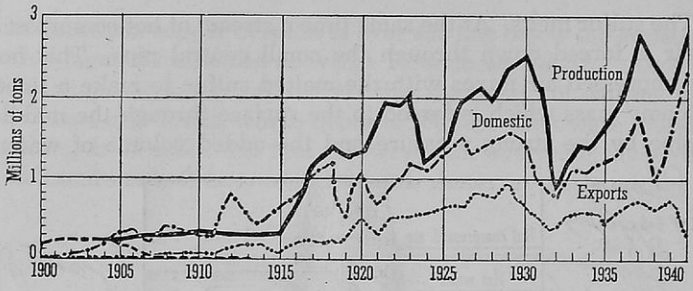

87. PRODUCTION OF SULFUR IN THE UNITED STATES

Sulfur enables you to drive cars on tough rubber tires; it enables you to use and enjoy a wealth of important products. Sulfur is used in the manufacture of tires for your car. Sulfur puts "life" into tires. The raw rubber, as it is produced from rubber trees, is a gummy mass which is sticky and shapeless. When raw rubber and sulfur are heated together an action takes place which is known as vulcanization. The amount of sulfur added and the temperature and length of time of vulcanization, determine how elastic or how hard the rubber product will be. Rubber bands are strong and elastic, hot-water bottles and laboratory tubing are pliable and impermeable to moisture, and a rubber comb or ruler is fairly rigid.

When unusual strength and ability to withstand wear is required, rubber is reinforced by textile fabrics. This enables you to use such useful products as automobile tires, fire hose, door mats, belts for power transmission, overshoes, raincoats, and insulated wire. Rubber heels for your shoes are springy but able to withstand wear. Your eraser may contain some abrasive to increase its usefulness.

While sulfur plays an important part in the rubber industry, a much larger part of the sulfur produced goes into the manufacture of sulfuric acid. This is one of the most important acids, since it is used in many of our largest industries.

Much sulfur is also used in the preparation of spray mixtures—insecticides for controlling harmful insects, and fungicides for controlling plant diseases. One of the common spray

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materials of this sort is lime-sulfur; it is prepared by boiling sulfur with slaked lime. It is a mixture of calcium sulfides which on exposure to air deposits fine sulfur upon the branches and leaves of the plant to which it is applied. Such fine sulfur is effective in killing many harmful insects and in controlling many plant diseases, but it is harmless to the higher forms of life. Sulfur in the form of a fine dust is also frequently applied to ornamental trees, shrubs, or flowers as a means of controlling insect pests and plant diseases.

About 15 per cent of the sulfur produced is made into calcium bisulfite to be used in the preparation of wood pulp in the paper industry. (See page 520.) Sulfur is also used in the preparation of dyes, metallic sulfides, black gunpowder, and medicines for skin diseases.

What kinds of sulfur can you use?—allotropy. One of the many interesting things about sulfur is that this element exists in three different forms which show widely different physical properties. In the study of oxygen you will recall that we referred to the different forms of an element as *allotropic forms;* ozone is the allotrope of oxygen. Solid sulfur is known in three allotropic forms which are easily studied. These forms differ from one another in the way in which the molecules are held together. These different arrangements produce different shaped masses, different densities, different colors, and differences in solubilities, but their chemical behavior is quite similar. The three forms of sulfur are described in the following outline. In this outline, note the names applied to these three allotropic forms; then compare their colors and outward appearances which are given in (a) under each head. Next in (b) see how each is prepared. In (c) note the crystalline forms (if any). The remainder of the outline gives other interesting properties.

1. *Rhombic (roll) sulfur.*
   (a) Pale yellow, brittle solid, without taste or smell.
   (b) Prepared easily by dissolving sulfur in carbon disulfide, which evaporates on standing, leaving crystals.

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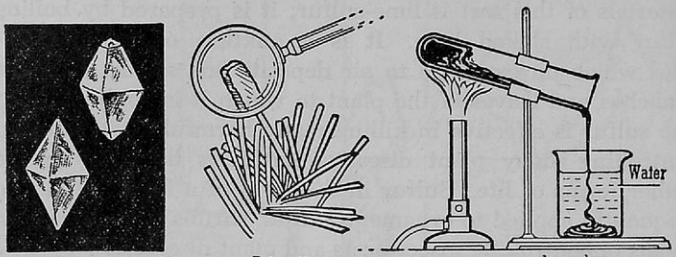

88. WIDELY DIFFERENT FORMS OF SULFUR AS REGULATED BY TEMPERATURE

(c) Crystals are rhombic or octahedral in shape. Many modifications are possible. (See Fig. 88.)
(d) Insoluble in water, but soluble in carbon disulfide.
(e) Density of crystals is about 2.06.
(f) Stable below 96° C. Melts at 112.8° C.

2. *Monoclinic (prismatic or needle-shaped) sulfur.*
(a) Waxy, glossy, hollow, brittle solid, without taste or smell.
(b) Prepared by heating sulfur just above its melting point and pouring the melted sulfur into a funnel fitted with moistened filter paper. Cool, and just before it is completely crusted over, pour out the excess sulfur.
(c) Needle-shaped crystals pointing toward center of cone. They are prismatic or monoclinic; but on standing, they change slowly to many small rhombic crystals. (See Fig. 88.)
(d) Insoluble in water; but in carbon disulfide changes to rhombic sulfur which dissolves in CS_2.
(e) Density of these crystals is 1.96.
(f) Stable between 96° and 119° C. Melts at 119° C.
(g) Changes to rhombic sulfur at 96° C.

3. *Plastic (amorphous) sulfur.*
(a) Tough, elastic, resembling India rubber. Can be molded between the fingers or drawn into threads.

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(b) Prepared by boiling sulfur and then cooling it quickly by pouring the molten sulfur into cold water. (The sulfur first melts at about 114° C., then becomes so thick [viscous] at about 180° C. that the test tube can be inverted. At 444° C., the liquid sulfur boils.)

(c) In the water it forms a gummy, elastic solid, varying in color from light amber to dark brown. It changes to the rhombic (stable) form on standing. (See Fig. 88.)

4. *"Flowers of sulfur" (powdered sulfur).*

(a) Light yellow, fine powder.

(b) True "flowers of sulfur" may be prepared by distilling sulfur and allowing the vapors to condense on the walls of a cool chamber. (Much commercial sulfur is rhombic sulfur ground to powder of desired fineness.)

(c) Partially amorphous, but largely rhombic or fractured rhombic crystals.

(d) Insoluble in water, but partially soluble in carbon disulfide.

Why is sulfur useful? One of the main reasons for the usefulness of sulfur is the fact that it forms a wide variety of compounds, many of which have properties that enable them to serve our needs.

Sulfur, when heated, unites directly with all the metals, except gold and platinum, to form sulfides. One example is the formation of iron sulfide (FeS):

$$Fe + S \rightarrow FeS$$

This action, in which sulfur combines with iron, liberates much heat. A strip of hot copper inserted in sulfur vapor glows brightly, forming black copper sulfide (Cu_2S) which becomes brittle on cooling. When ignited, powdered zinc and sulfur combine with explosive violence to form white zinc sulfide (ZnS).

The formulas of these sulfides resemble the formulas of the corresponding oxides. In fact, from the electronic structure of

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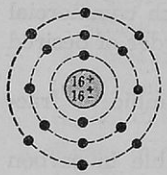
sulfur (S : 2, 8, 6) we should expect it to resemble oxygen (O : 2, 6) somewhat in its chemical properties since each of these two elements has six electrons in its outer orbit. (See Fig. 89.) Both elements exhibit a valence of —2 and react with metals and with nonmetals forming similar compounds as you will see from the following:

Ferrous sulfide	FeS	Ferrous oxide	FeO
Cupric sulfide	CuS	Cupric oxide	CuO
Zinc sulfide	ZnS	Zinc oxide	ZnO
Magnesium sulfide	MgS	Magnesium oxide	MgO
Carbon disulfide	CS_2	Carbon dioxide	CO_2
Hydrogen sulfide	H_2S	Hydrogen oxide	H_2O



89. SULFUR ATOM

However, the physical properties of these compounds, such as physical state and odor, may be as widely different as the physical properties of the elements themselves. This is at once plainly evident when we contrast the physical states of sulfur (solid) and oxygen (gas), hydrogen sulfide (gas) and hydrogen oxide (liquid water), and carbon disulfide (liquid) and carbon dioxide (gas).

Although sulfur ordinarily exhibits a valence of —2, it also exhibits a valence of either +4 or +6. This means that sulfur is not only able to borrow 2 electrons to complete its outer orbit, but it also can lend either 4 or 6 electrons. Consequently sulfur can lend electrons to oxygen. In other words, sulfur burns in air or oxygen to form the very pungent-smelling gas, sulfur dioxide.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. XI, pp. 205-225, "Rainy Day Apparel."

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XIV, pp. 185-187, "Sulfur."

DARROW, F. L. *The Story of Chemistry.* Chap. XII, pp. 433-436, "American Sulfur"; Chap. VIII, pp. 293-316, "Rubber."

GOLDBLATT, L. A. *Collateral Readings, Second Series.* Art. 14, pp. 90-92. Art. 15, pp. 92-98, "Sulfur Industry."

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 15, A, pp. 98-107, "Award of Perkin Medal to Herman Frasch."
HOLMES, HARRY N. *Out of the Test Tube.* Chap. X, pp. 116-127, "Brimstone or Cornerstone."
HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. XX, pp. 340-356, "Chemistry in the Rubber Industry."
ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. II, Chap. XXXIX, pp. 1108-1129, "Rubber."
SLOSSON, EDWIN E. *Creative Chemistry.* Chap. VIII, pp. 144-164, "The Race for Rubber."
TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXV, pp. 372-383, "Rubber."

Applying in Life What You Have Learned in Chemistry

A study hint: A good thinker makes diagrams to help him understand difficult or complicated processes.

One of the best ways to aid your thinking is by the use of diagrams. In this way you can pick out the main details of a process and understand and remember them better. You can see more clearly how the different parts are related and how they work together.

You may memorize sentences from the book and believe that, because you can repeat them, you know what you are talking about. This may not be true. However, if you study a process carefully until you can make a diagram of it, you will understand it and be able to explain it more satisfactorily.

In this unit you have several opportunities to learn to use diagrams to help you think straight.

Learn to use diagrams in your study and in your explanations.

Putting Chemistry to Work

A

(1) Why do people often say, "It smells like sulfur," when sulfur has no odor? (2) Explain why the method of obtaining sulfur in the United States is so different from that in Sicily. (3) Point out the importance of sulfur in connection with (a) the automobile industry, (b) the raising of fruits. (4) What advantages may you find in an element having allotropic forms as compared with one which has none? (5) After a rubber band has been used to keep a number of pieces of silverware together, a black mark is found underneath the band. Explain. (6) Choose from the list of uses of

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sulfur the one most common in your vicinity and discuss it briefly. (7) What have been the advantages to us of an American source of sulfur?

B

(8) Explain the similarity in the chemical behavior of sulfur and oxygen. (9) In getting sulfur from the Louisiana deposits, what three points did Frasch take into consideration? (10) See if you can make additions to the list of corresponding compounds of oxygen and sulfur. (See page 270.) Then compare their physical and chemical properties.

How Good Are You at Solving Problems?

(1) Indicate the valence of sulfur in each of the following: silver sulfide, rhombic sulfur, hydrogen sulfide, sulfur dioxide, sulfur trioxide, ferrous sulfide, antimony sulfide, and cuprous sulfide.

(2) A certain type of rubber contains 2 per cent of sulfur. How many pounds of sulfur are in 800 pounds of the rubber?

(3) Write equations for the formation (synthesis) of sulfur dioxide, ferrous sulfide, antimony sulfide, zinc sulfide, and cuprous sulfide. Then calculate the weight of the compound which can be prepared from 16 grams of sulfur in each case.

(4) How many grams of combined sulfur are present in 5.6 liters (S.T.P.) of sulfur dioxide?

Research and Activities That You Will Enjoy

A model: Devise a model or chart of the Frasch process. (Refer to: Lebowitz, "A Demonstration Working Model of the Frasch Process for Mining Sulfur," *J. Chem. Ed., 8,* 1630, Aug., 1931.)

An exhibit: Collect as many materials containing sulfur as you can find and show them to your class. Be able to give the common name of each, and the chemical composition.

A report: Look up the history of the work of Charles Goodyear which led to the discovery of vulcanization of rubber. Make a detailed report to the class. (See: Darrow, *Story of Chemistry,* Chap. 8.)

Herman Frasch: Organize a small group to plan and carry out a panel discussion interpreting for the class the difficulties, the importance, and the recompenses of Frasch's work in making available American sulfur. An excellent reference is: Goldblatt, *Collateral Readings in Inorganic Chemistry,* pages 98 to 107, or Chem. and Met. Eng., *48,* 104 (March 1941); Jour. Chem. Educ., *12,* 17, 83, 120 (1935).

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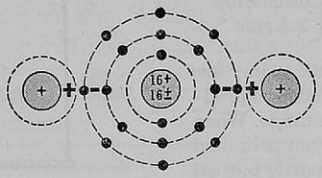
Problem 32

WHAT IS HYDROGEN SULFIDE; HOW CAN YOU USE IT?

Hydrogen sulfide is a gas with a spoiled-egg odor—a compound of sulfur and hydrogen. Your introduction to this compound of hydrogen and sulfur has usually been under circumstances which may have given you a rather distasteful feeling toward it. A whiff of it from the laboratory, or a visit to some sulfur spring may have aroused your curiosity. Hydrogen sulfide (H_2S) is a gas with a characteristic spoiled-egg odor. It is a product of the decomposition of proteins (which contain sulfur) and often may easily be detected in sewer gas.



90. HYDROGEN SULFIDE

The electronic picture of hydrogen sulfide is shown in Fig. 90. Note that each of two hydrogen atoms lends its electron to a sulfur atom thus completing the outer ring of the sulfur atom.

Other characteristics of hydrogen sulfide. Hydrogen sulfide is colorless and very poisonous. It may produce headache and nausea if a small amount is breathed, and in a larger amount it may cause the person breathing it to collapse suddenly. Hydrogen sulfide is slightly heavier than air (34/29 = 1.17), and is moderately soluble in water in which it dissolves to form a weak solution of hydrosulfuric acid.

How to prepare hydrogen sulfide. Hydrogen sulfide is prepared chiefly by the action of hydrochloric acid or sulfuric acid on ferrous (iron) sulfide, which in turn is a compound

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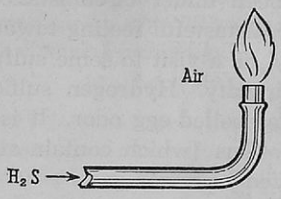
prepared commercially by fusing the elements, iron and sulfur.

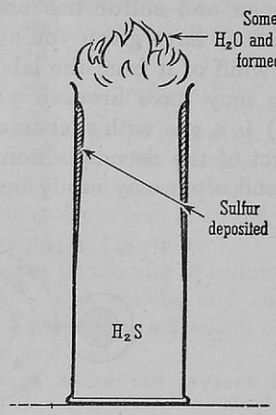
$$FeS + 2\ HCl \rightarrow FeCl_2 + H_2S\uparrow$$

Hydrochloric acid is usually used because the resulting ferrous chloride, being very soluble, is less likely to crystallize than the ferrous sulfate formed when sulfuric acid is used.



91. COMPLETE COMBUSTION OF HYDROGEN SULFIDE

Sulfur dioxide and water are the complete combustion products of hydrogen sulfide. When the supply of oxygen is limited the sulfur is only partly burned by reason of its higher kindling temperature.



92. PARTIAL COMBUSTION OF HYDROGEN SULFIDE

Hydrogen sulfide easily unites with oxygen but the products of oxidation are not always the same. Hydrogen sulfide burns in air or oxygen with a pale bluish flame. When it burns from a jet, as illuminating gas does, the burning gas is surrounded by a large amount of air (Fig. 91), so both the sulfur and hydrogen are oxidized to form water (steam) and sulfur dioxide, as shown by the following equation:

$$2\ H_2S + 3\ O_2 \rightarrow 2\ H_2O + 2\ SO_2$$

The products of oxidation are different, however, when hydrogen sulfide is burned in a small-mouth bottle. The amount of oxygen is limited, since it is available only at the mouth of the bottle. The heat produced by the burning decomposes other molecules of the unstable hydrogen sulfide into sulfur

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and hydrogen. The more combustible hydrogen unites with the small amount of oxygen available, thus leaving a coating of free sulfur on the sides of the bottle. (See Fig. 92.) The equation for this incomplete combustion of hydrogen sulfide is:

$$2\ H_2S + O_2 \rightarrow 2\ H_2O + 2\ S$$

Hydrogen sulfide enables you to identify certain metals. Hydrogen sulfide is used chiefly in laboratory analyses to prove the presence of certain metallic ions. When hydrogen sulfide gas is passed into solutions of the salts of various metals, colored metallic sulfides may be precipitated. The color and solubility of the sulfide make it possible to identify certain metals. The table on this page shows the colors and solubility of several metallic sulfides used in metal analysis.

THE COLOR AND SOLUBILITY OF SEVERAL METALLIC SULFIDES

When you pass hydrogen sulfide into a solution of a salt of an unknown metal,

if the precipitate has this color—↓	*and is soluble (S) or insoluble (I) in:*		*then the precipitate is—↓*	*and the metal is identified as—↓*
	HCl	*HNO_3*		
white	S	S	ZnS	Zinc
bright yellow	I	S	CdS	Cadmium
lemon yellow	I	oxidized	As_2S_3	Arsenic
orange	S (hot)	oxidized	Sb_2S_3	Antimony
black	I	S	CuS	Copper
black	S	I	HgS	Mercury
brown-black	I	S	PbS	Lead

How can you identify hydrogen sulfide? The distinctive colors of many sulfides may be used to prove the presence of hydrogen sulfide, providing the odor is not enough. The most commonly used test is to moisten a piece of filter paper in a solution of lead acetate (or nitrate) and expose this moistened paper to the gas in question. A shiny, brownish black

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coloration (lead sulfide) indicates the presence of hydrogen sulfide.

$$Pb(C_2H_3O_2)_2 + H_2S \rightarrow PbS\downarrow + 2\,HC_2H_3O_2$$

Hydrogen sulfide is often a nuisance—it tarnishes your silverware and often darkens the paint on your houses. Hydrogen sulfide also reacts directly with many metals to form sulfides. This is frequently objectionable as, for instance, when hydrogen sulfide tarnishes silver. The frequent cleaning of silverware in the home is necessary because we burn coal or natural gas in which sulfur is present; because so many of us live in cities where industrial plants are producing hydrogen sulfide; and because sulfur is a constituent of many of our foods, particularly eggs. We often see the action of sulfur upon the paint about our homes when white lead has been used as one of the components of the paint. The action of sulfur on the lead paint produces black lead sulfide. In a locality in which hydrogen sulfide is prevalent, the blackening may be prevented by use of zinc white, lithopone, or titanium paints.

Hydrogen sulfide dissolves in water to form hydrosulfuric acid. A solution of hydrogen sulfide tested with litmus paper, gives definite proof that the solution is acidic by turning the litmus paper red. The formula of this acid, H_2S, is the same as the formula of the gas. The acid is a binary acid. It is called *hydrosulfuric acid.*

Experiment shows that at room temperature and pressure (approximately 20° C. and 760 mm) less than three volumes of hydrogen sulfide gas dissolve in one volume of water; and the percentage of hydrogen ions in the solution is very small. These two facts indicate that we may expect hydrosulfuric acid to be a very weak acid. In the first stage of ionization the molecules break down into H^+ and HS^- ions; with further dilution, S^{--} and more H^+ ions form. Accordingly we have the equations:

$$H_2S \rightleftarrows H^+ + HS^-$$
$$HS^- \rightleftarrows H^+ + S^{--}$$

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

As an acid, hydrosulfuric acid reacts with bases, with metallic oxides, and with metals to form sulfides.

$$2\ NaOH + H_2S \rightarrow Na_2S + 2\ HOH$$
$$Na_2O + H_2S \rightarrow Na_2S + H_2O$$

The solution which we call hydrosulfuric acid plays a very small part in either laboratory or commercial work, since the gaseous hydrogen sulfide is the more efficient and convenient form to use. However, the salts of hydrosulfuric acid form certain important compounds, which on account of their intense colors are used as pigments.

The salts of hydrosulfuric acid are sulfides—many of them are important ores. Among the important sulfides are zinc blende (ZnS), galena (PbS), cinnabar (HgS), and iron pyrites (FeS_2).

The colored sulfides are used to give color to paint. For example, cadmium sulfide is a yellow pigment, zinc sulfide (ZnS) is a white solid sometimes used in paints, and mercury sulfide (HgS) is the brilliant red pigment known as vermilion. The sulfides of arsenic (As_2S_3 and As_2S_5) have been used as pigments since ancient times. Antimony sulfide (Sb_2S_3) is used in making matches and red rubber.

Sulfide ores are common in nature; they are the source of many of our metals. Sulfide ores must be roasted (heated in air). Both the metal and the sulfur are oxidized as illustrated in the roasting of lead sulfide:

$$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$$

Readings for Pleasure and Profit

Foster, William. *The Romance of Chemistry.* Chap. XII, pp. 184–186, "Sulfides."

Applying in Life What You Have Learned in Chemistry

"If your coalbin was empty this winter, it may comfort you to know that in 1306, King Edward I, of England, issued a proclamation making the use of coal as a fuel in London a capital offense.

"One case is on record when an accused was tried, found guilty of burning coal, condemned, and promptly executed.

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"The invisible, gaseous products of the combustion of coal were early pronounced detrimental to health and vegetation. Resentment became intense when ladies of rank, their fair faces made fairer by liberal applications of powder, underwent a curious change of complexion whenever they sat near a coal fire."[1]

What element probably present in the face powder and what element present in the coal may have caused the darkened complexion?

Putting Chemistry to Work

A

(1) If the gas that you use in cooking contained hydrogen sulfide, you would probably be driven out of the kitchen by the formation of another compound of sulfur. Explain. (2) Why are the walls of a chemical laboratory which have been painted with white lead paint likely to darken in a short time? (3) A solution of hydrogen sulfide soon becomes cloudy, then milky, and finally a solid settles out. What is it? Explain how oxygen causes this reaction.

B

(4) Given as starting materials sulfur, hydrochloric acid, and iron, how would you prepare hydrogen sulfide? (5) Refer to the table on page 275 and write equations for the formation of each sulfide, using soluble nitrates, sulfates, or chlorides of the metals. (6) Make a comparison of the useful qualities of hydrogen sulfide with its harmful qualities. How can the harm be prevented? (7) How can you identify an unknown substance as a sulfide?

How Good Are You at Solving Problems?

(1) Compare the weight of hydrogen sulfide with the weight of air. What is the weight of a liter of hydrogen sulfide at standard conditions?

(2) How many liters of hydrogen sulfide can be prepared by the action of hydrochloric acid on 36 grams of ferrous sulfide?

(3) How many liters of water vapor and of sulfur dioxide will be formed by the combustion of 6 liters of hydrogen sulfide?

(4) How many liters of hydrogen sulfide have been oxidized if 100 grams of sulfur are collected from the water leading from a sulfur spring?

(5) Air containing more than 0.02 per cent by volume of hydrogen sulfide is dangerous. Suppose thirty pupils who are preparing

[1] *The Catalyst*, Jan., 1938.

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hydrogen sulfide permit four liters of the gas to escape from each flask generator into a laboratory whose dimensions are $10 \times 8 \times 5$ meters. Assuming that there is no ventilation, calculate the approximate percentage of hydrogen sulfide in the room.

Research and Activities That You Will Enjoy

A safety council: Appoint a committee to draft a set of safety rules for working with hydrogen sulfide. (Send for *Safe Practice, Sheet No. 2,* prepared and distributed by the Chemical Division of the National Safety Council, 20 N. Wacker Drive, Chicago.)

A working model: Construct a Kipp (continuous) hydrogen-sulfide generator. First read about this type of generator and note diagrams of it.

A color chart: Prepare a color chart showing the colors of the various precipitates produced when hydrogen sulfide is passed through solutions of compounds of metals.

A field trip: Is there a sulfur spring near where you live? Visit it, and bring back a sample of the water. Ask your instructor about tests to find whether it contains any sulfur.

Problem 33

HOW IS SULFUR DIOXIDE A USEFUL SERVANT: HOW CAN YOU MAKE IT?

If you were to visit the vicinity of the crater of Mauna Loa on the Hawaiian Islands, the fumes of sulfur dioxide quite likely would distress you for this gas is produced by active volcanoes. The odor of sulfur dioxide also can often be detected near manufacturing plants. Coal usually contains some sulfur and the oxidation of this sulfur produces sulfur dioxide.

What makes some electric refrigerators cool? If you pass gaseous sulfur dioxide into a tube surrounded with a salt and ice mixture (about —10° C.), you soon have a fine sample of liquid sulfur dioxide. Do not expect to keep it very long in an open dish. At room temperature a strong, tightly stoppered bottle is required to keep it from evaporating. A few drops of water put into the liquid sulfur dioxide will freeze

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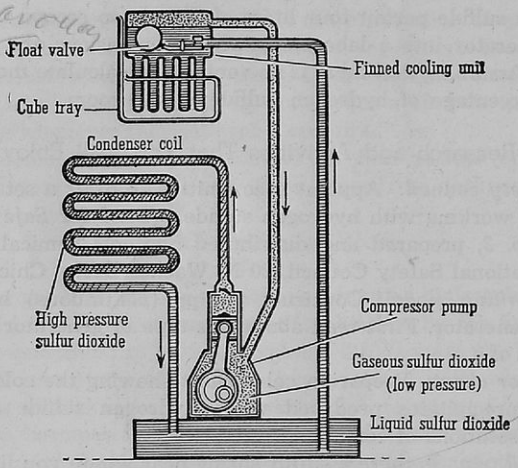
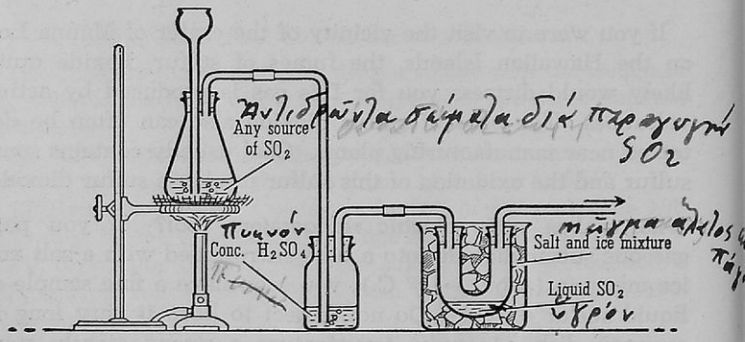


93. SULFUR DIOXIDE IN THE HOME REFRIGERATOR. Sulfur dioxide is easily liquefied. When it vaporizes it absorbs heat. This heat is taken from the refrigerator and its contents. After evaporating, the sulfur dioxide can again be liquefied. Starting at the compressor trace the course of the gas through each step.



94. LIQUEFACTION OF SULFUR DIOXIDE. Sulfur dioxide is an easily liquefied gas. It is liquefied by cooling at ordinary pressure.

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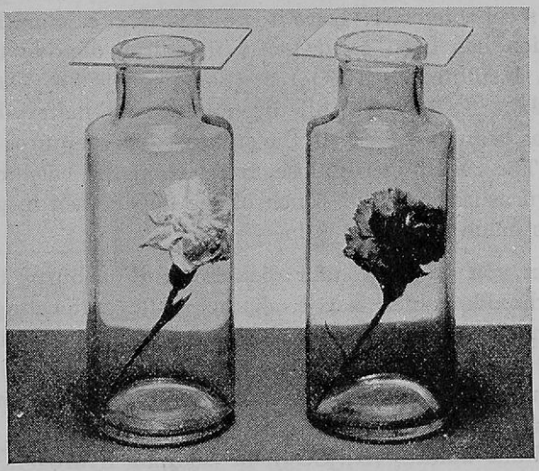
immediately. Can you associate several facts you have learned about evaporation this year and explain how sulfur dioxide may be used to make electric refrigerators cool? (See page 280.)



95. BLEACHING WITH SULFUR DIOXIDE. Two red carnations were placed in these bottles. The bottle on the left contained sulfur dioxide.

What makes your new straw hat white? If you were to investigate why your new straw hat is so white, you very likely would find that sulfur dioxide had been used to bleach it. This bleaching action is due to the fact that sulfur dioxide is a good reducing agent and consequently withdraws oxygen from the compounds that compose the coloring matter in the straw. It is interesting to place a moistened colored flower or apple peeling in sulfur dioxide gas and notice the color gradually fade. (See Fig. 95.) Colorless compounds are thus formed within the flower or apple peeling.

Straw, silk, wool, hair, and paper are often bleached by the reducing action of moist sulfur dioxide, but the bleaching as a rule is not very permanent. Can you tell why a straw hat

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

that is white in June may become brown by September? Why does it remain white under the band?

How was the paper in this book prepared? An important use of sulfur dioxide is the preparation of paper pulp from wood. The wood, usually spruce, is cut to small chips and put into a large steel converter. Here it is mixed with calcium hydroxide which has been saturated with sulfur dioxide to form calcium bisulfite, $Ca(HSO_3)_2$. (See page 520.) The wood is cooked with this until all the noncellulose material in the wood has been dissolved (in the sulfite). This requires several hours. The resulting cellulose, freed from the calcium salts, is known as sulfite pulp. Much of the paper used in printing books is made from this pulp.

How can you prepare sulfur dioxide? Sulfur burns to form sulfur dioxide which has a characteristic suffocating odor. For commercial purposes, much sulfur dioxide is obtained by burning sulfur or roasting sulfide ores. (See page 678.) However, for study in the laboratory, one of the following two methods is more convenient.

1. Sodium sulfite (Na_2SO_3) or sodium hydrogen sulfite ($NaHSO_3$) may be treated with dilute sulfuric acid or dilute hydrochloric acid, in a generator as shown in Fig. 96.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SO_3$$
$$\hookrightarrow H_2O + SO_2\uparrow$$

$$NaHSO_3 + HCl \rightarrow NaCl + H_2SO_3$$
$$\hookrightarrow H_2O + SO_2\uparrow$$

The sulfurous acid (H_2SO_3) thus formed is so unstable that at the temperature of the reaction, it decomposes into sulfur dioxide and water. The sulfur dioxide is collected by air displacement. Is it lighter or heavier than air?

2. Another method sometimes preferred is to reduce concentrated sulfuric acid with copper. Gentle heating of the flask generator is necessary to start the action. It is convenient to think of the concentrated sulfuric acid as giving up a part of its oxygen to the copper to form copper oxide, which

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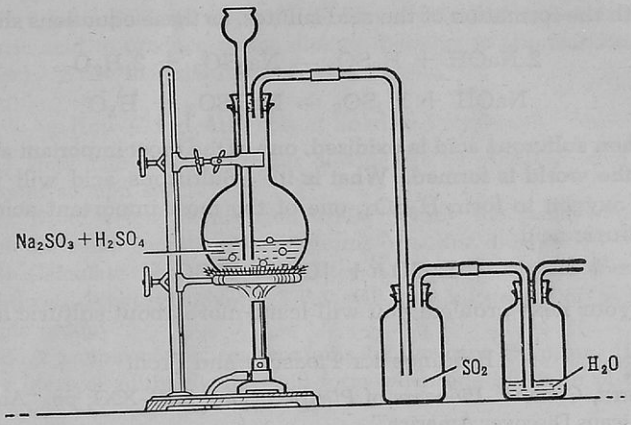

96. LABORATORY PREPARATION OF SULFUR DIOXIDE. The stronger sulfuric acid decomposes and dehydrates the weaker sulfurous acid.

further reacts with sulfuric acid as shown by the following step equations:

First step: $Cu + H_2SO_4 \rightarrow [CuO] + H_2O + SO_2\uparrow$

Second step: $[CuO] + H_2SO_4 \rightarrow CuSO_4 + H_2O$

Final equation: $Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow$

How can you use sulfur dioxide to prepare sulfurous acid? By passing sulfur dioxide gas into water, or by placing water in a bottle of sulfur dioxide and shaking it with the palm of the hand over the mouth of the bottle, you discover that this gas is very soluble. The use of litmus paper convinces you that the solution is acidic, consequently you know that sulfur dioxide is an acidic anhydride. (See page 104.) Its reaction with water indicates that the acid formed is sulfurous acid.

$$H_2O + SO_2 \rightleftarrows H_2\,SO_3$$

Sulfurous acid is unstable, so the reaction is reversible as shown by the double arrow.

This acid neutralizes bases with the formation of normal sulfites, or (in the presence of an excess of sulfurous acid)

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with the formation of the acid sulfites, as these equations show:

$$2\ NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2\ H_2O$$

$$NaOH + H_2SO_3 \rightarrow NaHSO_3 + H_2O$$

When sulfurous acid is oxidized, one of the most important acids in the world is formed. What is it? Sulfurous acid will take on oxygen to form H_2SO_4, one of the most important acids—sulfuric acid.

$$H_2SO_3 + [O] \rightarrow H_2SO_4$$

In your next problem you will learn more about sulfuric acid.

Readings for Pleasure and Profit

BORTH, CHRISTY. *Pioneers of Plenty.* Chaps. XVI-XXI, pp. "Americans Discover America."

Applying in Life What You Have Learned in Chemistry

Henry's mother sent him to the grocery store to get a can of molasses, a bottle of maraschino cherries, and a package of dried apricots. When he returned home, he found on the label of each package a statement that sulfur dioxide had been used in the preparation. Can you tell why sulfur dioxide was used in each case?

Putting Chemistry to Work

A

(1) When moist hydrogen sulfide and sulfur dioxide are mixed, a deposit of sulfur forms. Write the equation for the reaction. What connection do you see with the formation of sulfur around the mouths of volcanoes? (2) Starting with sulfur, oxygen, sodium, and water show by equations how you could prepare sodium sulfite. What is the "by-product" in your preparation? (3) By means of chemical tests how can you distinguish hydrogen chloride, hydrogen sulfide, and sulfur dioxide? (4) Why are the materials which have been bleached with sulfur dioxide sometimes washed with a very dilute solution of a base? (5) When colorless sulfurous acid is added to purple potassium permanganate solution ($KMnO_4$), a colorless solution results. What action do you think occurs?

B

(6) Why is sulfur dioxide called an acidic anhydride? (7) Point out several properties of sulfur dioxide which make it desirable for

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use in a household refrigerator. (8) Zinc reacts with concentrated sulfuric acid to produce sulfur dioxide (similar to the reaction of copper). Write the equation for the reaction.

How Good Are You at Solving Problems?

(1) How many liters of sulfur dioxide can be prepared from 42 grams of sodium sulfite?

(2) What weight of nitrogen would occupy the same volume under the same conditions as 16 grams of sulfur dioxide?

(3) Calculate the weight of one liter of sulfur dioxide at standard conditions. What volume (S.T.P.) will ten kilograms of sulfur dioxide occupy?

(4) A sample of soft coal contains 1.2 per cent of sulfur. How many liters of sulfur dioxide will form when one kilogram of this coal burns?

Research and Activities That You Will Enjoy

A demonstration: Show the class how to liquefy sulfur dioxide in a U-tube surrounded by a freezing mixture of ice and salt or solid carbon dioxide.

A diagram and report: Draw a diagram of a sulfur-dioxide household refrigerator and explain how it operates.

A forum: See how much outside information you can gain on different types of household refrigerators and then discuss with your class the advantages and disadvantages of each type.

Problem 34

MILLIONS OF TONS OF SULFURIC ACID ARE USED EACH YEAR. HOW IS IT USED; HOW IS IT MANUFACTURED?

Many years ago sulfuric acid was called "oil of vitriol" because the concentrated acid is a thick, syrupy, or "oily" liquid which has a "cutting" or biting effect. Pure concentrated sulfuric acid is a colorless liquid with a density of 1.84 (almost twice as heavy as water), but the common commercial acid is dark in color and has a density of about 1.71. The concentrated acid is often referred to as 66° Baumé, while the crude acid is generally about 60° Baumé, an arbitrary scale for

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measuring density of liquids. Sulfuric acid may be diluted with water but remember, when diluting this acid, *always pour the acid into the water* while stirring it. Water poured into concentrated sulfuric acid is quickly changed into steam which may spatter hot acid about, with danger to you or your clothing.

Sulfuric acid is a strong acid; it reacts with bases, metals, metallic oxides, and carbonates to form sulfates. This important acid affects indicators as other acids do and neutralizes bases to form water and salts (in this case, sulfates). Under ordinary conditions sulfuric acid also reacts as a typical acid with bases, metals, metallic oxides, and carbonates.

With bases: $2\,NaOH + H_2SO_4 \rightarrow 2\,HOH + Na_2SO_4$

With metals: $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

With metallic oxides: $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$

With carbonates: $Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$

The reactions reviewed above are possible because sulfuric acid liberates hydrogen ions (H^+). Since sulfuric acid contains two hydrogen ions, it is capable of ionizing in two different ways, as follows:

H_2SO_4 (in water) $\rightleftarrows H^+ + HSO_4^-$ (hydrogen sulfate ion)

$\uparrow\!\!\hookrightarrow H^+ + SO_4^{--}$ (sulfate ion)

This means that when both of the hydrogen ions are replaced by a metal, a *normal salt* such as Na_2SO_4 is formed. If only one hydrogen ion is replaced by sodium, the salt is formed by the combination of the sodium ion (Na^+) and the bisulfate ion (HSO_4^-). The resulting *acid salt* ($NaHSO_4$) is more properly known as sodium hydrogen sulfate. Can you now suggest a formula for potassium hydrogen sulfate? for calcium hydrogen sulfate?

Sulfuric acid may react with certain metals in two different ways. Dilute sulfuric acid and concentrated sulfuric acid react differently. Metals *below hydrogen* in the displacement series do not react with the dilute acid. Metals *above hydrogen* react with *dilute* sulfuric acid to form hydrogen and a *sulfate.*

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Most metals, regardless of their activity, reduce *concentrated* sulfuric acid to form a *sulfate, sulfur dioxide,* and *water.* Can you contrast by means of equations the effect of dilute and concentrated sulfuric acid on such metals as zinc, aluminum, magnesium, copper, and silver?

How you can identify the sulfate ion. In your laboratory work you may have demonstrated the action of barium chloride (or nitrate) on a soluble sulfate to form *insoluble* barium sulfate:

$$(Ba^{++} + 2\,Cl^-) + (2\,H^+ + SO_4^{--}) \rightarrow BaSO_4\downarrow + (2\,H^+ + 2\,Cl^-)$$

The insoluble, un-ionized barium sulfate thus formed is insoluble in hydrochloric acid. This property distinguishes barium sulfate from other insoluble barium salts such as the sulfite, carbonate, or phosphate. These insoluble barium salts dissolve in hydrochloric acid, while barium sulfate remains undissolved. Therefore, to test for the sulfate ion, add a solution of barium chloride and hydrochloric acid. The formation of a white precipitate indicates a sulfate:

$$Ba^{++} + SO_4^{--} \rightarrow \underset{\substack{\text{(insoluble}\\ \text{in HCl)}}}{BaSO_4\downarrow}$$

Sulfuric acid has an affinity for water; it is an excellent dehydrating agent. Concentrated sulfuric acid unites with water "eagerly." For this reason, you can dry gases by passing them through concentrated sulfuric acid—unless they unite chemically with the acid, as ammonia does. You have already learned that when sugar ($C_{12}H_{22}O_{11}$) is heated strongly, its hydrogen and oxygen are given off as water, and carbon (charcoal) remains. If, instead of heating the sugar, you place concentrated sulfuric acid with it, you find that a mass of carbon is formed. The sulfuric acid absorbs the elements hydrogen and oxygen as water.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{concentrated } H_2SO_4} 12\,C + 11\,H_2O$$

Other organic compounds, such as cellulose ($C_6H_{10}O_5$) in wood or paper, starch ($C_6H_{10}O_5$), and other kinds of sugars

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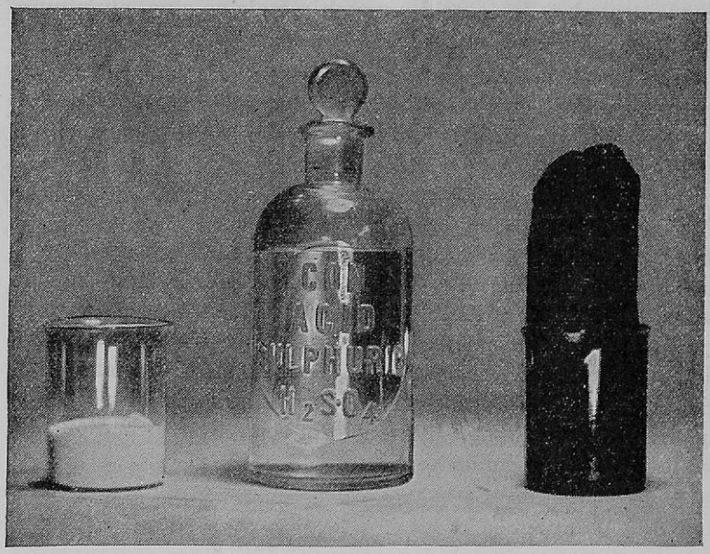
($C_6H_{12}O_6$) are charred in a similar manner when brought into the presence of concentrated sulfuric acid.



97. SULFURIC ACID AS A DEHYDRATING AGENT. Concentrated sulfuric acid removes the elements of water from a carbohydrate, leaving uncombined carbon. The carbohydrate shown here is sugar. This illustrates the great tendency of sulfuric acid to absorb water. Consequently sulfuric acid is often used to dry gases or to keep the air dry in balance cases. The water combines with the acid to form a hydrate.

Sulfuric acid is used in the preparation of hydrochloric acid and other acids. Compared with other acids, concentrated sulfuric acid has a high boiling point, about 338° C. When it is heated with a salt of another acid, a double decomposition reaction occurs in which the other acid is formed. By taking advantage of their lower boiling points, the acids which are formed in this manner are separated from any by-product by distillation; they boil off easily from the mixture. The common acids of commerce are usually prepared in this way. The following

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equations represent typical reactions which may be carried out in the laboratory:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3\uparrow$$

However, with more heat and an excess of salt, an additional quantity of the acid can be produced. These reactions are carried out mainly in commercial operations in large furnaces:

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl\uparrow$$

The addition of sulfuric acid to an unknown salt may indicate the negative ion that is present in the salt. Thus it is possible to detect a chloride, a sulfide, or an acetate by the odor of the corresponding acid which is released as a gas.

$$2\ NaC_2H_3O_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HC_2H_3O_2$$

Sulfuric acid surrenders part of its oxygen and is therefore an oxidizing agent. When concentrated sulfuric acid is heated alone, it decomposes into sulfur trioxide and water:

$$H_2SO_4 \rightarrow H_2O + SO_3$$

The sulfur trioxide is released as dense, white, and very suffocating fumes. An oxidizing agent already has been defined as a substance willing to part with its oxygen, providing some other element or compound (a reducing agent) withdraws the oxygen and combines with it. In the case of concentrated sulfuric acid, each molecule of the acid (H_2SO_4) is willing to part with one atom of oxygen. This leaves sulfurous acid (H_2SO_3) which, being unstable, breaks down into sulfur dioxide and water. Thus you have the equation:

$$H_2SO_4 \rightarrow H_2SO_3 + [O] \text{ or}$$

$$H_2SO_4 \rightarrow H_2O + SO_2\uparrow + [O]$$

The oxygen which is very active in its atomic form will combine readily with any reducing substance which is present, as for example with copper:

$$Cu + [O] \rightarrow CuO$$

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

You know that metal oxides, such as CuO, react with acids to form water and salts. In this case, a molecule of sulfuric acid now acts as a typical acid, according to the equation:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

The step reaction is thus complete, and bringing the steps together and canceling out formulas of those substances which appear on opposite sides of the reactions, you have:

$$H_2SO_4 \rightarrow H_2O + SO_2 + \cancel{[O]}$$
$$Cu + \cancel{[O]} \rightarrow \cancel{CuO}$$
$$\cancel{CuO} + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

Final equation: $Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + 2\ H_2O + SO_2\uparrow$

If the reducing agent is a nonmetal, such as carbon, the equations by steps will become:

$$H_2SO_4 \rightarrow H_2O + SO_2\uparrow + [O]$$

Now the carbon will combine with the oxygen, but since two atoms of oxygen are required to form one molecule of carbon dioxide, two molecules of sulfuric acid are necessary to furnish these two atoms of oxygen, thus:

$$2\ H_2SO_4 \rightarrow 2\ H_2O + 2\ SO_2\uparrow + 2\ \cancel{[O]}$$
$$C + 2\ \cancel{[O]} \rightarrow CO_2\uparrow$$

Since carbon dioxide is a gas, it will leave the receptacle so no further reaction is possible. You have the final equation:

$$C + 2\ H_2SO_4 \rightarrow 2\ H_2O + 2\ SO_2\uparrow + CO_2\uparrow$$

Tons of sulfuric acid are used in industry to furnish you with a great variety of products. More than 8 million tons of sulfuric acid have been manufactured and used in the United States in a single year. If we compare the tonnage of sulfuric acid used in the United States during the last fifty years with the rise and fall in the nation's business during that period, we find that sulfuric acid has earned the right to be called "a barometer of the nation's business."

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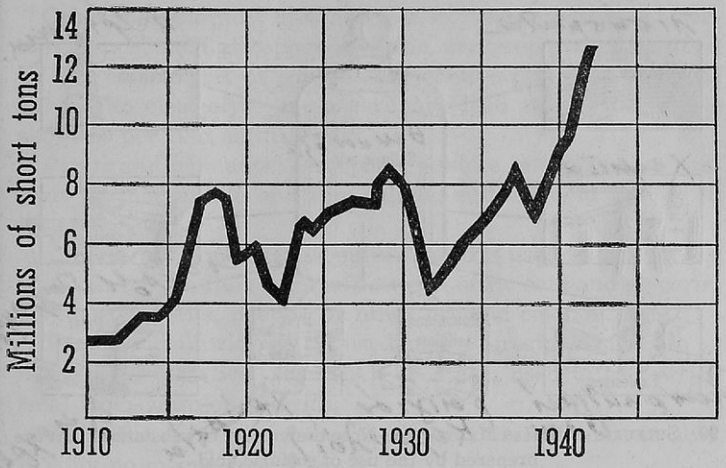

98. PRODUCTION OF SULFURIC ACID IN THE UNITED STATES

Some of the most important uses of sulfuric acid are listed as follows:

Sulfuric acid helps plants to produce more food for you—the manufacture of fertilizers. Sulfuric acid reacts with by-product ammonia (from coke plants) to form ammonium sulfate, a substance used as a fertilizer. With insoluble calcium phosphate, sulfuric acid forms soluble calcium hydrogen phosphate which is also used as a fertilizer. (See page 599.) In 1937 approximately 29 per cent of the sulfuric acid produced in the United States was used in the manufacture of fertilizers. (See Fig. 100.)

Sulfuric acid helps produce gasoline to run your car. Originally all gasolines were washed with concentrated sulfuric acid to remove objectionable colors and to produce clear, noncorrosive gasoline. More recently this method is applied only to gasoline produced by the cracking process. (See page 465.) Fig. 100 shows the percentage of sulfuric acid produced in the United States in 1937 that was used in the refining of petroleum.

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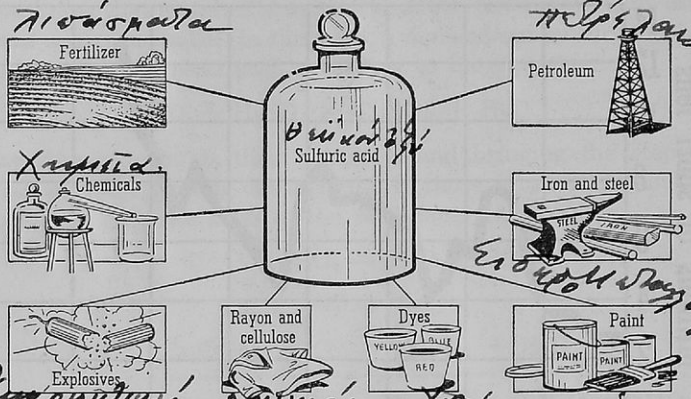
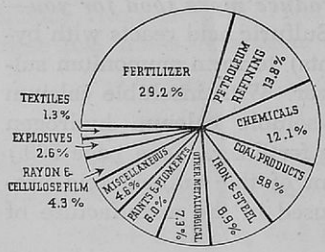


99. SULFURIC ACID HAS MANY USES. Note the variety of substances that are prepared by the use of sulfuric acid.

Sulfuric acid was used to manufacture many of the chemicals on your laboratory shelves. Hydrochloric acid and nitric acid are made from the corresponding sodium salts reacting with sulfuric acid. Sulfates of many of the metals, such as aluminum sulfate (clay + H_2SO_4), copper sulfate (Cu + H_2SO_4), and ferrous sulfate (Fe + H_2SO_4 or iron rust + H_2SO_4) are also made.



100. USES OF SULFURIC ACID

Sulfuric acid has many other uses. Manufacture of dyes and drugs. Dyes and drugs come mainly from coal tar and its products. Sulfuric acid is required in their preparation, often as a dehydrating agent. Concentrated sulfuric acid is used as a dehydrating agent in the preparation of many other organic chemicals.

Iron and steel manufacture. Before coating steel or iron with zinc (galvanizing), tin, or enamel, the steel (or iron) is dipped into a "pickling" bath of acid to free the metal of scale and iron rust.

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Other metallurgical uses and use in storage batteries. Certain metals, such as copper and zinc, are prepared or purified by the electrolysis of solutions of their sulfates. (See page 681.) The electrolyte in the ordinary lead storage battery is about 20 per cent sulfuric acid.

Paints and pigments. Lithopone, a white interior paint, contains barium sulfate and zinc sulfide; sulfuric acid is used in its preparation.

Explosives. Concentrated sulfuric acid is used to take up the water formed in the reactions between nitric acid and glycerin, cellulose, toluene, phenol, or other organic compounds.

Textiles. Sulfuric acid is used in the precipitating bath in making rayon. (See page 569.) It is also used in recovering wool from worn-out fabrics.

While the above list shows the largest uses of sulfuric acid, it is by no means complete.

HOW IS SULFURIC ACID MANUFACTURED?

Although nature has provided large deposits of sulfates, such as calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), sodium sulfate (Na_2SO_4), and others, man has found no cheap acid to release the sulfate ion. He usually starts with free sulfur for the preparation of sulfuric acid.

The essential reaction upon which the production of sulfuric acid is based is the oxidation of the free sulfur, first to sulfur dioxide,

$$\overset{0}{S} + \overset{0}{O_2} \rightarrow \overset{+4-2}{SO_2}$$

and then the further oxidation of the sulfur dioxide to sulfur trioxide:

$$2\ \overset{+4-2}{SO_2} + \overset{0}{O_2} \rightarrow 2\ \overset{+6-2}{SO_3}$$

Sulfur trioxide is the acid anhydride of sulfuric acid. Sulfur

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

trioxide, therefore, unites with water under suitable conditions to form the acid.

Two important industrial methods have been developed for the manufacture of sulfuric acid. They are the lead chamber process and the contact process. The chief difference in the two processes lies in the manner of effecting the oxidation of SO_2 to SO_3. In the older lead chamber process the oxides of nitrogen are used to oxidize SO_2 to SO_3. In the newer contact process platinum or vanadium pentoxide are the catalysts commonly used to promote the direct union of sulfur dioxide and oxygen.

Dilute and impure sulfuric acid is manufactured by the lead chamber process. Note the diagram of this process (Fig. 101) to get a general idea of its mechanical features. Sulfur is burned in the burners forming sulfur dioxide. The hot sulfur dioxide, mixed with air (nitrogen and oxygen), passes upward through the Glover tower which is filled with loose brick or tile. Oxides of nitrogen also are introduced into the tower. This mixture of gases (SO_2, O_2, N_2, NO, and NO_2) passes from the Glover tower into the first lead-lined chamber where steam or atomized water is admitted. The following equations represent in simple form the changes which take place:

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

The sulfuric acid falls to the bottom of the lead chamber as a heavy mist. The process requires an excess of water and as a result the acid formed is dilute. The lead walls of the chamber are only slightly attacked by dilute sulfuric acid since whatever lead sulfate is formed on the walls acts as a protective coating much as paint does on a metal or wooden surface.

The gases which do not react in the first chamber pass through other chambers until all the SO_2 is used up. The number of chambers usually is from three to five. Finally,

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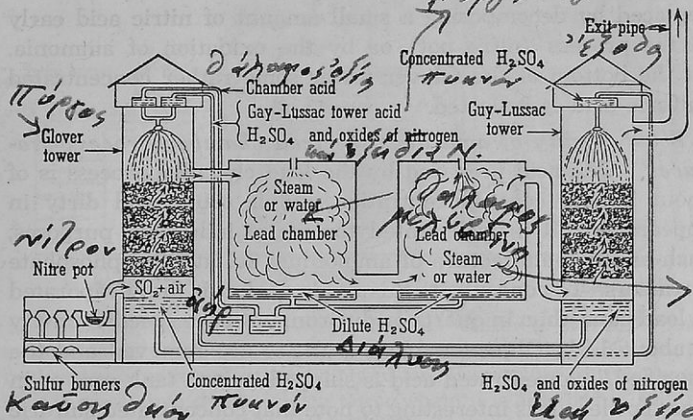


101. SULFURIC ACID BY THE CHAMBER PROCESS. Sulfur is burned to form sulfur dioxide. This is mixed with steam, an excess of air, and oxides of nitrogen in the lead chambers. Here sulfuric acid forms and condenses in the lead chambers. The oxides of nitrogen and the nitrogen of the air pass into the Gay-Lussac tower. Here a descending spray of sulfuric acid absorbs the oxides of nitrogen and the nitrogen passes out of the stack. The sulfuric acid containing the dissolved catalyst is brought to the top of the Glover tower and sprayed over the packing in it. Here it meets the hot gas from the sulfur burner which sets the catalyst free, where it can reenter the lead chambers. Trace the course of the gases through the system.

the remaining gases (nitrogen and oxides of nitrogen) pass into the Gay-Lussac tower. This is similar in construction to the Glover tower. Here cold concentrated sulfuric acid drips in from the top and dissolves the oxides of nitrogen. This solution is conveyed to the top of the Glover tower where it is diluted with water and sprayed over the brick with which the tower is filled. As the solution falls toward the bottom it meets the ascending current of hot gases as they enter the tower. Under these conditions the oxides of nitrogen are set free from the sulfuric acid solution and are ready to pass once more through the lead chambers and oxidize more SO_2 to SO_3. In this way the oxides of nitrogen are used over and over again, greatly decreasing the cost of the process. Usually there is a small loss of the oxides of nitrogen; these are

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

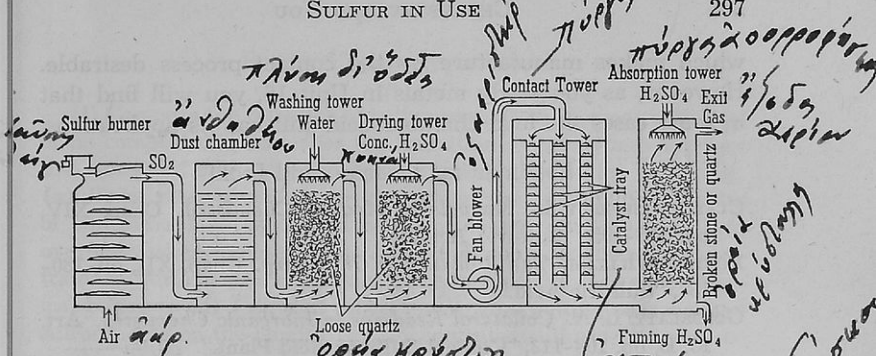
replaced by decomposing a small amount of nitric acid early in the process (nitre pot) or by the oxidation of ammonia. At the bottom of the Glover tower some rather concentrated sulfuric acid is collected.

What quality of acid does the lead chamber process produce? The acid prepared by the lead chamber process is of about 70 per cent concentration and is crude and dirty in appearance. It is well suited for many industrial purposes, such as the manufacture of ammonium sulfate and phosphate fertilizers. To concentrate this crude acid, it is first evaporated in lead pans, then in quartz or duriron, until the specific gravity is about 1.84. Objectionable impurities are removed and the "purified," concentrated acid is shipped in iron tank cars or in glass bottles. It is interesting to note that concentrated sulfuric acid will not dissolve iron, due to the fact that the iron sulfate coating which forms on the surface of the iron, acts as a protective "paint" and is not soluble in the concentrated acid.

Pure concentrated sulfuric acid is manufactured by the contact process. The lead chamber process calls for such large equipment, requires the recovery of such vast quantities of gas (oxides of nitrogen), and produces such a crude acid of low concentration, that a more direct method was sought. Just before 1900 the use of catalysts began to solve many of the chemist's problems, and experimentation showed that platinum, though expensive, was a very satisfactory catalyst for the oxidation of sulfur dioxide. The catalyst is prepared by soaking asbestos fibers in chloroplatinic acid (H_2PtCl_6) and heating the compound until it is decomposed thus leaving a deposit of finely divided platinum on the fibers. Silica gel may be used to support the platinum.

In the contact process (Fig. 102), sulfur is first burned just as it is in the chamber process, and the sulfur dioxide and air (oxygen and nitrogen) are passed through a dust collector to remove objectionable solid particles. These gases are then cooled and passed through a series of scrubbers which thoroughly rid them of impurities, especially arsenic. This is necessary because a platinum catalyst is very easily "poisoned"

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



102. SULFURIC ACID BY THE CONTACT PROCESS. Sulfur is burned to form sulfur dioxide. It is purified and dried and passed over the catalyst in the contact tower with a plentiful supply of air. Here sulfur trioxide forms. This is passed into the absorption tower where it is absorbed in sulfuric acid to form fuming sulfuric acid. This is diluted to form concentrated sulfuric acid.

and rendered ineffective. The gases are then heated and passed through contact chambers, in which sulfur dioxide is brought in intimate contact with the oxygen at a suitable temperature (400° C.) in the presence of the platinum catalyst. The resulting sulfur trioxide is then passed into some sulfuric acid of at least 98 per cent concentration. This concentration may be maintained by adding water as fast as sulfur trioxide is absorbed. If, however, no water is added as SO_3 is absorbed, the sulfuric acid may go beyond 100 per cent in its concentration forming "fuming" sulfuric acid, a substance which may be represented by the formula $H_2SO_4 \cdot SO_3$.

Recently it has been found that vanadium pentoxide is an effective catalyst for the contact process. It is now extensively used since it is less expensive and less easily poisoned than platinum.

The acid produced by this process is both pure and concentrated, requiring no further treatment before use. The equipment for the process requires less ground space, and to some extent is replacing the older chamber process as companies find they must renew equipment. Some of the later uses for sulfuric acid require a pure and more concentrated acid,

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

which makes manufacture by the contact process desirable. However, as you study metals in Unit 16, you will find that in some cases the lead chamber acid still has its applications.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XIV, pp. 188-195, "Sulfuric Acid."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XII, pp. 180-184, "Sulfuric Acid."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 15, B, pp. 108-112, "Contact Sulfuric Acid Plant."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. IV, pp. 107-175, "Sulfuric Acid."

Applying in Life What You Have Learned in Chemistry

Someone has said, "You can measure the degree of civilization by the amount of sulfuric acid that is consumed."

Says Ted, "Our family can't be very civilized, for I don't know when we have ever bought any sulfuric acid!"

Was Ted right? Explain.

Do the variations in the production curve for sulfuric acid (Fig. 98) justify its use as a "barometer" of business?

Disastrous results might occur if you used concentrated sulfuric acid, thinking that it was dilute. How can you determine if the sulfuric acid in a bottle is concentrated or dilute without consulting the label?

Even careful laboratory workers may get a spot of sulfuric acid on clothing. How and why is the clothing affected? If you spilled some dilute sulfuric acid on your clothes, what remedy would you apply?

You are a manufacturer of fertilizers. Will you likely use "chamber" acid or "contact" acid? Why?

Would you buy stock in a chemical concern which plans to make sulfuric acid from the huge deposits of naturally occurring sulfates? Many persons have become wealthy by taking chances in "impossible" processes. Remember Frasch. Explain.

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Putting Chemistry to Work

A

(1) Compare the quantity of sulfur used as an element with that of its compounds. How does the formation of compounds increase the service of sulfur to man? (2) Explain each of the following: (a) Black rings often appear on wooden shelves that hold bottles of sulfuric acid. (b) A full bottle of concentrated sulfuric acid overflows when exposed to air. (c) A beaker containing concentrated sulfuric acid is sometimes placed inside the case of a chemical balance. (d) Frightful burns result from getting concentrated sulfuric acid on the hands. (e) Concentrated sulfuric acid may be used in a desiccator instead of anhydrous calcium chloride. (3) How would you distinguish between a sulfite, a sulfate, and a sulfide? (4) Why is a white powder obtained, when a blue crystal of copper sulfate is left standing in concentrated sulfuric acid? (5) Research is making possible the purification of petroleum and the manufacture of phosphate fertilizers without the use of sulfuric acid. What effect may this have upon the sulfur industry?

B

(6) Explain how sulfurous acid (H_2SO_3) acts as a *reducing* agent while concentrated sulfuric acid (H_2SO_4) can act as an *oxidizing* agent. (7) In what way does the preparation of sulfuric acid differ from that of hydrochloric acid? Explain in detail the reason for this. (8) Write the ionic equation for the test for a sulfate. If you wish to precipitate all the barium ions from a solution, why do you add a slight excess of sulfuric acid? (9) Why does the behavior of hot concentrated sulfuric acid with metals differ from that of the dilute acid? (10) Write equations (if reactions occur) for the action of zinc, aluminum, copper, and silver on dilute sulfuric acid. (11) Write step equations for the action of silver on concentrated sulfuric acid. (12) Compare the action of dilute and concentrated sulfuric acid on iron. (13) Why must the temperature in the contact process be controlled?

How Good Are You at Solving Problems?

(1) How many grams of potassium hydroxide are necessary to neutralize 196 grams of sulfuric acid? How many grams of potassium sulfate will be formed?

(2) How many liters of sulfur dioxide (S.T.P) are released when aluminum reacts with 19.6 grams of concentrated sulfuric acid?

(3) How many tons of sulfuric acid can be made from one ton

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of sulfur which is 99 per cent pure? (Assume an 80 per cent yield.)

(4) The sulfur in a 10-gram sample of coal was oxidized and precipitated as 1.24 grams of dry barium sulfate. What is the percentage of sulfur in the coal?

(5) Two samples of zinc, each weighing 6.5 grams, are weighed out. One sample reacts with concentrated sulfuric acid, the other with dilute sulfuric acid. Determine the weight of zinc sulfate formed in each case. Also compare the number of liters of the gaseous products formed in each case.

Research and Activities That You Will Enjoy

A model: Plan and build a working flask model to demonstrate how sulfuric acid is prepared either by the contact process or by the chamber process. (Consult: Fowles, *Lecture Experiments in Chemistry* for excellent ideas.)

A guest speaker: Invite an industrial chemist to discuss briefly with your class the importance of sulfuric acid in industry or interview him and write for the class a summary of what he tells you.

A diagrammatic chart: Prepare a chart on the chamber process for manufacturing sulfuric acid and explain it to the class.

Problem 35

HOW CAN A STUDY OF SULFURIC ACID ENLARGE YOUR IDEA OF OXIDATION-REDUCTION REACTIONS?

Many times in recent units you have seen that reactions involving oxidation and reduction are important and useful ones. You have seen that all forms of ordinary burning are oxidation and that many metals are obtained from their ores by reduction. Thus far the terms, oxidation and reduction, have been used in a rather limited sense as the addition or withdrawal of oxygen. Let us now see how this idea of oxidation-reduction can be enlarged so as to include some of the other elements.

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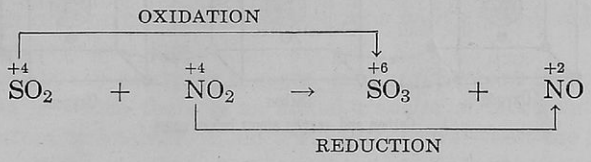
How does the valence of an element change when it is oxidized? when it is reduced? In the lead chamber process for manufacturing sulfuric acid (page 294), the essential reaction may be written simply as:



The sulfur dioxide is oxidized to sulfur trioxide while the nitrogen dioxide is reduced to nitric oxide. The valence changes are also noticeable here. The *oxidation* of sulfur dioxide is accompanied by an *increase in valence* of sulfur from +4 in SO_2 to +6 in SO_3. The *reduction* of nitrogen dioxide is brought about by a *decrease in valence* of nitrogen from +4 in NO_2 to +2 in NO. This idea of oxidation as an increase in valence and of reduction as a decrease in valence is no doubt a new one for you. Consequently, note how it may be applied to other similar reactions.

In your earlier experimental work magnesium burned in air (oxygen) and iron combined with sulfur with a show of much heat and light. Likewise antimony burns in chlorine. The equations are:

$$2\,\overset{0}{\mathrm{Mg}} + \overset{0}{\mathrm{O_2}} \rightarrow 2\,\overset{+2-2}{\mathrm{MgO}}$$

$$\overset{0}{\mathrm{Fe}} + \overset{0}{\mathrm{S}} \rightarrow \overset{+2-2}{\mathrm{FeS}}$$

$$2\,\overset{0}{\mathrm{Sb}} + 3\,\overset{0}{\mathrm{Cl_2}} \rightarrow 2\,\overset{+3-1}{\mathrm{SbCl_3}}$$

Here we are interested to see that these three similar combination reactions are all oxidation-reduction reactions. The valence of the metal in each case has increased. (Remember that the valence of an uncombined element is zero.) Thus *each metal has been oxidized* although only the first (Mg) united with oxygen. Sulfur and chlorine are oxidizing agents

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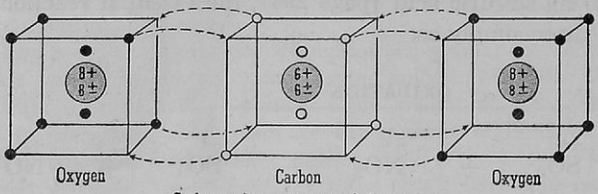
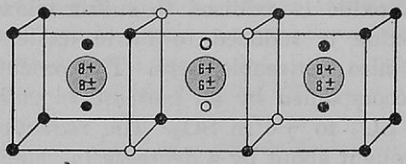
just as truly as oxygen is an oxidizing agent. Likewise, each nonmetal has been reduced, since its valence decreased.



Carbon and oxygen atoms before union



A molecule of carbon dioxide

103. CUBIC DIAGRAM OF THE OXIDATION OF CARBON

When an element is oxidized, what happens to its electrons? When carbon is oxidized to form carbon dioxide, one atom of carbon unites with two atoms of oxygen to form one molecule of carbon dioxide. We believe that this chemical reaction is produced by some sort of shift between the electrons in the outer shells of these three atoms. Figure 103 is a diagram by means of which we may explain what happens to these electrons. Notice that oxygen, before the reaction takes place, has six electrons in its outer shell, and needs two more to complete this shell. The carbon atom has four electrons in its outer shell. (For convenience in identification we represent the electrons in carbon as circles and the electrons in oxygen as black dots. Is there any actual difference between the electrons in carbon and those in oxygen?)

When carbon burns in oxygen we believe that each carbon atom shares its outer electrons with the two atoms of oxygen, as shown diagrammatically in the figure. Since these four electrons which came from the atom of carbon now belong *in part*

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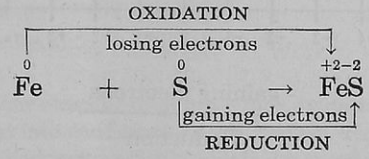
to the oxygen atoms, we may think of the carbon atom as having lost electrons. Since all electrons are negative, we conclude that the atom of carbon in carbon dioxide is more positive than before the union. So we say that carbon in carbon dioxide has a valence of +4, although we must remember that in this case carbon *shares* its electrons with oxygen and does not entirely lose them.

The shift of electrons is more easily understood if we take a case in which there is an actual transfer of electrons from one atom to another. Such a change occurs when the metal lithium burns in the active gas fluorine. This change, which is similar to burning carbon in oxygen, is represented in Fig. 61, in which we see that an atom of lithium gives up its one outer electron thus completing the outer shell of the atom of fluorine. Lithium is oxidized although there is no oxygen involved in the process. Consequently, we may say that when an element is oxidized, it loses electrons either by giving them up entirely or by sharing them with other atoms.

Notice again the three equations on page 301. You can see that each metal is oxidized because it loses electrons either by sharing them or by giving them up entirely. When magnesium combines with oxygen, each atom of magnesium loses two electrons (by sharing), while each atom of oxygen gains two electrons. In the second reaction each atom of iron loses two electrons, each atom of sulfur gains two. When antimony and chlorine unite, each atom of antimony loses three electrons and each atom of chlorine gains one electron. The metals are oxidized; they lose electrons. We conclude, then, that *oxidization is the loss of electrons.* Similarly, the nonmetals are reduced; they gain electrons. *Reduction is the gain of electrons.*



The preceding equation illustrates oxidation and reduction.

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What is an enlarged conception of oxidation? of reduction? *Oxidation* is a chemical reaction in which an element loses electrons (e) and thus increases in (positive) valence. In its simplest form the above oxidation reaction becomes:

$$\overset{0}{\text{Fe}} - 2\ e \rightarrow \overset{++}{\text{Fe}}$$

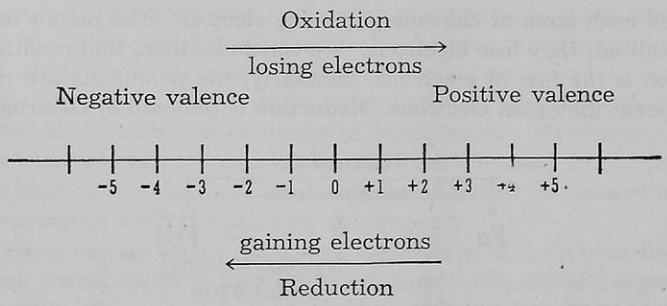
Reduction is a chemical reaction in which an element gains electrons and thereby decreases in valence.

$$\overset{0}{\text{S}} + 2\ e \rightarrow \overset{--}{\text{S}}$$

Oxidation and reduction always take place together.

The following diagram shows clearly how oxidation-reduction reactions are related to loss-gain of electrons and to valence changes.

Oxidation of an element means—↓	*Reduction of an element means—↓*
1. The element loses electrons.	1. The element gains electrons.
2. The valence of the element is raised or increased.	2. The valence of the element is lowered or decreased.
3. The substance before its oxidation was a reducing agent.	3. The substance before its reduction was an oxidizing agent.



104. OXIDATION AND REDUCTION

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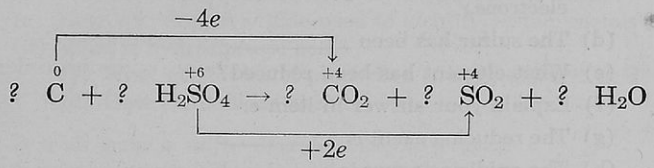
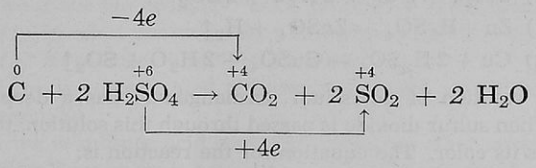
In every oxidation-reduction reaction the loss in electrons by one substance equals the gain in electrons by the other substance; likewise the gain in valence of one substance must equal the loss in valence of the other.

How can you use electron transference to balance equations for oxidation-reduction reactions? When carbon and hot concentrated sulfuric acid react, carbon dioxide, sulfur dioxide, and water are formed. This oxidation-reduction reaction can be expressed with the *unbalanced* equation thus:



Here the carbon atom loses (shares) four electrons, while the sulfur atom gains only two electrons. Since *the loss and the gain of electrons must be the same,* two atoms of sulfur are needed. This means that two molecules of sulfuric acid are needed and that two molecules of sulfur dioxide and two molecules of water are formed. The balanced equation becomes:



Try to balance the reaction between copper and concentrated sulfuric acid by a similar method.

Putting Chemistry to Work

A

(1) Why must an element undergo either oxidation or reduction when it is brought into combination? (2) Explain why oxidation and reduction are studied together. (3) Explain, by the electron exchange method, the formation of sulfuric acid.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

B

(4) Sulfur, with its common valences of −2, +4, and +6, offers a good opportunity to illustrate oxidation and reduction in reactions.

In the following correctly balanced equation answer these questions.

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S$$

(a) Valence of sulfur in H_2S.

(b) Valence of free sulfur.

(c) Sulfur has (lost, gained) _____(how many?) electrons.

(d) The sulfur has been _____.

(e) What element has been reduced?

(f) Explain your answer in item *e*.

(g) The reducing agent is _____.

(h) The oxidizing agent is _____.

(5) Follow the same procedure as given in item 4 in each of the following:

(a) $S + O_2 \rightarrow SO_2$

(b) $H_2 + CuO \rightarrow Cu + H_2O$

(c) $2\,SO_2 + O_2 \rightarrow 2\,SO_3$

(d) $Na_2SO_4 + 2\,C \rightarrow Na_2S + 2\,CO_2$

(e) $2\,H_2S + 3\,O_2 \rightarrow 2\,H_2O + 2\,SO_2$

(f) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

(g) $Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow$

(6) A solution of potassium permanganate has a deep purple color. When sulfur dioxide is passed through this solution, the solution loses its color. The equation for the reaction is:

$$2\,KMnO_4 + 5\,SO_2 + 5\,H_2O \rightarrow K_2SO_4 + 2\,H_2SO_4 + 3\,H_2O + 2\,MnSO_4$$

Explain how the sulfur dioxide is acting as a reducing agent and how both reduction and oxidation are taking place together.

Looking Back into Unit 7

Be sure you know the purpose of this unit. Read again the material on page 262, "Looking Ahead into Unit 7." Then study the following Summary Test.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Summary Test

1. *How is sulfur obtained and used?*
   (a) How is sulfur obtained and purified in other countries?
   (b) How is American sulfur produced?
   (c) What are important uses for elementary sulfur?
   (d) What are the chief differences in the allotropes of sulfur?
   (e) What chemical properties make sulfur useful?

2. *What is hydrogen sulfide; how is it used?*
   (a) What are the sources of hydrogen sulfide?
   (b) What are the products when hydrogen sulfide burns?
   (c) How is hydrogen sulfide used to identify certain metals?
   (d) What is hydrosulfuric acid?
      (1) What are the chief properties of hydrosulfuric acid?
      (2) How are sulfides useful?

3. *In what ways is sulfur dioxide a useful servant?*
   (a) How is sulfur dioxide useful—
      (1) In an electric refrigerator?
      (2) In bleaching?
      (3) In making paper?
   (b) How can you prepare sulfur dioxide?
   (c) How is sulfur dioxide related to sulfurous acid and to sulfites?

4. *How is sulfuric acid used and made?*
   (a) What are the ordinary "acid" properties of sulfuric acid?
      (1) In what two ways does sulfuric acid react with metals?
      (2) How can you test for a sulfate?
   (b) How is concentrated sulfuric acid useful as a dehydrating agent?
   (c) How is sulfuric acid useful in preparing other acids?
   (d) How does sulfuric acid act as an oxidizing agent?
   (e) In what ways is sulfuric acid useful in industry?
   (f) How is sulfuric acid made—
      (1) In the chamber process?
      (2) In the contact process?

5. *How have you enlarged your ideas of oxidation-reduction reactions?*
   (a) How does the valence of an element change when it is oxidized? when it is reduced?

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(b) When an element is oxidized what happens to its electrons?
(c) What is your enlarged conception of oxidation and of reduction?
(d) How can you use electron transference to balance equations for oxidation-reduction reactions?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

Sulfur is *valuable* in *industry* and *agriculture.* Chemically it is oxygen's nearest relative. Fortunately sulfur is *plentiful* and widely *distributed.*

To the average person, there are no outward indications of why *sulfur* and *sulfuric acid* should be *"barometers of business."* However, the person with a knowledge of chemistry knows that sulfur and sulfur compounds fill a very important place in the industrial world.

After studying this unit, you should have an appreciation of the importance of sulfur in the manufacture of *rubber products* and in *spray materials* for plant diseases and insects. You, no doubt, do not like the odor of *hydrogen sulfide,* but you should see its value in *metal analysis. Sulfur dioxide* is offensive, but it *bleaches* goods including straw goods; it is sometimes used as a *refrigerant;* and tons of it are *oxidized* and combined with *water* to form the most important acid of commerce—*sulfuric acid.*

You find that *sulfuric acid* has some very important uses that depend on definite *properties* of the acid. So as an acid, it is used to prepare the *fertilizers* ammonium sulfate and calcium superphosphate, to clean metal (steel) surfaces for *galvanizing* and *tinning,* and to make many common laboratory and commercial *chemicals.* As a *dehydrating agent,* the concentrated acid is used to remove *water* in the manufacture of *dyes, explosives,* and in *petroleum refining.* And as an acid of *high boiling point,* it is used to prepare other *acids* such as nitric acid and hydrochloric acid.

You also learn of the excellent *oxidizing* properties of *concentrated sulfuric acid.* This leads you into a new conception of *oxidation and reduction*—in which the explanation is based on loss and gain of electrons or the increase or decrease in *valence.*

Yes! With your study in this unit on *sulfur* you are brought

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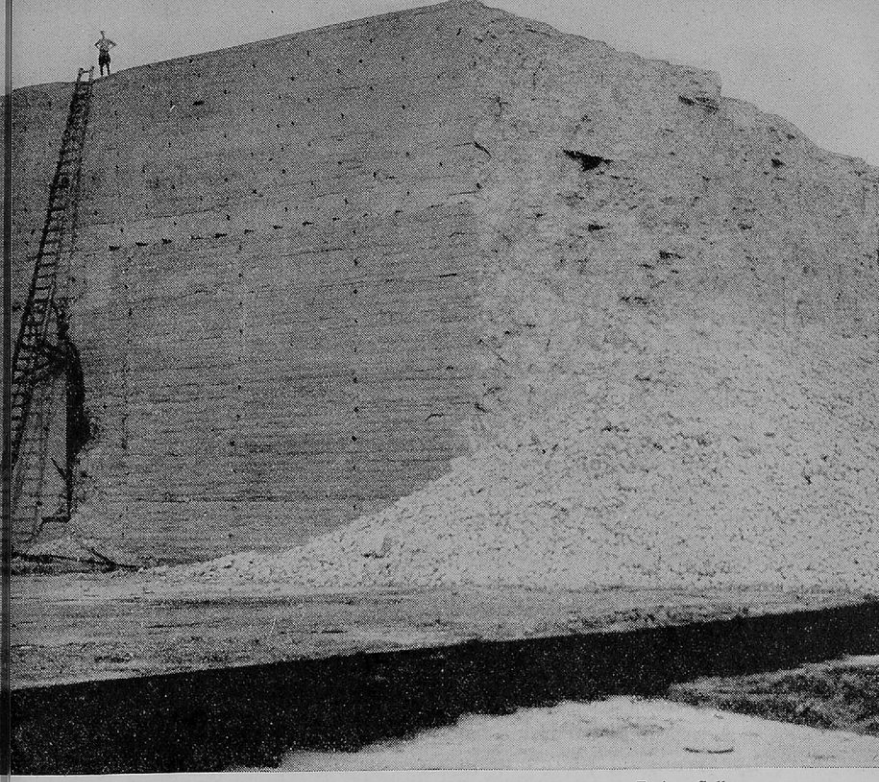

Ewing Galloway

SULFUR STORAGE. Sulfur, oxygen, and water make the universally used sulfuric acid which in turn is the source of other sulfur compounds, even the sulfa- drugs that help fight our battles against disease.

face to face with some *real chemistry.* Do the *basic laws* and *concepts* that you have previously studied still hold true? Do you see how the *theoretical concepts* of science form the backbone of the *industrial world?*

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Looking Ahead into

Unit Eight

In your study of the elements as the "building blocks" of the world, you have been primarily interested in the separate elements and their compounds. You have noted especially the differences in their properties and have seen how these differences cause the elements and their compounds to have different uses. Little attempt so far has been made to bring similar elements together into groups in order to simplify their study.

In Unit Five you saw how helpful it is to group many *compounds* into three groups—acids, bases, and salts. In this present unit you will learn that many of the *elements* likewise can be arranged in groups according to a natural plan. This grouping simplifies your study of chemistry a very great deal by permitting you to let one element serve as a typical example of the entire group or family.

A practical gardener frequently saves much time and effort by arranging plants in groups according to their needs for water, soil, sunlight. His grouping is a practical classification. The periodic table of the elements that you will study in this unit is both a practical classification and a natural one. It is a great convenience and a great timesaver. The periodic table is one of the most important and useful generalizations in chemistry.

Problem 36. *How Is Chlorine a Typical Member of a Family of Nonmetallic Elements?*

Problem 37. *How Are the Halogens a Typical Chemical Family?*

Problem 38. *How Can the Family Tree of Elements Be Represented by the Periodic Chart?*

Problem 39. *How an Observation, an Accident, and an Error Led to the Discovery of a Series of Radioactive Elements.*

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A Family Tree: How the Relationship of Elements in Groups Is Shown by the Periodic Table

Problem 36

HOW IS CHLORINE A TYPICAL MEMBER OF A FAMILY OF NONMETALLIC ELEMENTS?

You no doubt have heard statements such as these: "It runs in the family," "She has the features of her mother," or "They must be brothers; they look so much alike." As you know, there are often striking similarities among different members of a family. However, such persons are never exactly alike in every way. They may be similar in many respects, but they are not identical.

What is meant by "a chemical family"? On the basis of their similar chemical behavior, some of the elements can be placed in groups or families. This does not mean that they have identical chemical properties. The chemical properties of a family of elements usually vary in a more or less regular fashion. However, their chemical properties vary more in *degree* than they do in *kind*.

You already have studied the inert gases of the atmosphere. They constitute a chemical family of similar elements. Some reference also has been made to other families. Arranging the elements in families in this way is very convenient. It enables you to organize chemical facts and to make general statements that apply to the different members of the same family. For example, from your knowledge of sodium you can say that the other members of the sodium family (the alkali metals) react with water, releasing hydrogen; that they form strong bases; and that their ions have a valence of positive one. However, do not try to make or apply a general statement

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that is not warranted by the facts—the differences among members of a family are often as important as their similarities.

Why do elements that are in the same chemical family resemble each other? The chemical properties of an element depend on the number of electrons in the outer shell of the atom. For example, if the atoms of each of two elements have seven electrons in their outer shells, the elements react in a similar manner—both tend to gain one electron, both have a valence of negative one, and consequently both elements form similar compounds. Two such elements are fluorine (F: 2, 7) and chlorine (Cl: 2, 8, 7). They are the first two members of the chlorine family which includes also bromine and iodine. It is thought that the recently reported element alabamine also belongs to this family.

Before you study the chlorine family as a group, you should get a better basis for comparison by first concentrating on a typical member of this family—chlorine.

Since chlorine is a very active element, it is not found uncombined in nature. It must be obtained from its compounds. Chlorine can be obtained from sodium chloride or from hydrochloric acid which is prepared from sodium chloride.

How chlorine, a typical member of the halogen family, is prepared from hydrochloric acid. The usual method of preparing chlorine in the laboratory is by oxidizing hydrochloric acid. In this process the oxygen "steals" hydrogen from the hydrochloric acid, thus releasing chlorine. This is a striking example of the attraction that oxygen displays for hydrogen.

Any good oxidizing agent, such as potassium permanganate ($KMnO_4$), lead dioxide (PbO_2), or concentrated nitric acid, may be used with the hydrochloric acid if the products formed are not troublesome. Manganese dioxide (MnO_2) is commonly used. It is immersed in hydrochloric acid and heated gently. (See Fig. 105.) The following reaction occurs:

$$4\ HCl + MnO_2 \rightarrow MnCl_2 + Cl_2\uparrow + 2\ H_2O$$

Scheele first prepared the gas in 1774 by this reaction, but he did not recognize the gas as an element. Later Davy

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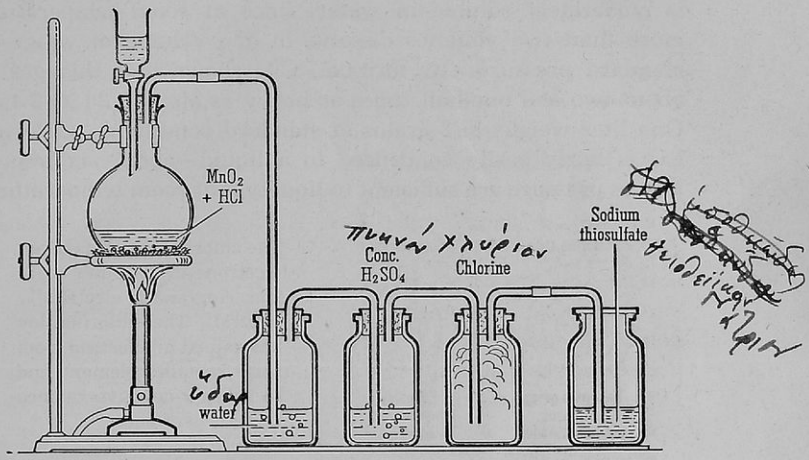
named the gas chlorine from a Greek word meaning greenish-yellow.



105. Laboratory Preparation of Chlorine. The oxidation of hydrochloric acid yields chlorine. Note that in this case manganese dioxide is an oxidizing agent and not a catalyst.

How chlorine is prepared from sodium chloride. Chlorine may be prepared in the laboratory directly from sodium chloride by treating a mixture of manganese dioxide and sodium chloride with sulfuric acid. In this reaction it is convenient to think of the sulfuric acid as acting on the sodium chloride to form hydrochloric acid which then is oxidized by the manganese dioxide. The final equation is:

$$2\,NaCl + 2\,H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2\uparrow$$

Chlorine also may be prepared by the *electrolysis* of sodium chloride. When a direct current of electricity is passed through a solution of sodium chloride (or through the *melted* salt), chlorine is released at the positive terminal (anode).

What the properties of chlorine are. Chlorine is a greenish-yellow gas with a disagreeable, irritating odor. When breathed in too large quantities, it causes an inflammation of the mucous

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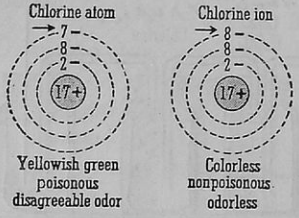
linings of the nose, throat, and lungs. The resulting congestion of these delicate tissues may prove fatal. Chlorine is moderately soluble in water, since at room temperature more than two volumes dissolve in one volume of water at standard pressure. Its formula, Cl_2, shows that this gas is about two and one-half times as heavy as air (71/29 = 2.45). One liter weighs 3.22 grams at standard conditions. Chlorine gas is fairly easily condensed to a liquid—about six atmospheres pressure are sufficient to liquefy it at room temperature.



The chlorine atom has seven electrons in its outer electron ring and is electrically neutral. The chlorine ion has gained an electron from some metallic element and so it has a negative valence of one.

106. THE CHLORINE ATOM AND THE CHLORINE ION

The electron arrangement of chlorine (Cl: 2, 8, 7) indicates that the element should behave as a nonmetallic element; and therefore it is not surprising to find that, in the presence of other suitable elements, each chlorine atom gains one electron and changes to a stable form by completing its outer shell of electrons. Chlorine atoms gain electrons very readily and consequently this element is highly active. It is even more active than oxygen.

Chlorine combines with hydrogen—a true case of combustion though there is no trace of oxygen present. When a jet of burning hydrogen is lowered into a bottle of chlorine, the hydrogen *continues to burn* by uniting with the chlorine, even though there is no trace of oxygen present in the jar. Hydrogen chloride is formed. A mixture of hydrogen and chlorine may be kept in the dark without danger, but in the sunlight the two gases combine vigorously, producing a violent explosion.

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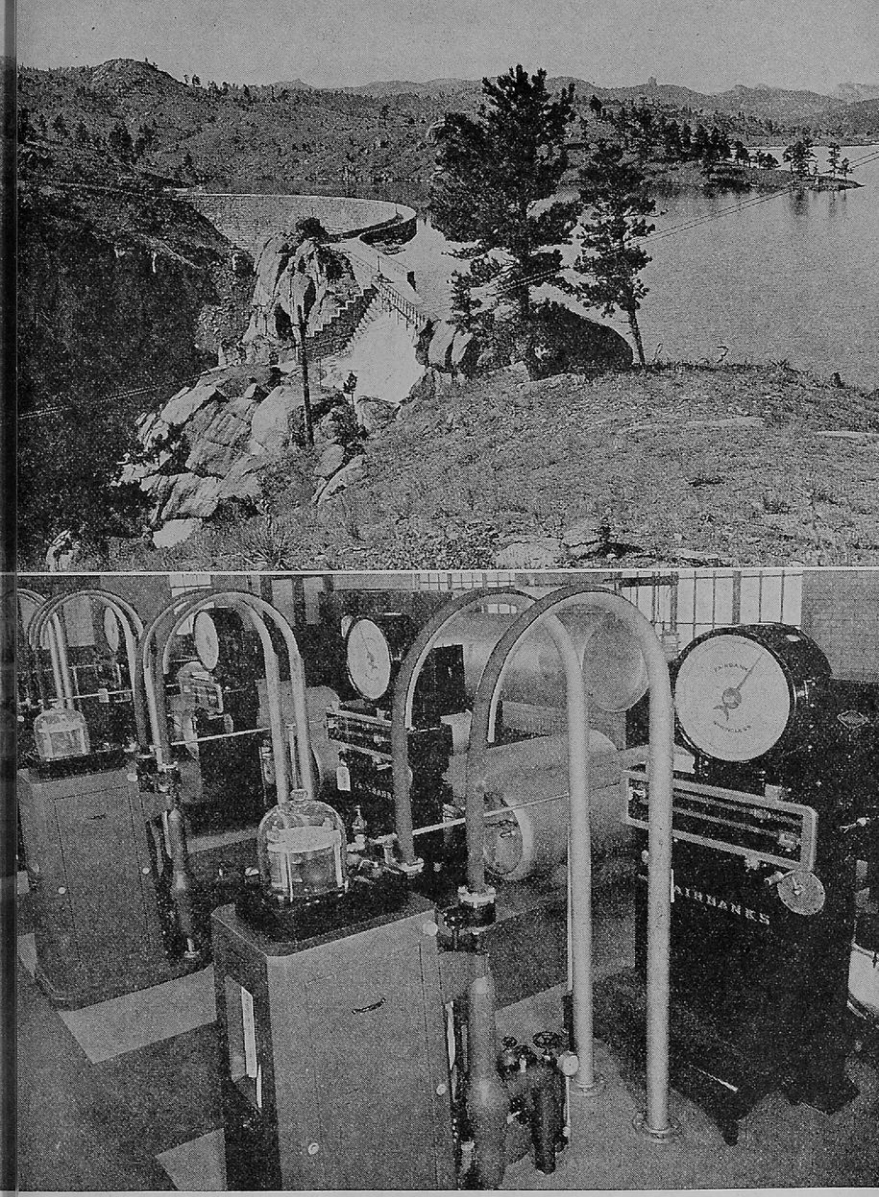

Top Picture—Courtesy, Board of Water Commissioners, Denver, Colorado
Bottom Picture—Courtesy, Water Purification Division, Chicago, Illinois

WATER SUPPLY AND CHLORINATING PLANT. The top picture shows a water supply for Denver, Colorado. The bottom picture shows a chlorinating plant in one of Chicago's pumping stations. Why is water purification a greater problem in Chicago than it is in Denver?

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Chlorine combines with metals; powdered antimony burns spontaneously in chlorine even though there is no oxygen present. Chlorine combines vigorously with many metals, releasing much energy. Powdered antimony burns spontaneously in chlorine. A white cloud of antimony trichloride ($SbCl_3$) is formed. A strip of warm copper foil likewise burns in chlorine with the formation of cupric chloride ($CuCl_2$). Chlorine also forms chlorides with many nonmetals such as phosphorus trichloride (PCl_3) and carbon tetrachloride (CCl_4).

Chlorine "steals" the hydrogen from hydrogen compounds. Chlorine acts on hydrogen compounds by withdrawing hydrogen from them. This action is demonstrated by placing in chlorine a piece of filter paper which has been dipped in warm turpentine ($C_{10}H_{16}$). A heavy cloud of black smoke is produced as the carbon is liberated. The chlorine combines with the hydrogen forming hydrogen chloride:

$$C_{10}H_{16} + 8\ Cl_2 \rightarrow 10\ C + 16\ HCl$$

Other compounds of hydrogen and carbon (hydrocarbons) act in a similar manner.

Chlorine enables you to wear white clothing. A colored *dry* cloth placed in chlorine gas retains its color. If the cloth is *wet*, the color is soon bleached white (Fig. 107); water appears to play a part in the bleaching act.

In order to bleach clothing or other materials, why must chlorine gas be dissolved in water? Here is a fine opportunity for you to do a piece of chemical "detective work." You might start solving the problem by remembering that chlorine is a nonmetallic element; *it reacts with water to form acids:*

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{HOH} \rightarrow \underset{\text{hydrochloric acid}}{HCl} + \underset{\text{hypochlorous acid}}{HClO}$$

Note the following facts concerning the preceding equation: (1) Chlorine gas by itself will not bleach materials, (2) neither will water. When these two substances—chlorine and water—get together, they react, forming hydrochloric acid and hypochlorous acid. But (3) if you put a colored cloth in a solution

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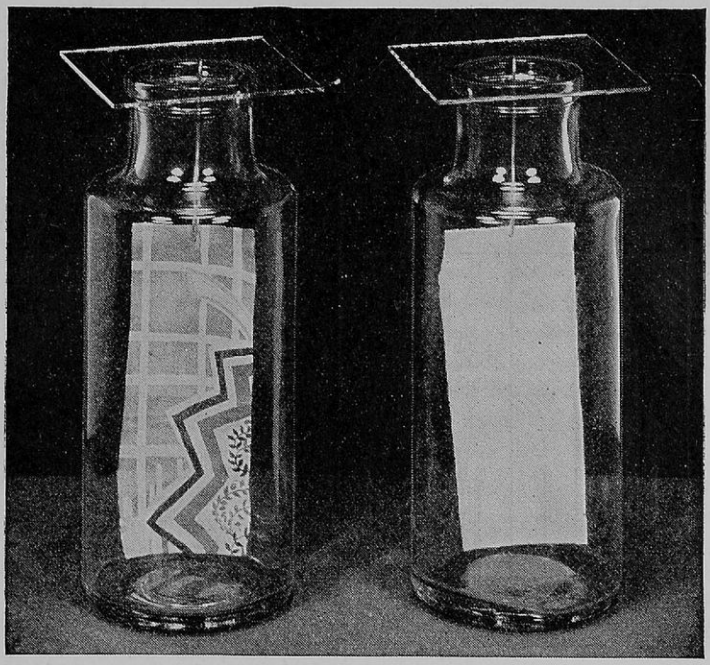

107. Bleaching with Chlorine. Two pieces of colored cloth were lowered into bottles of chlorine. The piece in the bottle on the right had been wet with water.

of hydrochloric acid, the cloth is not bleached. (4) The active agent, therefore, must be the *hypochlorous* acid. The reactions that lead to bleaching may be summed up as follows:

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

$$HClO \longrightarrow HCl + \underset{\text{atomic oxygen}}{[O]}$$

Coloring matter + [O] → colorless compound

Is it the chlorine that does the bleaching or the atomic oxygen which is liberated from hypochlorous acid? If you place a solution of chlorine (a mixture of hydrochloric acid and hypochlorous acid) in the sunlight, oxygen is given off.

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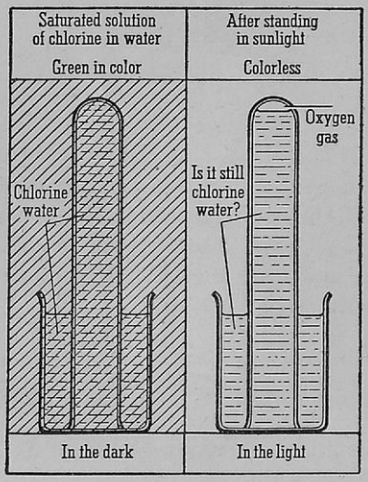
This oxygen does not come directly from the water (H_2O), for water is too stable to decompose under these conditions. The oxygen, therefore, must come from the unstable hypochlorous acid as it decomposes—for this is the only other possible source.



If a solution of chlorine in water is placed in the sunlight the yellow color of the solution disappears and a gas gathers at the top of the tube. Tests show that the gas is oxygen and that hydrochloric acid is present in the solution. The chlorine has reacted with the water to form hydrochloric and hypochlorous acids. The hypochlorous acid is unstable and under the action of sunlight decomposes forming atomic oxygen and hydrochloric acid. The oxygen thus liberated is very active.

108. THE ACTION OF CHLORINE ON WATER

You already have learned that the oxygen of the air (O_2) slowly bleaches many colored substances. From these facts you can deduce that the good bleaching qualities of a solution of hypochlorous acid is not due directly to chlorine but to the oxygen that is released when the unstable hypochlorous acid (HClO) decomposes, yielding atomic oxygen. When the released oxygen comes in contact with colored substances, instead of becoming molecular oxygen (O_2), it combines chemically with them and forms products that are colorless.

Chlorine helps to kill germs that endanger your health. Even very dilute solutions of chlorine kill bacteria and other minute forms of life. Consequently, many cities sterilize their drinking water by adding comparatively small amounts of chlorine to the

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water. As little as one pound of the element dissolved in a million gallons of water is usually sufficient to kill typhoid germs. Water of swimming pools often is chlorinated for similar reasons. This effect is due to the oxidizing properties of hypochlorous acid.

In order to protect public health, many cities specify that restaurants and other public eating places wash their dishes in water containing chlorine or an active chlorine compound. The purpose of this requirement is to kill disease germs that might otherwise be passed from one person to another. Although chlorine is highly effective for this purpose, it must be given an opportunity to come in contact with possible germs on glassware or dishes. Merely "sloshing" the dishes in a chlorine solution may not be adequate since such substances as modern lipstick may adhere to glasses and keep the chlorine solution from contacting the surfaces underneath.

Readings for Pleasure and Profit

Beery, Pauline. *Stuff.* Chap. IV, pp. 60-72, "Chlorine—Water Purification—Bleaching."

Clarke, Beverly L. *Marvels of Modern Chemistry.* Chap. XIII, pp. 178-184, "The Redheaded Halogens."

Foster, William. *The Romance of Chemistry.* Chap. VIII, pp. 111-117, "Chlorine, Bleaching and Disinfecting."

Goldblatt, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 11, pp. 67-71, "Worthwhile Economies in Producing Chlorine and Caustic Soda."

Kendall, James. *At Home among the Atoms.* Chap. XI, pp. 159-171, "Gentlemen Prefer Blondes."

Rogers, Allen. *Manual of Industrial Chemistry.* Vol. I, Chap. X, pp. 287-308, "Chlorine and Its Preparation."

Slosson, Edwin E. *Creative Chemistry.* Chap. XII, pp. 221-237, "Fighting with Fumes."

Applying in Life What You Have Learned in Chemistry

A submarine story described a serious accident in which ocean salt water flooded the storage batteries containing sulfuric acid and lead dioxide (PbO_2). Can you name and account for the poisonous gas formed?

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Heavy storms had brought much flood water to the river town of Milford. In order to protect the citizens against typhoid fever, the city officials had directed that the water supply be more heavily chlorinated. Many persons were grumbling about the taste of the water.

One boy who had studied chemistry suggested the use of ozone which would not only sterilize the water but also remove odors and tastes as well.

Tell why you think the suggestion was or was not practical.

A study hint: In order to think well you must learn how to compare substances and to compare processes.

How can you apply the preceding statement in your study of this problem?

Putting Chemistry to Work

A

(1) Why do vegetables cook faster in salt water than in fresh water? (2) Make a comparison chart that will enable you to avoid the error (frequently made by students) of confusing chlorine with hydrogen chloride gas. (3) Tell why chlorine and some of its compounds are used in many laundries. (4) In preparing chlorine, why is the method used in the laboratory usually different from the methods used commercially? (5) How would you expect a fresh solution of chlorine water to react with litmus? Explain any difference you would expect to find after the chlorine water had stood in the sunlight for several days.

(6) A small piece of antimony metal showed no appreciable change when placed in a bottle of chlorine. Does this agree with your findings in the laboratory concerning the action of chlorine on antimony? Explain. (7) After chlorine is used to bleach cotton, an antichlor, frequently sodium thiosulfate ("hypo"), is used to destroy any chlorine which may have been left in the fiber. Why? (8) What must a manufacturer consider when he chooses materials from which to manufacture a substance on a large scale? Show how these points apply in the manufacture of industrial chlorine.

B

(9) Give an example of combustion without oxygen. Tell what product is formed. (10) Why is chlorine water usually kept in dark bottles? Why does the color of chlorine water fade on standing for a few days in the light? Write an equation for the change which

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occurs. (11) Manganese dioxide is used in the preparation of oxygen from potassium chlorate and also in the preparation of chlorine from hydrochloric acid. Explain how the function of the manganese dioxide differs in these two cases. (12) Name seven kinds of particles (molecules and ions) present in chlorine water. (13) What is the difference between combined chlorine, molecular chlorine, atomic chlorine, and the chloride ion?

How Good Are You at Solving Problems?

(1) How many liters of chlorine (S.T.P.) can be prepared from 11.7 grams of common salt? Show that the choice of the method for liberating the chlorine will or will not make a difference in the volume of the chlorine obtained.

(2) How many grams of chlorine can be obtained when 19.33 grams of pyrolusite (90% pure MnO_2) are heated with an excess of hydrochloric acid?

(3) Tin cans may be detinned by treatment with chlorine. If 18.5 pounds of stannic chloride ($SnCl_4$) are obtained, how many pounds of tin may be recovered?

(4) When 100 tons of chlorine are prepared by electrolysis, how many tons of sodium hydroxide are formed?

Research and Activities That You Will Enjoy

A model or a chart: Design and prepare either a model or a chart showing the main parts of a Nelson (Vorce) cell for the electrolytic production of chlorine from brine.

"Chemistry as a hobby" talk: (For one who is really enthusiastic about his home "Chem. Lab.") Tell the class how you became interested in chemistry as a hobby, how you went about building your laboratory, how you obtained chemicals and apparatus, and about any interesting problems you have encountered and solved.

A panel discussion: Select a small group of students to bring before the class the different ways in which chlorine and chlorine compounds protect the health of your community.

Can any of the other halogens be used for the same purposes that chlorine is used? If so, why is chlorine used mostly?

Sir Humphry Davy: Sir Humphry Davy and Michael Faraday, assistant to Davy at one time, made valuable contributions to chemistry and physics. Find and report what Davy did in connection with chlorine.

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Problem 37

HOW ARE THE HALOGENS A TYPICAL CHEMICAL FAMILY?

How are the elements of the halogen family alike; how are they different? The elements fluorine, chlorine, bromine, and iodine form a typical family of elements. They are all nonmetallic elements, having a valence of negative one. Fluorine, bromine, and iodine, therefore, form compounds that are similar to those of chlorine. For example, the sodium salts of fluorine, bromine, and iodine closely resemble table salt which is the binary sodium salt of chlorine. For this reason, these four elements are known collectively as the *halogens,* which means "formers of sea salt." Salts of the halogens are present in sea water. Binary metallic salts of the halogens and their hydrogen compounds are known as halides. In nature the halogens are found only in combined forms.

All the halogen elements are poisonous and corrosive. Their formulas are written F_2, Cl_2, Br_2, and I_2 since in the gaseous form their molecules contain two atoms.

Fluorine combines with all other elements except the inert gases. It is doubtful if any of you have seen this gaseous element; few persons have. Fluorine gas (F_2) is pale yellow and exceedingly poisonous and corrosive. Since it is extremely active, it combines with all other elements except the inert gases. Hence, it is difficult to prepare and keep. It reacts vigorously with water. The most common compound of fluorine is calcium fluoride (CaF_2) or fluor spar from which the element fluorine is named. Other fluorine compounds are cryolite ($3\ NaF \cdot AlF_3$) and fluorapatite [$CaF_2 \cdot 3\ Ca_3(PO_4)_2$]. These three compounds occur naturally as minerals.

Chlorine is the most common of the halogens. Chlorine (Cl_2) is a greenish-yellow gas. Its occurrence and properties have been discussed in the preceding problem. As you study the properties of the other halogens, compare them with chlorine.

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Bromine is more than three times as heavy as water. Bromine (Br_2) is a brownish-red liquid that is more than three times as heavy as water. It is the only nonmetallic element which is liquid at ordinary temperatures. The liquid element and its vapor are extremely corrosive, attacking the skin to form painful burns. Hence, bromine should be handled with great care. Do not breathe gaseous bromine; it attacks the lining of the nose and throat even more seriously than chlorine. Its peculiar suffocating odor is responsible for the name, bromine, which means "stench." Bromine occurs in combined form as sodium bromide and magnesium bromide, small amounts of which are found in certain salt deposits and in sea water.

Iodine is a steel-grey, metallic-looking solid. Iodine may remind you of cutting your finger when you perhaps use an alcoholic solution of the element—tincture of iodine—as an antiseptic to sterilize the wound. Usually this common drug-store solution is misnamed "iodine." You could obtain the solid, steel-grey, metallic-looking iodine by permitting the alcohol to evaporate. Upon being heated gently, solid iodine sublimes to a beautiful purple vapor. The word *iodine* means "violet-colored."

Iodine occurs as iodides in some salt deposits and to a small extent in sea water. Formerly, iodine was obtained from the ashes of certain seaweeds. Now one of the chief sources is sodium iodate ($NaIO_3$) in Chile saltpeter. A new source of supply which has recently become available is from oil-well brines of California.

A small amount of iodine—only about 50 milligrams—is present in the human body in combined form. About one-third of this is found in the thyroid gland in the neck. Even this small amount of iodine is extremely important in normal development and growth. A deficiency of iodine may result in goiter, an enlargement of the thyroid gland.

Foods from plants grown in certain localities, such as the Great Lakes region, may be deficient in iodine since iodine compounds, being very soluble, are easily washed out of the soils. Sea foods are rich in iodine.

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Two of the halogens are gases; one is a liquid; and one is a solid—some interesting physical properties of the halogen elements. For convenience some of the simple properties of the halogens are shown in the table given below. Note the progressive changes in physical properties from fluorine to iodine as the atomic weights increase. The physical states of the halogen elements vary: two of them are gases; one is a liquid; and one is a solid. As you read the table from left to right, the colors become darker; the densities become greater; and the boiling points rise in a regular fashion.

COMMON PROPERTIES OF THE MEMBERS OF THE HALOGEN FAMILY

Name of element	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
Formula	F_2	Cl_2	Br_2	I_2
Atomic number	9	17	35	53
Ring structure	2, 7	2, 8, 7	2, 8, 18, 7	2, 8, 18, 18, 7
Usual valence	−1	−1	−1	−1
Atomic weight	19	35.5	80	127
State and color	pale yellow gas	greenish-yellow gas	dark red liquid	purplish-black solid
Density	1.31 (air = 1)	2.49 (air = 1)	3.19 (water = 1)	4.93 (water = 1)
Boiling point	−187° C.	−33.6° C.	58.7° C.	184.4° C.
Derivation of name	Fluor spar—a rock that "flows" (melts easily)	Greek word—"greenish-yellow"	Greek word—"a stench"	Greek word—"violet-colored"
Approximate *relative* abundance	100	200	1	1

How are the hydrogen halides similar in properties? Since the halogen elements have a valence of negative one, they form hydrogen compounds which have the formulas HF, HCl, HBr, and HI. These are known as hydrogen halides. You already have found that hydrogen chloride (HCl) is a colorless gas. The other hydrogen halides also are colorless gases. The

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hydrogen halides fume in moist air, which shows that they are all very soluble. Like hydrogen chloride, they dissolve in water but do not combine with it. The solutions are all strong acids whose names, as you would expect, are characterized by *hydro- ic: hydro*fluoric acid, hydrochloric acid, hydrobromic acid, and hydriodic acid.

How can you prepare the hydrogen halides? Recalling the preparation of hydrogen chloride (page 179) will aid you in the preparation of the other hydrogen halides. The principle employed is the action of high-boiling point sulfuric acid on the most common *metal* halides. This process can be used only for the preparation of the stable hydrofluoric and hydrochloric acids. Note carefully the similarities and differences of the following equations:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF\uparrow$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$$

$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr\uparrow$$

$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI\uparrow$$

} not practical

These four reactions show you that great care must be used in noting the exceptions to general statements. If you attempt to prepare pure hydrogen bromide by the above method, a brownish-red vapor is formed and the odor of sulfur dioxide is noted. Similarly, if you attempt to prepare pure hydrogen iodide by the above method, a violet vapor appears and the odor of hydrogen sulfide is evident. How can we account for these unexpected facts?

The brownish-red vapor is free bromine, which shows that some of the hydrogen bromide has decomposed. This indicates that hydrogen bromide is not so stable as hydrogen chloride. But when hydrogen bromide decomposes, free hydrogen, a vigorous reducing agent, is released. The free hydrogen reduces some of the sulfuric acid to sulfur dioxide. This same idea may also be stated in this way: Sulfuric acid, an oxidizing agent, oxidizes hydrogen bromide thus liberating free bromine.

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$$2\ HBr + H_2SO_4 \rightarrow 2\ H_2O + SO_2\uparrow + Br_2\uparrow$$

You will recognize the above reaction as an oxidation-reduction reaction since the valence of bromine increases from —1 in hydrobromic acid to zero in free bromine. Also the valence of sulfur decreases from +6 in sulfuric acid to +4 in sulfur dioxide. Each bromine atom loses one electron (oxidation) while the sulfur atom gains electrons (reduction).

Hydrogen fluoride is stable; its heat of formation is about 64,000 calories—how stable are other hydrogen halides? The relative stability of the hydrogen halides may be determined by comparing their heats of formation. You will remember that the heat of formation of a compound is the number of calories of heat liberated when one gram-molecular weight of the compound is formed. The heat of formation also indicates the amount of energy required to separate the compound into its elements. The heats of formation of the hydrogen halides, shown in the accompanying table, indicate the relative stability of these compounds.

HEATS OF FORMATION OF THE HYDROGEN HALIDES

Name of compound	*Formula*	*Heat of formation*	*Stability*
Hydrogen fluoride	HF	63,991 calories	Very stable
Hydrogen chloride	HCl	22,031 calories	Stable
Hydrogen bromide	HBr	8,650 calories	Unstable
Hydrogen iodide	HI	−5,926 calories[1]	Very unstable

Fluorine and chlorine are so active that they are better oxidizing agents than oxygen—what is the relative activity of the halogens? A mixture of fluorine and hydrogen explodes violently even in the dark. Chlorine and hydrogen combine slowly in the dark, somewhat faster in ordinary light, and explosively in the sunlight. Bromine and hydrogen unite when heated, but the reaction is reversible and never complete. Some iodine

[1] A negative heat of formation shows how much energy must be *added* to form the compound. Compounds with negative heats of formation are very unstable and may decompose spontaneously, liberating heat. (See pp. 253-255.)

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and hydrogen unite when heated moderately, but the union is slow and incomplete. These facts indicate the relative activity of the halogens.

Without a doubt fluorine is the most active halogen. Its intense activity is further shown by the manner in which it attacks water, withdrawing the hydrogen and releasing oxygen. (So much energy is involved that some ozone also is formed.) Fluorine is the most active nonmetal and the most vigorous oxidizing agent known. Next in order comes chlorine. It, too, is more active than oxygen and is a better oxidizing agent than oxygen for, in the sunlight, it slowly withdraws hydrogen from water. Bromine is less active than oxygen but more active than iodine. Iodine is low in the activity series of the nonmetals.

You will recall that each halogen atom has seven electrons in its outer shell. One additional electron is needed to make the outer shell complete. The relative activity of the halogens indicates that the fluorine atom attracts most vigorously the one electron it needs to complete its outer shell of eight and holds tightly to the "eighth electron" when it is once attained. On the other hand, the iodine atom attracts its needed electron only slightly and holds on to it but weakly. This difference in the activity of fluorine (F: 2, 7) and of iodine (I: 2, 8, 18, 18, 7) is best explained by drawing their "atomic pictures" and then observing the difference in the electron shells of their atoms. The outer completed shell of the fluorine atom is pictured as being much closer to the positively charged nucleus than the relatively distant outer shell of the iodine atom. Consequently, the negative electrons of the outer shell of the fluorine atom are held more tightly by the positive nucleus and are lost with greater difficulty.

Chlorine will "oust" bromine from bromine compounds; bromine will "oust" iodine from iodine compounds—how does this demonstrate the relative activity of these halogens? Probably the most convincing proof of the difference in the activity of the halogens is the order in which they replace each other from solutions. Fluorine is omitted from such a study because of the difficulty and dangers in handling it. When a

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few drops of chlorine water are added to solutions of sodium bromide and sodium iodide that are in separate test tubes, the changes in color show that bromine and iodine have been liberated from their compounds and replaced by the chlorine:

$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2$$

$$2\ NaI + Cl_2 \rightarrow 2\ NaCl + I_2$$

The free bromine imparts a characteristic deep red-brown color to carbon tetrachloride, carbon disulfide, or chloroform which is shaken with the solution. In a similar manner the free iodine forms a beautiful purple solution. The color of the solution may be used as an identifying test for *uncombined* bromine or iodine. You should remember that combined bromine or iodine does not give these colored solutions.

On the other hand, when a few drops of bromine water are placed in solutions of sodium chloride and sodium iodide that are in separate test tubes, the iodine is replaced by the bromine but the chlorine is not replaced by the bromine:

$$2\ NaI + Br_2 \rightarrow 2\ NaBr + I_2$$

$$2\ NaCl + Br_2 \rightarrow \text{no reaction}$$

These replacements again show that an atom of chlorine is more eager to complete its outer shell than atoms of bromine or of iodine.

How are the members of the halogen family prepared? Bromine and iodine are not prepared in the laboratory by using hydrobromic or hydriodic acids since these acids are too unstable to be kept on the laboratory shelves. However, the acids may be prepared by the action of concentrated sulfuric acid on the sodium or potassium salts of these acids. You can, therefore, prepare and oxidize the acids in a single operation by heating gently a mixture of the salt, sulfuric acid, and manganese dioxide. (See page 312 for chlorine.) The action of the sulfuric acid on the salt forms the acid which is then oxidized by the manganese dioxide, thus liberating the free halogen. See the completed equations on the next page.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

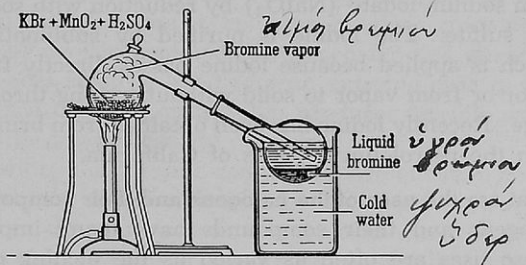
$$CaF_2 + H_2SO_4 + MnO_2 \rightarrow \text{No fluorine is set free}$$

$$2\ NaCl + 2\ H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2\ H_2O + Cl_2\uparrow$$

$$2\ NaBr + 2\ H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2\ H_2O + Br_2\uparrow$$

$$2\ NaI + 2\ H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2\ H_2O + I_2\uparrow$$

Fluorine cannot be liberated in the above manner because fluorine reacts with water, forming hydrofluoric acid. To prepare fluorine you, therefore, must use a method that is suitable for all extremely active elements—electrolysis. Elementary fluorine is prepared by electrolyzing a mixture of potassium hydrogen fluoride (KHF_2) and liquid anhydrous hydrogen fluoride in an apparatus made of platinum, copper, or graphite.



109. Laboratory Preparation of Bromine. Sulfuric acid and a bromide form hydrobromic acid. This acid is easily oxidized by manganese dioxide to liberate bromine. Gentle heating vaporizes the bromine and it is condensed in the water-cooled flask. Compare this method with that used in preparing chlorine.

How industry prepares the halogens. These elements are prepared on a commercial scale by the oxidation method described above or by using chlorine to replace them from their naturally occurring salts. This latter method is employed in obtaining bromine from sea water. The Ethyl-Dow bromine plant on the Cape Fear river in North Carolina can produce 15,000 pounds of bromine daily from 37 million gallons of ocean water. Bromine is obtained from Michigan brine (containing $MgBr_2$) by electrolysis. This method is not practical in obtaining iodine. At present, most of the iodine is obtained

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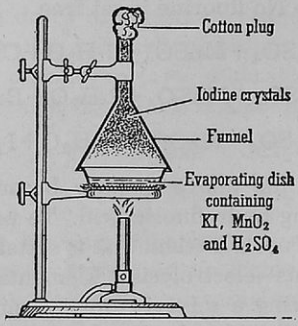

Sulfuric acid and an iodide form hydriodic acid. This acid is oxidized using manganese dioxide as the oxidizing agent. Gentle heating vaporizes the iodine and the purple vapor condenses forming steel-gray iodine crystals on the inner surface of the funnel. The iodine may be purified by resubliming it.

110. LABORATORY PREPARATION OF IODINE

from sodium iodate ($NaIO_3$) by reduction with sodium hydrogen sulfite. The iodine is purified by sublimation, a name which is applied because iodine passes directly from solid to vapor or from vapor to solid without passing through a liquid stage. Recently iodine has been obtained from brines occurring with the petroleum deposits of California.

What are the uses of the halogens and their compounds? The halogens and their compounds have many important uses. These uses are often as varied as the etching of glass and the preparation of medicine.

Compounds of fluorine cool many electric refrigerators and "frost" electric light bulbs. One of the most useful compounds of fluorine is calcium fluoride, or fluor spar (CaF_2). It is found in extensive deposits along the Ohio river in Illinois and Kentucky.

Recently dichloro-difluoro-methane (Freon, CCl_2F_2) has come into use as a nontoxic safe refrigerant to use in household refrigerators.

Another useful compound of fluorine is hydrofluoric acid which is employed in etching glassware and "frosting" lamp bulbs. This action depends on the ability of hydrogen fluoride to react with silicon dioxide or the silicates (glass) forming silicon fluoride (SiF_4) a gas which escapes thus completing the action. Typical equations are shown on the next page.

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$$SiO_2 + 4\ HF \rightarrow 2\ H_2O + SiF_4\uparrow$$

$$Na_2SiO_3 + 6\ HF \rightarrow 2\ NaF + 3\ H_2O + SiF_4\uparrow$$

$$CaSiO_3 + 6\ HF \rightarrow CaF_2 + 3\ H_2O + SiF_4\uparrow$$

The object to be etched is coated with a thin layer of paraffin and the design is scratched through the paraffin, exposing the glass. The paraffin-covered object is then subjected to the action of hydrofluoric acid or to hydrogen fluoride gas, prepared by the action of sulfuric acid on powdered calcium fluoride. The paraffin is not affected but the exposed glass is attacked as shown by the equations above. Electric light bulbs are "frosted" on the inside in a similar manner with hydrofluoric acid and ammonium bifluoride. It is easily seen why hydrofluoric acid cannot be kept in glass containers. Usually wax or ceresin containers are used for this purpose. Hydrofluoric acid must be handled with extreme care in the laboratory, since this acid on the skin produces terrible sores which heal with great difficulty.

Minute quantities of fluorine compounds are effective moth and insect powders. Calcium fluoride is used as a flux in making steel and in the manufacture of enameled ware. Sodium aluminum fluoride (Na_3AlF_6) also known as cryolite, is used as the solvent for aluminum oxide in the electrolytic preparation of aluminum.

Chlorine kills germs in city water systems. The uses of chlorine in water purification, in bleaching, in preparing pure hydrochloric acid, and in disinfecting have been discussed on pages 315-318. Why not review these uses at this point? You can now add to this list the use of chlorine in freeing bromine from its compounds.

Bromine enables you to use the photographic films in your kodak. Elementary bromine is used in the preparation of dyes, tear gases, and chemicals and as a mild oxidizing agent. Silver bromide is sensitive to light, so this compound is used on photographic films and plates. Sodium, potassium, and ammonium bromides are used in medicine as nerve sedatives (rest medicine). A great deal of bromine is used in

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111. POSITIVE PRINT



112. NEGATIVE PRINT

Silver halides are used on photographic plates because they are partially reduced by sunlight. On the negative, after development, light places are shown as dark spots and vice versa. On the positive print, light and shade are shown in their proper values.

making antiknock gasoline. This gasoline contains tetraethyl-lead $(C_2H_5)_4Pb$ and ethylene dibromide $(C_2H_4Br_2)$. The ethylene dibromide is added to remove the lead so the spark plugs and pistons will not become fouled.

Iodine gives you a common antiseptic, tincture of iodine. The most widely known use of iodine is as an antiseptic. For this purpose a tincture of iodine is used. The tincture is about a 7 per cent solution of iodine in alcohol. Iodine compounds are employed in the treatment of goiter, which should always be done under the advice of a physician. "Iodized" table salt contains a small amount (about 0.01 per cent) of sodium iodide. Iodoform (CHI_3) is used as an antiseptic dressing, and potassium iodide is extensively used in medicine, photography, and in the chemical laboratory.

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How can you distinguish a halogen compound from other compounds? A fluorine compound may be identified by the etching test. All other halogen binary compounds of metals may be tested separately by the action of silver nitrate solution on their soluble salts. When a solution of silver nitrate is mixed with different sodium halide solutions, characteristic precipitates are formed as shown by the following reactions:

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow$$

white — soluble in NH_4OH, insoluble in HNO_3

$$NaBr + AgNO_3 \rightarrow NaNO_3 + AgBr\downarrow$$

pale yellow—moderately soluble in NH_4OH, insoluble in HNO_3

$$NaI + AgNO_3 \rightarrow NaNO_3 + AgI\downarrow$$

brighter yellow—insoluble in NH_4OH and HNO_3

The colors of silver bromide and silver iodide may be somewhat difficult to distinguish. If so, a little chlorine water may be added to some of the original solution to liberate the halogen. The solution is then shaken with carbon tetrachloride and the color of the lower layer is noted. (See page 328.) A violet color indicates an iodide and a brown color indicates a bromide.

A *mixture* of halogen compounds cannot be identified in the above manner, since the colored precipitates "cover up" the white silver chloride.

Readings for Pleasure and Profit

Beery, Pauline. *Stuff*. Chap. IV, pp. 72-81, "Fluorine, Bromine, and Iodine."

Clarke, Beverly L. *Marvels of Modern Chemistry*. Chap. XIII, pp. 178-184, "The Redheaded Halogens."

Foster, William. *The Romance of Chemistry*. Chap. VIII, pp. 118-128, "Bromine, Iodine, and Fluorine."

Goldblatt, L. A. *Collateral Readings in Inorganic Chemistry*. Art. 14, pp. 88-97, "Commercial Extraction of Bromine from Sea Water."

Rogers, Allen. *Manual of Industrial Chemistry*. Vol. I, Chap. X, pp. 312-314, "Bromine and Iodine."

Weeks, Mary Elvira. *The Discovery of the Elements*. Chap. XVII, pp. 253-274. "The Halogen Family."

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Applying in Life What You Have Learned in Chemistry

If a customer asks for it, drugstores will sell "stainless or white iodine," which is prepared by clearing a solution of iodine with sodium thiosulfate. Why is "white iodine" worthless as an antiseptic?

You are getting ready to charge your auto storage battery but cannot determine which is the positive terminal. To one terminal you connect a metal plate on which is a thin paste of starch and potassium iodide. A wire attached to the other terminal makes a dark blue mark as it is drawn through the paste. Which is the positive terminal? How do you know? Explain what occurs.

"Just look at that dress!" cried Annabelle. "I tell you it's ruined. I just spilled 'iodine' all over the front of it."

"That's easy," answered her chemically minded brother, coming to the rescue. "Just wait a minute while I touch up all the spots with these moistened crystals. . . . There, it's as good as new." And so it was.

How would you remove "iodine" spots from a dress?

How would you remove "iodine" spots from a washbowl?

Putting Chemistry to Work

A

(1) Snow and ice gradually disappear even when the temperature remains below freezing. What process occurs? (2) Suggest a method for preparing silver bromide and silver iodide to be used in photographic materials. (3) Why is great care used in etching glass? (4) If you were provided with alcohol, potassium iodide, manganese dioxide, and sulfuric acid, how could you prepare a solution of iodine to be used as an antiseptic? (5) Give specific instances in which the idea of a chemical family has helped you in your chemistry work. Predict how it will further aid you. (6) Why does the state of Michigan require that all table salt sold shall contain a small amount of combined iodine? (7) Suppose you have a white solid that you know is either a chloride, a bromide, or an iodide. How could you determine which halide it is?

B

(8) After recalling the method used in obtaining chlorine by the oxidation of hydrochloric acid, suggest a method for preparing

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bromine. Can you apply the same reasoning to the preparation of iodine? (9) Why was the preparation of the element, fluorine, by Moissan "one of the most difficult problems in modern chemistry"? (10) Why does a bottle of hydriodic acid turn brown? (11) Would you expect the preparation of bromine and iodine to require more energetic or less energetic oxidizing agents than one used in the preparation of chlorine? (12) Using the electron theory, show why (a) fluorine is a better oxidizing agent than chlorine; (b) fluorine cannot be prepared by ordinary oxidation methods; (c) bromine replaces iodine; (d) the iodide ion is easily oxidized to free iodine. (13) Which one of the following compounds is richest in iodine, NaI, CHI_3, AgI, or $NaIO_3$?

Research and Activities You Will Enjoy

A demonstration: It is claimed that iodine vapor gently blown against latent fingerprints causes them to show up quite clearly. See if you can learn more about the technique employed and then demonstrate for your class.

A guest speaker: Suggest to your family physician that your class would appreciate having him explain why the body needs iodine and how iodine is related to goiter. If he is too busy to visit your class for a few minutes, report to the class all he says.

A "field" trip: During its "slack" hours visit a drugstore that specializes in filling prescriptions. Inquire about the different chlorides, bromides, and iodides carried in stock for medicinal uses.

Problem 38

HOW CAN THE FAMILY TREE OF ELEMENTS BE REPRESENTED BY THE PERIODIC CHART?

Suppose that some outsider had come into your class and required each of you to sit, not in the usual alphabetical order, but in some other order he had in mind—say in the order of your increasing weights. Would you not be greatly astonished after looking around your class to find the lazy boys in a row all by themselves, the active athletes in another row, all the brunettes in a third row. the redheads all together in

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another, and so on? "An accident," you might say. Possibly, but there is no doubt that you would be impressed and interested, perhaps to the point of being scientifically curious to know how it happened.

It may be even more surprising to know that all of the ninety-two elements in the world can be arranged in related groups in a *periodic chart* and that this chart is one of the most useful "tools" in chemistry.

What early attempts were made to group the elements? Many of the early chemists insisted that it was a mistake to consider the elements as incidental and unrelated. They hoped to show that the elements are related according to some undiscovered plan of nature and that they could be arranged in some natural fundamental manner. About the time Dalton proposed his now famous atomic theory, Prout (1815) suggested that all the elements were composed of hydrogen and that, therefore, all atomic weights should be whole numbers. But after atomic weights were determined with greater accuracy, it was evident that they were not all whole numbers. For example, the atomic weight of chlorine is 35.5. Conservative scientists laughed at Prout's idea; they little realized how closely his hypothesis had come to a great fundamental truth, discovered years later.

Döbereiner (1829) observed an interesting relationship among the atomic weights and simple properties of certain groups of three elements. For example, he noted that the atomic weight of bromine (80) is approximately the average of the atomic weights of chlorine (35.5) and iodine (127). Likewise, the similar chemical properties of bromine show a sort of halfway ground between the properties of the other two elements. Other triads (threes) were noted, such as the similar elements calcium, strontium, and barium.

The idea of octaves—"eights." A great advance was made in classifying the elements when Newlands (1865), using atomic weights as a common property, arranged some of the elements *in the order of their increasing atomic weights.* He found that every eighth element repeated the properties of a

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preceding one, in somewhat the manner of musical octaves. The following periods of elements will illustrate this idea.

Period 1	Li	Be	B	C	N	O	F
	7	9	11	12	14	16	19
Period 2	Na	Mg	Al	Si	P	S	Cl
	23	24	27	28	31	32	35.5

The worth-while characteristic of this arrangement lies in the fact that elements of similar chemical properties come together in the same vertical columns. Look for the very similar elements fluorine and chlorine; lithium and sodium; oxygen and sulfur. In spite of the fact that Newlands did not go far enough and that his grouping was not entirely satisfactory, his idea was a great one, because it was a start in the right direction.

How did Mendeléeff successfully form a family tree of elements? After studying and withholding judgment for many years in the true scientific spirit, the Russian chemist Mendeléeff (1869) published his table of the sixty-three known elements. Like Newlands, he placed the elements in groups on the basis of increasing atomic weights. The elements were arranged in eight vertical columns so that those of similar chemical properties would fall together. This arrangement, brought up to date to include all ninety-two elements, is known as the Periodic Classification of the Elements, or more briefly as the Periodic Chart. (See page 339.) *Periodic* means occurring again and again in a regular fashion, such as the hours in a day or the seasons. The horizontal rows across the chart are numbered from one to six as *periods*, or series. The vertical columns are numbered from zero to eight as *groups*.

Mendeléeff likewise distinguished himself as a master thinker by using rare scientific judgment in changing his original plan to account for new and unexpected facts. He soon noted that the elements in certain groups do not belong to the same

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family. So he divided these groups into two families as you will see by the sodium and copper families in group I. Again, when he came to iron, instead of trying to make this element fit in group I under potassium (where it obviously does not fit), he divised a *long period.* In this way iron, cobalt, and nickel started a new group and the second half of the period was continued with copper in group I. (Group 0 was not known in Mendeléeff's time.) He arose to the heights of real scientific vision by leaving blank spaces for undiscovered elements and by accurately predicting the properties of these elements which nobody had ever seen.



113. A STAMP HONORING DMITRI IVANOVICH MENDELEEFF. This Russian postage stamp honors Mendeléeff, the founder of the periodic law. Note that while the print on the stamp is in the Russian alphabet, the symbols on the periodic table on the background are in Roman type. Chemical symbols form an international language.

How can you interpret the periodic chart as a family tree? This orderly arrangement of the elements is one of the most important and useful generalizations (principles) in chemistry. Consequently, it is much to your advantage to study it until you understand it throughly and can use it easily. By referring to this chart frequently as you study the following pages, you will soon get clearly in mind the positions of the most common elements. This will aid you greatly in chemistry.

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Periods	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Type Formulas →		E_2O ECl	EO ECl_2	E_2O_3 ECl_3	EO_2 ECl_4	E_2O_5 EH_3	EO_3 H_2E	E_2O_7 HE	Transition Elements
Families →		A B	A B	A B	A B	A B	A B	A B	
0	The Inert Gases	1 Hydrogen H=1.008							
1	2 Helium He=4	3 Lithium Li=6.94	4 Beryllium Be=9.02	5 Boron B=10.82	6 Carbon C=12.01	7 Nitrogen N=14.01	8 Oxygen O=16	9 Fluorine F=19	
2	10 Neon Ne=20.18	11 Sodium Na=23	12 Magnesium Mg=24.32	13 Aluminum Al=26.97	14 Silicon Si=28.06	15 Phosphorus P=31.02	16 Sulfur S=32.066	17 Chlorine Cl=35.46	
3	18 Argon A=39.94	19 Potassium K=39.10	20 Calcium Ca=40.08	21 Scandium Sc=45.10	22 Titanium Ti=47.90	23 Vanadium V=50.95	24 Chromium Cr=52.01	25 Manganese Mn=54.93	26 Iron Fe=55.84 / 27 Cobalt Co=58.94 / 28 Nickel Ni=58.69
		29 Copper Cu 63.54	30 Zinc Zn 65.38	31 Gallium Ga 69.72	32 Germanium Ge 72.60	33 Arsenic As 74.91	34 Selenium Se 78.96	35 Bromine Br 79.92	
4	36 Krypton Kr=83.7	37 Rubidium Rb=85.48	38 Strontium Sr=87.63	39 Yttrium Y=88.92	40 Zirconium Zr=91.22	41 Columbium Cb=92.91	42 Molybdenum Mo=95.95	43 **Technetium** Tc 99	44 Ruthenium Ru=101.70 / 45 Rhodium. Rh=102.91 / 46 Palladium Pd=106.7
		47 Silver Ag=107.88	48 Cadmium Cd=112.41	49 Indium In=114.76	50 Tin Sn=118.70	51 Antimony Sb=121.76	52 Tellurium Te=127.61	53 Iodine I=126.92	
5	54 Xenon Xe=131.3	55 Cesium Cs=132.91	56 Barium Ba=137.36	57 to 71 Rare Earths	72 Hafnium Hf=178.6	73 Tantalum Ta=180.88	74 Tungsten W=183.92	75 Rhenium Re=186.31	76 Osmium Os=190.2 / 77 Iridium Ir=193.1 / 78 Platinum Pt=195.23
		79 Gold Au=197.2	80 Mercury Hg=200.61	81 Thallium Tl=204.39	82 Lead Pb=207.21	83 Bismuth Bi=209.00	84 Polonium Po=210 (?)	85 At 211 **Astatine**	
6	86 Radon Rn=222	87 **Francium** Fr 223	88 Radium Ra=226.05	89 Actinium Ac=227 (?)	90 Thorium Th=232.12	91 Protoactinium Pa=231	92 Uranium U=238.07		

5	57 Lanthanum La 138.92	58 Cerium Ce 140.13	59 **Praseodymium** Pr 140.92	60 **Neodymium** Nd 144.27	61 **Illinium** Il 146 (?)	62 Samarium Sm 150.43	63 Europium Eu 152.0	64 Gadolinium Gd 156.9	65 Terbium Tb 159.2	66 Dysprosium Dy 162.46	67 Holmium Ho 164.94	68 Erbium Er 167.2	69 Thulium Tm 169.4	70 Ytterbium Yb 173.04	71 Lutecium Lu 174.99
6	89 Actinium Ac 227.05	90 Thorium Th 232.12	91 **Protactinium** Pa 231	92 Uranium U 238.07	93 **Neptunium** Np 237	94 **Plutonium** Pu 239	95 **Americium** Am 241	96 **Curium** Cm 242							

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How six "periods" and nine "groups" are used in the periodic chart. All of the elements, except hydrogen which stands alone, fall into six horizontal rows called periods. These are numbered from 1 to 6. The first two periods are short, since they contain only eight elements each. The other periods are long and the full periods contain eighteen elements or more. Each long period is divided into two series which are separated by three transition elements (Fe, Co, Ni, etc.).

All of the elements likewise are arranged in nine vertical columns known as groups. These are numbered from 0 to VIII. On the basis of valence electrons and other similar chemical properties, the elements within most of the groups fall naturally into two subgroups, or families, such as the chlorine family in group VII. Each family is moved to the left (A) or to the right (B) in its vertical column. (See Li, Na, K, etc., in the sodium family, Cu, Ag, Au in the copper family, Ca, Sr, Ba in the calcium family, and so on.)

How valence and group numbers correspond in the periodic chart. In general, the number of a group indicates the number of valence electrons in an atom of each element in the group. To an extent this accounts for the similar chemical properties of the elements within a group, more particularly within a family. Thus, it is possible to write type formulas for each group. General formulas for the oxides and the chlorides (or hydrides) are shown near the top of the chart. "E" represents any element in a family. Of course, it must be remembered in this connection that several elements have variable valences.

Since all of the elements in group 0 (the inert gases in the helium family) have been discovered since Mendeléeff made his chart, there was no numbered column for them. They are sometimes placed in group VIII, since they all have eight electrons in their outer shells. However, it seems more convenient to list these elements in a zero group since they all exhibit a valence of zero; that is, they do not unite to form compounds.

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How base-forming and acid-forming elements are arranged in the periodic chart. With the exception of group 0, the elements on the left-hand side of the chart are metals. The "A" families are the chief base-forming elements. Look for the sodium family in group I and the calcium family in group II. The nonmetallic elements are found on the right-hand side of the chart in the "B" families. Many of these elements form strong acids, as illustrated by the chlorine and oxygen and nitrogen families. A diagonal line drawn from beryllium through aluminum to tungsten will come near several of the elements which show both basic and acidic properties. The most metallic element is found in the lower left-hand corner, while the most nonmetallic element is found in the upper right-hand corner.

As you go from left to right with increasing atomic weights, the basic properties of the elements in a period decrease while the acidic properties increase in a regular fashion. Using the second period as the best example, recall the strong basic properties of sodium, the weaker basic properties of magnesium, the extremely weak basic properties of aluminum which also shows weak acidic properties, silicon as a weak acid-former, phosphorus as somewhat stronger, sulfur as forming a strong acid, and chlorine as a very strong acid-forming element.

How the properties of elements vary with their atomic weights. In general, both the physical and the chemical properties of the members of a family show gradual changes with atomic weights. However, usually the physical properties are more orderly. Recall the progressive changes in the physical properties of the halogens. (See page 323.) Another good example is the sodium family as shown by the table at the top of the next page.

Note that with increasing atomic weights of the elements in this family, the densities of the elements increase (except potassium), their melting points decrease, and their boiling points also decrease. It is interesting to note that cesium melts at only a little above room temperature.

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SIMPLE PHYSICAL PROPERTIES OF THE SODIUM FAMILY

Element	*Atomic Weight*	*Density*	*Melting Point*	*Boiling Point*
Lithium	6.94	0.53	186° C.	1400° C.
Sodium	23.0	0.97	97° C.	880° C.
Potassium	39.1	0.87	62° C.	760° C.
Rubidium	85.5	1.52	38.5° C.	696° C.
Cesium	132.9	1.87	26.4° C.	670° C.

How can you use the periodic chart of elements? "The primary object of classification is to arrange facts so we can acquire the greatest possible command over them with the least possible effort." For this reason the periodic chart is widely used today. This periodic arrangement of the elements has greatly aided the progress of chemistry in the past. Here are some of the uses of the chart:

1. *It simplifies your study of many related elements* by grouping them into a few families. You already have seen how such a family grouping is helpful. By getting well in mind the chemistry of chlorine as a representative of its family, you more easily learned and remembered useful facts about the other members of the family. Furthermore, from your knowledge of one member you can predict with reasonable certainty in a general way how the other members of the family will behave.

2. *It helps in writing formulas,* since a group number usually indicates the common valence of the elements in the group. It is well to note and remember the exceptions to this general rule. As you would expect, the formulas of the compounds of the elements in a group are very similar. For instance, knowing the formula of sodium sulfate (Na_2SO_4), you can be more certain of the less-known compound potassium chromate (K_2CrO_4). Knowing carbonic acid (H_2CO_3) helps you write silicic acid (H_2SiO_3).

3. *It indicates the properties of new elements recently discovered.* In 1871 Mendeléeff called attention to the blank space

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which was left between calcium (40) and titanium (48). He predicted that an element to fit this space would have an approximate atomic weight of 44 and, like aluminum above it, would have a valence of three. Knowing the properties of the elements around this blank space, he very shrewdly predicted many physical and chemical properties of this unknown element and its compounds. When scandium (Sc = 45) was discovered in 1879, its properties closely agreed with the predicted ones. The discovery and the prediction of the properties of other elements have been encouraged in a similar manner.

4. *It is a check on atomic weights* and the physical properties of elements when there is uncertainty about them. After radium was discovered, its equivalent weight was found experimentally to be 113. However, since this element was chemically similar to barium with a valence of two, it was placed in group II, and the atomic weight 226 (that is, 2×113) was assigned to it.

What imperfections are in the periodic chart? In their enthusiastic use of this helpful arrangement of the elements, people often fail to recognize several imperfections or defects in it. In noting these limitations it should be remembered that they do not make the chart less useful, but serve to show that the complete story of the structure and classification of the atoms undoubtedly is not yet known.

The grouping in the chart accounts for only one, or at best only two, valence numbers of the elements. It is well known that many elements have a variable valence. In a few instances the group number does not agree with the most common valence of an element. These exceptions should be noted carefully.

In some cases the similarity of elements within a family are weak. For example, copper does not resemble gold nearly so closely as it does mercury which is in a different family. Fifteen rare earth elements are herded into one space in group III. There is no satisfactory place for the important element hydrogen which is chemically a metal, but physically a nonmetal.

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There is a lack of agreement between the activity series of the metals and the nonmetals and the complete grouping in the periodic chart. These important activity series (see pages 72 and 326) summarize many properties and explain many reactions among the elements which are scattered without regularity throughout the chart. Exceptions to this lack of uniformity are found within certain families such as the sodium and chlorine families.

Finally, a careful inspection of the chart will reveal three pairs of elements which are slightly "out of place" according to their atomic weights. These pairs are argon and potassium, tellurium and iodine, and cobalt and nickel. When placing them in the chart, preference was given to their chemical behavior instead of their increasing weights. In the next few paragraphs note how the brilliant work of a young English physicist met this objection and at the same time shed new light on the structure of the atoms.

What is the basis for the new periodic chart? By the use of X-ray spectra (described on page 158) Moseley started the experimental work which now enables us to number all the elements from 1 to 92. This natural serial number of each atom is known as its *atomic number.* It represents the total number of planetary electrons in the atom, or the number of free protons in its nucleus. Thus, the atomic number becomes the most distinctive characteristic of an atom; it determines its structure which in turn governs its chemical behavior.

When the elements are arranged in the periodic chart on the basis of their increasing atomic numbers, each element falls into a space where it belongs according to its chemical properties. No exceptions (such as A and K, Te and I in Mendeléeff's chart) have to be made. Furthermore, the position of each element between hydrogen (At. No. 1) and uranium (At. No. 92) is definitely fixed. Since an element corresponding to each of the ninety-two spaces has now been found we believe that all of the ninety-two different "building blocks of the world" have been discovered. We see also that atomic numbers are more fundamental than atomic weights,

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so the new periodic classification of the elements is based on their atomic numbers.

The Periodic Law

The chemical properties of elements are periodic functions (not of their atomic weights, but) *of their atomic numbers.*

What is meant by "isotopes"? All atoms are composed of protons and electrons as you have seen, but the weight of all the electrons in any atom is negligible compared with the weight of its protons. Since the relative weight of a proton (a hydrogen nucleus) is 1, it would seem that the atomic weights of all the elements should be whole numbers. This idea was first suggested by Prout a long time ago. (See page 336.) As atomic weights were determined more and more accurately, it was found that many of them certainly were *not* whole numbers. Prout's idea, which gained little recognition, was dropped until about 1910. Soddy, an English physicist, revived it by suggesting that all atomic weights *could* be whole numbers, if elements like chlorine (Cl = 35.46) were considered as mixtures of two kinds of atoms. Suppose they are Cl = 35 and Cl = 37, mixed in such amounts as to make their average Cl = 35.46. Shortly after this astounding prediction two different kinds of chlorine atoms were discovered by the use of the mass spectrograph and, as predicted, they had atomic weights of 35 and 37. Recently a third kind of chlorine has been reported with atomic weight 39. It is very rare and its existence has been questioned. These three different kinds of chlorine atoms have the same atomic number so they are identical in their chemical properties; they differ only in atomic weights. They are called *isotopes*, have the same atomic number, and occupy the "same space" in the periodic chart.

The nuclear structures of the three isotopes of chlorine are shown in Fig. 115. Of course, the arrangement of the planetary electrons is the same in all, Cl: 2, 8, 7. Note that the isotope Cl = 35 has 17 protons and 18 neutrons in its nucleus which

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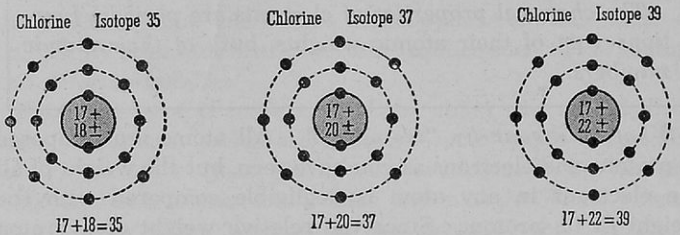
give it a weight of 35, and an atomic number of 17. Isotope Cl = 37 has 17 protons and 20 neutrons in its nucleus, and its atomic number is also 17. If isotope 39 exists, it has 17 protons and 22 neutrons, so again its atomic number is 17.



115. ISOTOPES OF CHLORINE. Note that in these diagrams the number and arrangement of the electrons are the same in all cases. This means that the chemical properties of the element are the same. Note however that the *nuclei* are different which makes the weights of these isotopes different.

Isotopes of many other elements have been, and continue to be, found. A few elements that are known to have isotopes are listed in the table on the next page.

One of the most interesting isotopes recently discovered (1932) and prepared is called deuterium (D) or "heavy hydrogen" (H = 2), because this isotope is twice as heavy as ordinary hydrogen. The weights of "heavy hydrogen" compounds are noticeably greater than the weights of compounds of ordinary hydrogen. Other properties likewise may be affected. For example, "heavy water" ($D_2O = 20$) is one-tenth heavier than ordinary water, has a higher freezing point and a higher boiling point, and is believed to be poisonous to plant life and small animals. It is difficult to predict just how the properties of other compounds containing this isotope of hydrogen may be changed. A whole new field of chemistry may result.

Isotopes of hydrogen and of nitrogen have given physiological chemists a new "tool" for their work. They use these atoms in "tagging" fat or protein molecules so they may follow them more easily in physiological processes.

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Isotopes of a Few Elements

(*In order of decreasing abundance for each element*)

Element	*Symbol*	*Atomic Number*	*Atomic Weight* (average)	*Weights of Isotopes*
Lithium	Li	3	6.94	7, 6
Neon	Ne	10	20.18	20, 22, 21
Zinc	Zn	30	65.38	64, 66, 68, 67, 70
Bromine	Br	35	79.92	79, 81
Tin	Sn	50	118.7	120, 118, 116, 119, 117, 124, 122, 121, 112, 114, 115
Lead	Pb	82	207.2	208, 206, 207, 205, 212, 210, 204, 202, 203, 211, 201, 209, 216, 215, 214, 213

Readings for Pleasure and Profit

Clarke, Beverly L. *Marvels of Modern Chemistry.* Chap. IX, pp. 131-148, "Classification of the Elements."

Darrow, F. L. *The Story of Chemistry.* Chap. II, pp. 45-50, "Periodic Systems."

Foster, William. *The Romance of Chemistry.* Chap. XVI, pp. 239-260, "Classification of the Elements."

Holmes, Harry N. *Out of the Test Tube.* Chap. XI, pp. 128-136, "The Grand Plan."

Jaffe, Bernard. *Crucibles.* Chap. XI, pp. 199-218, "Mendeléeff"; Chap. XV, pp. 289-311, "Moseley."

Tilden, Sir William. *Chemical Discovery and Invention in the 20th Century.* Chap. VI, pp. 107-130, "The Elements of the Chemist."

Putting Chemistry to Work

A

(**1**) How is a knowledge of the periodic table useful? (**2**) Explain the relation of a row of elements that make a period. (**3**) How can you tell where the end of a period is? (**4**) Why are the periods put under one another? (**5**) Explain both words in the phrase "periodic classification." (**6**) Point out ways in which the periodic classification of the elements has made your work in chemistry more systematic. Give specific instances. (**7**) Why is Mendeléeff given credit for the periodic classification although Newlands' work

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preceded his? (8) Point out three valuable scientific traits shown in Mendeléeff's work. To what extent do you possess them? (9) What justification is there for calling atomic numbers the *natural serial numbers* of the atoms?

B

(10) The atomic number of selenium is 34. You can therefore expect selenium to be (a) an acid-forming element; (b) a base-former; (c) an inert gas; (d) an amphoteric element; (e) a transition element. Give your reasoning for the answer you choose. (11) List the following scientists in chronological order: Moseley, Dalton, Arrhenius, Mendeléeff. (12) Draw "pictures" of the isotopes of neon; of hydrogen and deuterium. (13) Why was it so difficult for scientists to discover isotopes of elements? (14) Why and to what extent is the periodic chart based on atomic numbers more helpful than a chart based on atomic weights?

Research and Activities That You Will Enjoy

A "sales" talk: Organize a committee of eight to present to the class Kendall's "apartment-house" conception of the grouping of the elements. (See Kendall, *At Home among the Atoms.*) Very interesting and clever points may result if each member sponsors one apartment and tries to "rent" it to the class by showing the service qualities of the elements in it.

Problem 39

HOW AN OBSERVATION, AN ACCIDENT, AND AN ERROR LED TO THE DISCOVERY OF A SERIES OF RADIOACTIVE ELEMENTS [1]

About the end of the nineteenth century many self-satisfied scientists were grumbling, "All the great discoveries have been made; if we had only lived sooner." They little realized that three important discoveries were waiting for diligent workers and keen observers—discoveries which would open up an entirely new field of practical and theoretical science,

[1] Special information concerning atomic energy is given on page 793.

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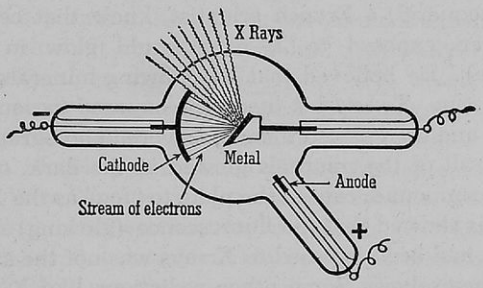
to help heal the sick, to help solve the mystery of matter, and even to indicate the age of the earth itself. These scientific achievements read more like fiction than fact.

How Crooke's cathode-ray tube led the way to an important discovery. This important series of events started with a discovery by Sir William Crookes, an English scientist. He observed that a powerful electric discharge in a high-vacuum tube produces a greenish-yellow glow (fluorescence) at the end of the glass tube opposite the cathode. It was evident that the mysterious rays coming from the cathode of the tube were not ordinary light rays because they were deflected by a magnet. Later, Sir Joseph J. Thomson showed that these cathode rays are a stream of fast-moving electrons, the same negative particles that are produced in your radio tubes today.



116. Diagram of an X-ray Tube. Electrons are shot off from the cathode at high velocity. When they strike the tungsten target they give rise to X rays.

How Roentgen accidentally discovered X rays. The second link in this marvelous chain of events was the result of an accident. But fortunately for all of us this accident occurred to a keen observer with a scientific insight and experimental ability. Wilhelm Roentgen, a German physicist, was working with a Crookes (cathode-ray) tube in his laboratory. Nearby lay an unexposed photographic plate well covered with heavy black paper. One may well imagine that a bunch of keys or

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some object rested on the covered plate. In any event, when quite by accident this plate was developed along with others, it showed a shadow image. Of course, Roentgen repeated the experiment, and he obtained a picture of the bones of a hand. Here were new mysterious rays which, unlike ordinary light, could penetrate certain solid objects like paper, wood, flesh, but not metals. Because the nature of these rays was unknown, Roentgen called them *X rays*. We now know that X rays are very similar to light waves except they are much shorter and, therefore, more penetrating. In the modern X-ray tube, when fast-moving electrons are stopped suddenly by a target of dense tungsten metal, these powerful radiations appear. X rays are generated by the impacts of electrons on solids.

How an error gave radium to the world. The third scene in this scientific drama was the result of an error in reasoning. Henri Becquerel, a French scientist, knew that certain minerals when exposed to X rays would glow in the dark (fluoresce). He believed that the glowing minerals were giving off X rays. To test his theory he exposed various minerals to X rays and then placed them on covered photographic plates. Although all of the minerals glowed in the dark, only one, a uranium compound, caused the plate to "fog" as the X rays had done. This showed that the fluorescence (glowing) of the minerals that had been exposed to X rays was not the same as the X rays themselves. Some other radiations like X rays were "fogging" the plate. Although Becquerel's theory was wrong, he was on the trail of a great discovery. He tried other uranium compounds and found that they all emitted radiations which, like X rays, could penetrate solid objects. Here was a new and strange property of matter—the ability to emit radiations which could go through solid objects. This is called *radioactivity*.

How the Curies obtained radium from pitchblende. While studying pitchblende, an ore containing uranium, Becquerel found that it had an even greater effect on a photographic plate than other uranium compounds he had tried. He suspected that the unexpectedly great effect was due to a new and unknown element in the pitchblende. Madame Marie

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Curie and her husband undertook to find the cause. The unbelievably difficult task of the Curies consisted of separating the many substances in pitchblende. They boiled and cooked a ton of the ore which was supplied by the Austrian government. By ordinary chemical analysis, using many tons of reagents, they precipitated, filtered, and separated impurity after impurity, always checking each portion to see that the cause of the radioactivity was not lost. Finally, after almost endless work, they found two residues, one with bismuth and the other with barium, that contained more activity than any of the other materials. In the bismuth fraction the activity was due to a new element which they called *polonium*. The name *radium* was given to the new radioactive element in the barium residue.

But the work was far from completed. There remained the difficulty of separating the radium compound from the barium impurities which it closely resembled chemically. After repeated *fractional crystallizations* (page 130) about 0.2 gram of a radium salt was obtained which was judged to be pure. Its radioactivity was about one million times greater than that of uranium. Twelve years later (1910) Madame Curie completed her important work by isolating metallic radium itself by electrolysis. In most respects chemically it is like calcium and barium, so it belongs in this family of elements. Since radium tarnishes rapidly in air, only its compounds, usually radium bromide, are in use. These compounds are usually meant when the term radium is used.

Madame Curie received the following tribute from Professor Holmes, of Oberlin College. "Twice awarded the Nobel Prize, elected to succeed her husband as Professor of Physics at the Sorbonne, twice given a gram of the costly radium by the citizens of the United States, honored by kings, presidents, and the great scientists, Marie Sladowska Curie, simple and unassuming, will forever hold a unique place in history. Yet, like Faraday, she had first been engaged to wash dishes in a great laboratory."[1]

[1] "Out of the Test Tube," by Holmes.

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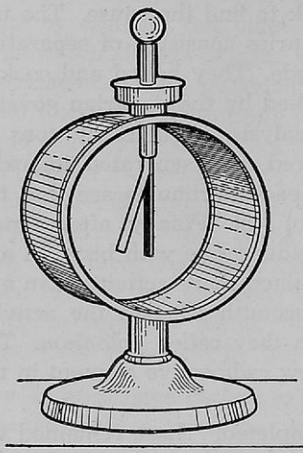

An electroscope consists of two leaves of gold leaf supported by a rod and inclosed in a case. When charged with static electricity, the leaves are widely separated because similar charges repel each other. When discharged, the leaves hang together. Ionized gases, by bringing ions to the electroscope, can neutralize the charge on the leaves. Radioactive substances ionize the gases in the air. Hence their presence can be detected by the electroscope.

117. ELECTROSCOPE

WHAT ARE THE QUALITIES OF RADIUM AND OTHER ELEMENTS IN THE RADIOACTIVE SERIES?

Since the discovery of the radioactivity of uranium, polonium, and radium, many other heavy elements have been found to possess these qualities. Whatever is said here of radium applies also to other radioactive elements, except with differences in degree.

Radium ionizes gases. This is shown when a minute quantity of radium is brought near a sensitive electroscope that has been charged with static electricity. (See Fig. 117.) When the radium is brought near the electroscope, the gases in the air nearby become ionized—that is, they break up into ions having electric charges. The charged electroscope attracts the ions of opposite charge and therefore it is discharged by them.

The electroscope was very useful in the discovery of radium and other similar elements. In hospitals small tubes of radioactive materials are frequently used for the treatment of certain diseases. If a tube is overlooked or thrown out with

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waste materials, hospital attendants go on a search with a charged electroscope. When it discharges, they know that they are near the lost radioactive materials.

Radium compounds glow in the dark. Madame Curie herself tells of this property. "One of our joys was to go into our workroom at night; we then perceived on all sides the feebly luminous silhouettes of the bottles or capsules containing our products. It was really a lovely sight and always new to us. The glowing tubes looked like faint fairy lights." Radium compounds also cause certain other compounds, such as zinc sulfide, to glow in the dark. This property is utilized in luminous watch dials and similar objects. A minute quantity of some radium (or other radioactive) compound is mixed with a large amount of zinc sulfide (about 1 to 100,000). The mixture is then used to paint the hands and figures on the dial. A similar effect is observed when a minute quantity of radium is brought near a zinc sulfide screen; the screen glows in the dark. This glow, when viewed through a microscope, is seen to consist of numerous tiny flashes of light. Such an arrangement is called a *spinthariscope*.

Radium gives off "rays." The preceding and many other experimental studies of radium and other radioactive elements show that they emit three kinds of "rays," or emanations. These are called *alpha rays, beta rays,* and *gamma rays.* The first two types of emanations are streams of charged particles. This is shown when these rays are allowed to come under the influence of a magnetic field. The alpha and beta rays are deflected in opposite directions since they are oppositely charged. The gamma rays are not deflected by a magnetic field since they are pulsations and contain no charged particles.

How alpha, beta, and gamma rays are identified. Alpha (α) *rays* have been identified as a stream of the nuclei of helium atoms. They are helium atoms without their two outer electrons, so each particle has a positive charge of two. They are shot out of the radium atoms in straight lines with a velocity that is about one-tenth of the velocity of light. Alpha particles are the least penetrating of the three kinds of "rays,"

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being able to pass through only a few centimeters of air. A very thin sheet of aluminum foil (0.1 mm) or a sheet of paper can stop them. But they produce an intense ionization of the gases through which they pass as shown by the rapid discharge of an electroscope. Alpha rays produce severe burns.

Beta (β) *rays* are streams of fast-moving electrons, like cathode rays, sometimes approaching the speed of light (186,000 miles a second). Consequently, they have a much greater penetrating ability than alpha rays; they can pass through a sheet af aluminum several millimeters in thickness.

Gamma (γ) *rays,* which are a sort of super X rays, are generated by the impacts of electrons on surrounding substances. Gamma rays travel with the speed of light and are very penetrating. They can go through several centimeters of ordinary metals almost as easily as light passes through glass. Gamma rays are waves like light waves but are much shorter.

Atoms of radioactive elements disintegrate spontaneously. Here is the explanation given to the unusual behavior of radium, uranium, and other radioactive elements: Radioactivity is not at all like ordinary chemical changes. It is the result of atomic explosions—minute nuclear volcanic eruptions. Alpha or beta particles are hurled out of the nucleus of a radioactive atom with tremendous force. Man can do little about this process; he cannot stop it and until recently could not start it. Even so, he has very little control over them as he does have over most chemical changes. Ordinary chemical changes occur between atoms or ions; changes involving radioactivity occur *within* the atoms.

The preceding explanation is based upon a large number of observations and ideas in addition to the ones previously mentioned. (1) All radium compounds produce a gas, called *radon,* which is the residue left when atoms of radium lose alpha particles (helium). (2) Radon itself is also radioactive and disintegrates, leaving a solid residue which in turn is radioactive. (3) Every uranium ore always contains both radium and radon, and the amounts depend upon the quantity of uranium in the ore. (4) Pure uranium compounds emit only

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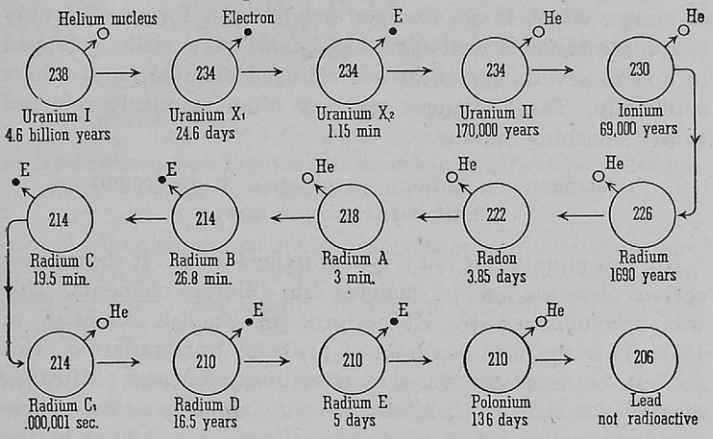
alpha particles, but after a time, due to the formation of intermediate radioactive products, beta particles also are given off. Likewise, pure radium compounds and radon emit only alpha particles but soon their disintegration products throw off beta particles. (5) All uranium ores contain inactive lead; the end of the trail for radioactive elements is lead (Fig. 118).



118. Uranium Series of Radioactive Elements

• *What is the "half-life" of a radioactive element?* You have seen that uranium is the starting point, or parent-element, for a whole series of radioactive elements. As each disintegrates, losing an alpha or a beta particle, a new element is formed, which by disintegration in turn furnishes another element. Each radioactive element has its own rate of disintegration. This is often expressed as the "half-life period," or the time in years, days, minutes, or seconds before a given amount of the substance will have decreased to half of the original amount. The figure on this page shows this period for each element. It also shows the successive disintegration products caused by the loss of alpha particles (helium nuclei) or beta particles (electrons).

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• *How can one element be changed into another?* Many years ago the alchemists dreamed of changing one element into another. Here we have it occurring in nature but in a far different manner from that which anyone even dared to dream:

radium → radon + helium (natural transmutation)

This means that we can no longer define an element as a form of matter which is not changed into simpler forms. Not only is transmutation a well-established fact, but man has stepped in and in several instances has changed elements into others artificially. These changes are now often popularly referred to as "smashing" atoms.

nitrogen + helium → oxygen + hydrogen
(artificial transmutation)

No, this equation is not a typographical error. It shows how certain elements may be changed into different elements. This was accomplished by Rutherford, an English scientist, in 1919. It is the first example of artificial transmutation. But do not be mislead; this is no ordinary change. Nitrogen atoms were shot at (bombarded) with alpha particles of tremendous energy. Most of the shots were misses, that is, the alpha particles failed to hit the nucleus of a nitrogen atom. But about one out of a million alpha particles hit its mark, stayed in the nucleus but knocked out a proton, and thus left an atom of an isotope of oxygen. The previous equation, showing the atomic number above and the atomic weight below each element, is as follows:

7		2		8		1
nitrogen	+	helium	→	oxygen	+	hydrogen
14		4		17		1

It should be remembered that such a change is not an ordinary chemical change which involves only the outer electrons of an atom. A transmutation, such as this one, occurs when particles are rearranged within the nucleus of an atom. This shows that an atomic nucleus is far more complicated than

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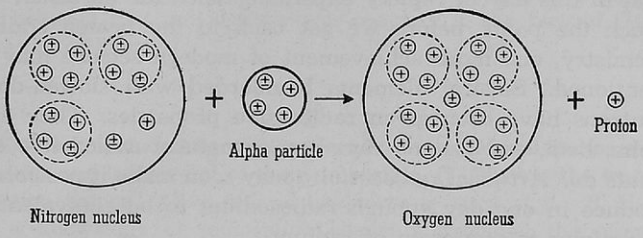
was previously believed. The following "picture equation" may give you a better idea how such transmutations of elements are possible. It is a study in *nuclear chemistry.*



119. Transmutation of Elements. If an alpha particle can be added to a nitrogen nucleus, an oxygen nucleus and a proton will result.

Several other similar artificial transmutations have been performed. Thus, boron has been changed to carbon, fluorine to neon, sodium to magnesium, aluminum to silicon, phosphorus to sulfur, and others.

• **What two new subatomic particles are recent discoveries?** The bombardment of beryllium with alpha particles resulted in a most unusual discovery. Particles having tremendous penetrating ability were emitted from the beryllium atoms. These particles carried no electrical charge; they were neutral. They are called *neutrons.* A neutron has almost the same weight as a hydrogen atom but it is much smaller. It is believed by some to be a compact bundle of one proton and one electron.

Still another kind of particle has been discovered in connection with cosmic ray studies. It is called a *positron,* or a positive electron. It seems that both neutrons and positrons are in the nuclei of atoms. If this is true, then we have four kinds of "universal building blocks": protons, electrons, neutrons, and positrons. You studied about all of these four kinds of "building blocks" in Unit 4 in this book. This lesson has given some of the evidence which has lead scientists to believe in the existence of these four different types of units of matter.

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This short study in nuclear chemistry has taken us far afield—to the very frontier of theoretical physical science. But who can say when a theoretical study will become practical in this day of rapidly expanding scientific horizons? To clinch the point, before we get back to the beaten trail of chemistry, one more achievement of modern science may be mentioned. Several elements bombarded with slowed-down neutrons have been given radioactive properties. They emit alpha, beta, and gamma rays just as natural radioactive elements do. *Artificial radioactivity* may soon make it possible to produce in one day enough radiosodium to be equivalent in its activity to one gram of radium.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. XX, pp. 383-397, "Radium"; Chap. XXI, pp. 409-421, "The Structure of Stuff"; Chap. XXII, pp. 422-433, "Seeing through Things."

DARROW, F. L. *The Story of Chemistry.* Chap. III, pp. 79-151, "Atoms, Electrons, and Protons."

DAVIS, WATSON. *The Advance of Science.* Chap. VII, pp. 75-82, "Heavy Hydrogen."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XV, pp. 218-238, "Wonders of Radium."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XII, pp. 137-158, "The Fall of the House of Uranium."

JAFFE, BERNARD. *Crucibles.* Chap. XIII, pp. 242-264, "Curie"; Chap. XIV, pp. 265-288, "Thomson"; Chap. XVI, pp. 313-338, "Langmuir."

KENDALL, JAMES. *At Home among the Atoms.* Chap. XV, pp. 204-220, "The First and Second Floors."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. VII, pp. 130-156, "Discovery and Properties of Radium"; Chap. VIII, pp. 156-169, "Structure and Disintegration of Atoms."

Putting Chemistry to Work

A

(1) In what two ways could you determine whether, or not, a substance is radioactive? (2) In what different ways can a chemist start or stop ordinary chemical reactions? Do these apply to the

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disintegration of radioactive elements? (3) What is meant by saying that "lead is the graveyard of radioactive elements"? (4) How did the fact that uranium oxide ore is more radioactive than pure uranium oxide help in the discovery of radium. (5) Why was it at first believed that radioactivity was contrary to the Law of Conservation of Energy?

B

(6) What is meant by *radioactivity?* Name several radioactive elements and list several of their properties. (7) What is the transmutation theory? Give several evidences to support it. (8) How has a knowledge of radioactive elements extended the atomic theory? (9) Using the half-life period as an indication of the intensity and permanence of the activity of radioactive elements, show why radium is a better source of radiations than radium A or uranium. (10) When a radioactive element loses an alpha particle or a beta particle, what happens to the atomic weight, the atomic number, and the valence of the product? (11) Point out several isotopes among the radioactive elements. (12) The use of neutrons as bombarding particles in artificial transmutation has what advantage over the use of other particles?

Research and Activities That You Will Enjoy

A helpful chart: Make a chart showing the various kinds of electromagnetic waves related to light. Include gamma rays and X rays. Explain the source of each kind of wave.

A report: After outside study and careful organization of the topic, tell the class about the commercial production of radium.

The Curies: Tell the class what you consider the most interesting and important points in "Marie Curie, My Mother," by Eve Curie. (Refer to the book or see *Ladies' Home Journal,* July, 1938, page 85.)

Looking Back into Unit 8

Be sure you know the purpose of this unit. Read again the material on page 310, "Looking Ahead into Unit 8." Then study the following Summary Test.

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Summary Test

1. *How is chlorine a typical member of a family of nonmetallic elements?*
   (a) What is meant by a chemical family?
   (b) How is chlorine prepared?
   (c) What are the properties of chlorine?
   (d) How is chlorine used—
      (1) In bleaching?
      (2) In killing dangerous bacteria?

2. *How are the halogens a typical chemical family of elements?*
   (a) How are the halogens alike? How do they differ?
   (b) How are the halogen hydrides similar in properties?
   (c) How is the activity of the halogens determined?
   (d) How are the halogens and their compounds used?
   (e) How can you identify the combined halogens?

3. *How can the family tree of elements be represented by the periodic chart?*
   (a) What early attempts were made to group the elements?
   (b) How did Mendeléeff successfully form a family tree of elements?
   (c) How can the periodic chart be interpreted as a family tree?
   (d) How is the periodic chart used?
   (e) What imperfections are in the periodic chart?

4. *How did an observation, an accident, and an error lead to the discovery of a series of radioactive elements?*
   (a) How did Crooke's cathode-ray tube lead the way to an important discovery?
   (b) What contribution did Roentgen make?
   (c) How was radium discovered?
   (d) What are the qualities of radium and other radioactive elements?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

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Closing the Unit

Man is constantly labeling and organizing the things of the world in which he lives. Have you, in your study of chemistry, followed this dramatic story of the *classification* and *discovery* of *matter?* The work of Newlands, Mendeléeff, Moseley, and others has culminated in the *periodic chart* as we now have it. This important chart helps to classify and organize an apparently chaotic world and more firmly establishes chemistry as an exact science. Again you find the *electron theory* strengthens the facts brought out by the *periodic chart.*

Large amounts of *chlorine* (or some of its *unstable* compounds) are used in *water purification,* in *bleaching,* in *disinfection,* and in *deodorizing.* These are worthy *peacetime* uses, but in times of *war,* chlorine is used as a dreadful poison in gas warfare, either directly or in such compounds as *phosgene* and *mustard gas.* Since this fact is true, some people condemn the progress of science. You and other intelligent people of the world should make every effort to see that the fruits of chemistry are directed into beneficial channels. This is a problem that has faced mankind for a long time.

The *compounds* of the *halogens* serve many of our greatest needs, sometimes directly and sometimes as the source material for other chemicals. *Sodium chloride* is the most widely distributed and the best-known *salt* in the world. You associate *bromine* and its compounds with such varying uses as antiknock *gasoline, photography, tear gas,* and *medicines. Iodine* has two chief uses, as an *antiseptic* and as a control for *goiter. Fluorine,* the most active nonmetal, produces compounds that are useful in *etching glass,* in *metallurgy,* and in *refrigeration.*

You no doubt like the story of *radium* and admire the devotion of *Madame Curie* to her work. You see in the study of radium further proof for a belief in an *electron theory.* You trust radium's usefulness in the *medical* world will grow. However, you should not let the more or less technical side of *radioactivity* discourage you. Rather, you should appreciate this glimpse into a field of chemical research that in the years to come may prove many of our theories of today.

During your lifetime you may expect and anticipate the solving of more of Nature's riddles. Perhaps you, too, can have a part in their solution. *Do you accept Nature's challenge?*

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Looking Ahead into

Unit Nine

"Boom!" went the stick of dynamite and a hundred million million atoms of unsociable nitrogen went flying and scampering back to their natural home in the air. What did it matter to them in their excitement and eagerness to get away if they lifted a ton of rock out of the hillside where a new concrete road is going through? They were tired of their "nitroglycerin" prison and when the slight jar from the detonating cap gave them their signal, away they flew back to their freedom in the air.

Here they will continue their lazy existence of doing little except getting in the way of busy, active, oxygen molecules. And they perhaps will continue their "loafing" until some energetic engineer recaptures them by his clever process of nitrogen fixation and puts them back to work.

When free atmospheric nitrogen is made to combine with other elements to form compounds which may be used by plants and animals, the process is called nitrogen fixation. Combined nitrogen is far more valuable than free nitrogen.

Two important compounds containing fixed nitrogen are ammonia, in which nitrogen is made to combine with hydrogen, and nitric acid, in which nitrogen is made to combine with both hydrogen and oxygen. In this unit you will learn more about nitrogen fixation and about nitrogen and several of its important and useful compounds. This unit also emphasizes the necessity of controlling industrial processes.

Problem 40. *What Should You Know about the Lazy Element, Nitrogen?*

Problem 41. *How Can You Prepare and Use Ammonia?*

Problem 42. *How Is Nitric Acid Prepared—What Are Its Properties?*

Problem 43. *Explosives—How Is Nitrogen Turned Loose?*

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Nitrogen: A Lazy Element That Must Be "Driven" to Work— Nitrogen and Its Compounds

Problem 40

WHAT SHOULD YOU KNOW ABOUT THE LAZY ELEMENT, NITROGEN?

Nitrogen is one of the most familiar substances on earth. It makes up 78 per cent of the air that is all about you. This means that over 20,000,000 *tons* of free nitrogen are pressing down on each square mile of the earth's surface and approximately 12 pounds of it are pressing down on each square *inch* of your body.

Nitrogen is found in combined form in a few mineral compounds, such as potassium nitrate and sodium nitrate, and in a host of complex organic compounds, called the proteins, which animals must use as food to build up their tissues.

How can you prepare nitrogen for study? The atmosphere contains great quantities of both nitrogen and oxygen. The nitrogen is very inactive or lazy; on the other hand the oxygen, as you have found, is very active and easily forms compounds with many other elements. This suggests a method of obtaining nitrogen by taking oxygen out of air and leaving the nitrogen. To do this, you can burn phosphorus in a volume of air under a jar that is standing in water. The phosphorus combines with the oxygen, forming phosphorus pentoxide which is a compound that readily dissolves in the water and leaves in the jar a volume of gas that consists *mainly* of nitrogen. This nitrogen, however, does contain about one per cent of a mixture of argon, neon, helium, krypton, and xenon, in addition to some moisture and carbon dioxide. (See page 24.)

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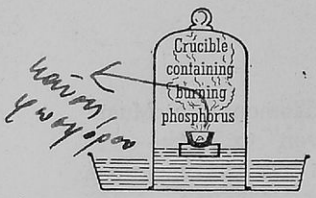
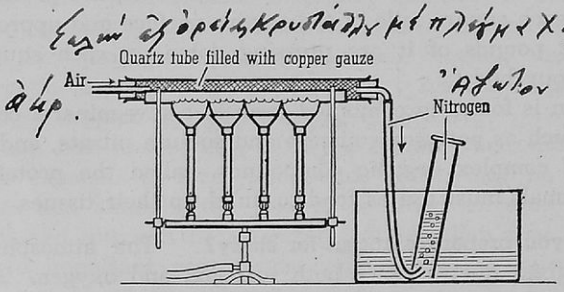


A simple way to obtain nitrogen from the air is to burn phosphorus in a jar over water. The phosphorus combines with the oxygen forming phosphorus pentoxide. This dissolves in the water leaving the nitrogen and the inert gases.

120. OBTAINING NITROGEN FROM THE AIR

It is also possible to remove the oxygen from air by passing the air slowly through a heated tube containing copper particles or copper gauze. The copper combines with the oxygen and leaves the nitrogen. However, copper does not react with oxygen as easily as does phosphorus, and this process consequently is much slower than the preceding one.



121. PREPARING NITROGEN FROM THE AIR FOR STUDY. Air is slowly passed through a quartz tube packed with hot copper gauze. The oxygen is removed by the copper. The nitrogen, with about one per cent of inert gases, passes into the collecting cylinder.

Each of these methods gives nitrogen that is *not* pure. Pure nitrogen may be obtained from the decomposition of certain nitrogen compounds. For example, if you pass *ammonia* (NH_3) through a tube containing hot copper oxide, the ammonia reduces the copper oxide to copper, and nitrogen and water vapor pass out of the tube:

$$2\ NH_3 + 3\ CuO \rightarrow 3\ Cu + 3\ H_2O + N_2\uparrow$$

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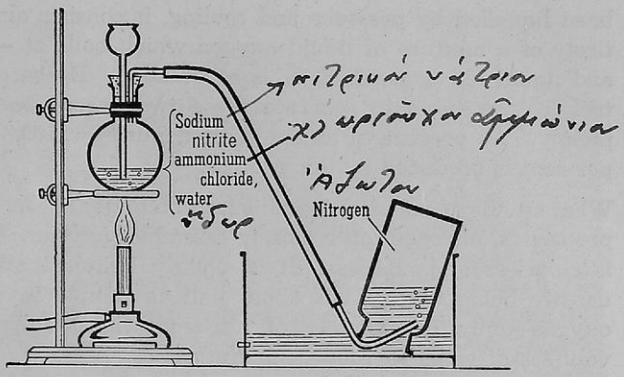

122. LABORATORY PREPARATION OF PURE NITROGEN. If pure chemicals are used pure nitrogen can be prepared by gently heating a mixture of sodium nitrite and ammonium chloride.

An even simpler method of preparing pure nitrogen is to heat a mixture of ammonium chloride and sodium nitrite. These substances react, and sodium chloride is formed; we say also that ammonium nitrite is formed. But ammonium nitrite is unstable. Therefore, water and inactive nitrogen are obtained instead of ammonium nitrite:

$$NH_4Cl + NaNO_2 \rightarrow NaCl + NH_4NO_2$$
$$\longrightarrow 2\,H_2O + N_2\uparrow$$

This reaction is interesting because it is an example of a decomposition reaction that *liberates energy*. After the reaction starts, enough heat is produced to keep the reaction going. This reaction often becomes so violent that, in order to control it, the flask must be cooled. If the reagents used are pure, the gaseous product will be pure nitrogen. The frequently used technical grade of reagents may produce some impurities having an odor.

How does industry get nitrogen for use? Industry meets its demand for nitrogen by obtaining it from liquid air. You found in Unit 2 that oxygen and nitrogen can be separated because of a difference in their boiling points. After air has

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been liquefied by pressure and cooling, it consists almost entirely of a mixture of liquid oxygen which boils at —183° C. and liquid nitrogen which boils at —195° C. By careful control it is possible to separate these two gases almost completely. At present, nitrogen with a purity of 99.8 to 99.9 per cent is produced by this process.

What are the physical characteristics of nitrogen? In physical properties, nitrogen quite closely resembles oxygen. Nitrogen is colorless and odorless. It is slightly lighter than air, its density being 0.967. It is about half as soluble in water as oxygen—only 1.5 volumes of nitrogen will dissolve in 100 volumes of water at room temperature.

What are the chemical characteristics of nitrogen? In sharp contrast with oxygen, nitrogen does not unite easily with other elements to form compounds. It must be forced into combination by using much energy. At high temperatures it can be made to combine with a few elements such as magnesium, lithium, and aluminum to form nitrides whose formulas are Mg_3N_2, Li_3N, and AlN.

Nitrogen can also be made to unite with oxygen by passing a mixture of nitrogen and oxygen through an electric arc. A small part of the nitrogen combines with oxygen to form nitric oxide. Similarly the energy of an electric spark can be used to force a small amount of nitrogen and hydrogen to unite, thus forming ammonia. Methods of preparing ammonia will be described later.

Nature has an important way of combining free nitrogen (nitrogen fixation). Upon the roots of beans, peas, clover, and other leguminous plants are nodules. When these nodules are examined under a powerful microscope, they are found to be the homes of great masses of "nitrogen-fixing" bacteria. The bacteria have the ability to extract nitrogen from the air and to convert it into soluble nitrates. These nitrates renew the fertility of soil since plants use them for food. Every plant must have nitrogen to live but no plant or animal can use free nitrogen; soluble *compounds of nitrogen* must, therefore, be present in every fertile soil.

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Courtesy, The Barrett Company

123. NITROGEN COMPOUNDS ARE FERTILIZERS. The field at the right in this illustration has been treated with nitrogen compounds as fertilizer. The field at the left was without nitrogen fertilizer.

Although the ability of nitrogen to unite with other elements is quite limited, whenever you do find a compound of nitrogen, you have a compound that will do something—one that has possibilities of doing good or evil. When nitrogen is combined with certain elements, we have *dyes* that rival the rainbow in the brilliance of their colors; while with other elements nitrogen forms *drugs* such as morphine, quinine, and acetanilid which ease pain and combat diseases. In other compounds nitrogen forms some of our most powerful *explosives* such as nitroglycerin and guncotton; and in still others it forms some of the deadliest poisons such as the cyanides and the ptomaines. Some of the compounds of nitrogen furnish us with pleasant-tasting flavors and with sweet perfumes; while others are so vile in taste and odor that they are beyond description. In nitric acid we find nitrogen in a strong acid and in ammonium hydroxide we have it in a well-known base.

Nitrogen compounds are in all fertile soils, for plants must have soluble nitrogen compounds for food. With these compounds the plants manufacture plant proteins which animals must use to build up their tissues. The physical basis of life

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is the plant or animal cell. The contents of this cell, the protoplasm, is a mixture of proteins—compounds containing nitrogen. Without nitrogen there could be no life.

Since nitrogen must be "over-persuaded" when it unites with other elements, it is very ready to withdraw from compounds, thus releasing the energy that went into the making of the compound, frequently with explosive violence. Because of these facts, nitrogen compounds in general are said to be unstable, reacting chemically by decomposition.

A Principle for You to Remember
Inactive elements form unstable compounds.

While nitrogen compounds are very numerous, only a few of the simpler ones will be described in this book. These are ammonia, ammonium compounds, nitric acid and its salts, and some of the oxides of nitrogen.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff*. Chap. II, pp. 39-44, "Nitrogen."

CLARKE, BEVERLY L. *Marvels of Modern Chemistry*. Chap. XI, pp. 159-161, "Nitrogen."

FOSTER, WILLIAM. *The Romance of Chemistry*. Chap. XIII, pp. 188-191, "Nitrogen."

Applying in Life What You Have Learned in Chemistry

A study hint: A good thinker learns how to explain processes to himself and to others.

Putting Chemistry to Work

A

(1) Since nitrogen, like water, can be obtained in the form of a gas, a liquid, or a solid, why do we say that water is a liquid but that nitrogen is a gas? (2) Suppose you were told that five bottles of gases contain oxygen, hydrogen, nitrogen, carbon dioxide, or argon. Give in detail the methods by which you would distinguish them. (3) When nitrogen is obtained from air by liquefaction and evaporation, what other elements of similar properties remain with it as impurities? (4) When nitrogen is obtained from NH_4NO_2, are

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

the inert gases present as impurities? Prove your answer by quoting a chemical law. (5) How could you determine, by very carefully weighing it, whether a sample of nitrogen came from air or from NH_4NO_2? (Hint: See the atomic weights of the inert gases.) (6) If you did not know the weight of a liter of nitrogen, how could you use the following facts to calculate it? Air is approximately one-fifth oxygen and four-fifths nitrogen by volume. One liter of air weighs 1.29 g; one liter of oxygen weighs 1.43 g. (Hint: What is the weight of five liters of air? What volume and what weight of these five liters is oxygen? What is the volume and the weight of the remaining gas?)

B

(7) Why is it incorrect to call nitrogen an inert gas? What term could you correctly apply to it? (8) Name some gases which will be present as impurities when nitrogen is prepared by passing air over heated copper. (9) What is wrong with the following: $2\,Ne + O_2 \rightarrow 2\,NeO$?

Problem 41

HOW CAN YOU PREPARE AND USE AMMONIA?

Ammonia (NH_3) is a simple compound of nitrogen and hydrogen which was known to the alchemists. They prepared it by distilling hoofs, horns, leather scraps, and other animal refuse. This process produced a bad-smelling mixture from which ammonia was separated. Since the alchemists thought that the best ammonia was obtained by distilling deer antlers, they called this nitrogen compound "Spirits of Hartshorn."

How does nature form ammonia? Nature forms ammonia by the decomposition of proteins. Proteins are complex organic substances of great molecular weight, containing approximately sixteen per cent of their weight in nitrogen. When they undergo decomposition, one of the decomposition products is ammonia. The odor of ammonia so often noticed around manure piles and other decaying organic matter comes from this source.

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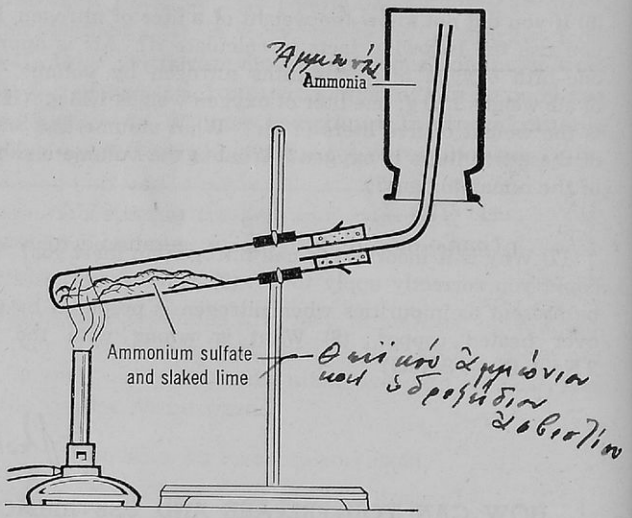
How can you prepare ammonia in the laboratory? You can prepare ammonia in the laboratory by allowing an ammonium compound to react with an active base. By gently heating



124. LABORATORY PREPARATION OF AMMONIA

a mixture of ammonium sulfate and slaked lime (calcium hydroxide), you get, by double decomposition, calcium sulfate and ammonium hydroxide. The ammonium hydroxide is unstable and decomposes, producing ammonia and water:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2\,NH_4OH$$
$$\hookrightarrow 2H_2O + 2NH_3\uparrow$$

A Principle for You to Remember

Any ammonium salt which furnishes ammonium ions (NH_4^+) will react with *any* active base which furnishes hydroxyl ions (OH^-) to produce ammonium hydroxide, which by its decomposition yields ammonia.

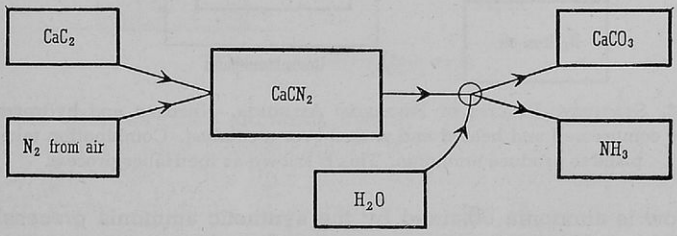
Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Sometimes when only small quantities of ammonia are needed, you can prepare it by gently heating a solution of ammonium hydroxide:

$$NH_4OH \rightarrow H_2O + NH_3\uparrow$$

How is ammonia obtained for industrial use? Until rather recently most of the ammonia used for industrial purposes was obtained by the distillation of coal. When coal is heated in a retort to produce coke, ammonia is given off with other gases. About five or six pounds of ammonia may be obtained from a ton of coal. The ammonia comes from the decomposition of nitrogen compounds in the fossil vegetation which makes up the coal.

This process does not supply enough ammonia to meet the demand, so new processes have been developed. Among these are the *cyanamide* process and the *synthetic* ammonia process. The production of fixed nitrogen from the atmosphere has increased nearly tenfold since 1923. (See Fig. 133, page 383.)



125. CYANAMIDE PROCESS OF PREPARING AMMONIA. Calcium carbide may be combined with nitrogen to form calcium cyanamide. This reacts with steam to form ammonia.

How is ammonia obtained by the cyanamide process? In the cyanamide process calcium carbide is heated with nitrogen in an electric furnace, producing calcium cyanamide and graphite (carbon):

$$\underset{\text{calcium carbide}}{CaC_2} + \underset{\text{nitrogen}}{N_2} \rightarrow \underset{\text{calcium cyanamide}}{CaCN_2} + \underset{\text{carbon}}{C}$$

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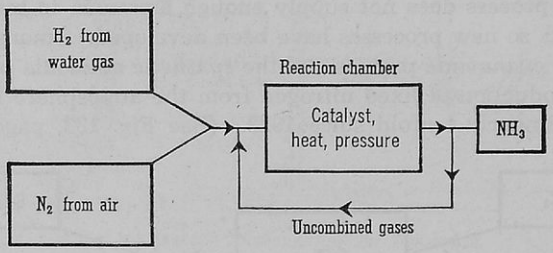
The calcium cyanamide, when treated with steam, yields ammonia:

$$CaCN_2 + 3\ H_2O \rightarrow CaCO_3 + 2\ NH_3\uparrow$$

One of the largest plants ever built for the production of ammonia by the cyanamide process is the plant of the American Cyanamide Company at Niagara Falls. Many nations are interested in ammonia since, as you will learn later in this unit, it can be converted into nitric acid for the manufacture of explosives.

Not all calcium cyanamide is used to prepare ammonia; some is sold under the trade name of "Nitrolime" as a nitrogenous fertilizer.



126. SYNTHETIC PROCESS OF PREPARING AMMONIA. Nitrogen and hydrogen are compressed and heated and passed over a catalyst. Combination takes place to produce ammonia. This is known as the Haber process.

How is ammonia obtained by the synthetic ammonia process? The synthetic ammonia process is at present by far the most important source of ammonia. This process is also known as the *Haber process*, a name taken from its inventor. A mixture of nitrogen and hydrogen, under great pressure, is heated to about 500° C. in the presence of a catalyst. Under these conditions about 15 to 20 per cent of the mixture of gases combines to form ammonia:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

The catalyst used in this process in this country consists of finely divided iron mixed with oxides of potassium and

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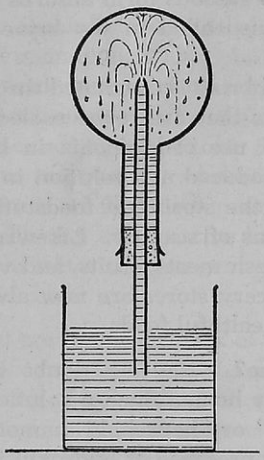
aluminum. This is the most efficient catalyst known for the purpose. Since the reaction is reversible, close attention must be paid to temperature and pressure, and the ammonia must be removed from the field of action as fast as it forms.



A flask is filled with dry ammonia gas. A rubber stopper fitted with a long jet tube is inserted. The lower end of the tube is placed in water. Soon the water spurts up. If the water is colored with red litmus solution, it becomes blue when it shoots up in the flask. The great solubility of the ammonia creates a partial vacuum, and the air pressure forces the water into the flask. The ammonia solution contains some ammonium hydroxide which changes the color of the litmus.

127. AN AMMONIA FOUNTAIN

What qualities make ammonia useful? Ammonia is a colorless gas with a strong, pungent odor. It is much lighter than air ($17/29 \doteq .586$). One liter under standard conditions weighs 0.78 gram. Ammonia is extremely soluble in water; about 1100 volumes of ammonia will dissolve in one volume of water that is at the freezing point. The critical temperature[1] of ammonia is quite high (132.4°), so the gas can be liquefied easily by pressure alone. Liquid ammonia boils at —33° C. and has a high heat of vaporization. One gram of liquid ammonia absorbs 327.1 calories of heat in changing its state from a liquid to a gas. Consequently it is a common substance used in artificial refrigeration plants. It also reacts readily with acids to form ammonium salts which have many important uses in industry.

[1] The critical temperature of a gas is the temperature above which it cannot be liquefied by pressure alone.

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How is ammonia used to make ice and to preserve your food? In ice plants ammonia is liquefied by a powerful compressor. After the liquid ammonia has cooled, it is allowed to evaporate and expand in metal pipes that are immersed in brine. The change of state from liquid form to gaseous form absorbs heat from the brine. Cans of water suspended in the brine are soon frozen into blocks of ice.

In refrigerating plants the cooled brine is circulated through pipes to the rooms or refrigerators that are to be cooled.

In recent years the widespread use of ammonia in large artificial refrigeration units has produced a revolution in our food habits. It has made possible the storing of foodstuffs in seasons of plenty for use in seasons of scarcity. Likewise, it has encouraged the shipment of fresh meats, fruits, and vegetables over great distances, so grocery stores are now always able to keep on hand a variety of healthful foods.

How is "ammonia" used in the home? You no doubt have seen a solution of ammonia in your home. Such a solution is commonly called "ammonia water" or "household ammonia." It turns litmus blue, indicating the presence of hydroxyl ions. This shows that some of the dissolved ammonia has reacted with the water to form *ammonium hydroxide:*

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

Ammonium hydroxide is a weak base; it furnishes so few hydroxyl ions that it does not injure fabrics or paint. It, therefore, can be used in the laundry and for household cleaning. Its value as a cleansing agent lies in its ability to emulsify grease. Upon evaporation, ammonium hydroxide leaves no residue. It is also frequently used to soften hard water; it precipitates the mineral salts which make the water hard.

Many of the household ammonias contain some oleic acid. This forms an ammonium soap which aids in the cleaning operation.

How does ammonia react with acids? Dry ammonia is not very active chemically. But with traces of moisture present, ammonia combines readily with acids to form ammonium com-

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pounds. In this way it forms ammonium chloride with hydrochloric acid, and ammonium sulfate with sulfuric acid:

$$NH_3 + HCl \rightarrow NH_4Cl$$
$$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

Note carefully the difference between the terms "ammonia" and "ammonium." Ammonia is a gas, a compound of nitrogen and hydrogen with the formula NH_3. On the other hand, ammonium applies to the radical NH_4 which exists only in compounds or in the ionic form.

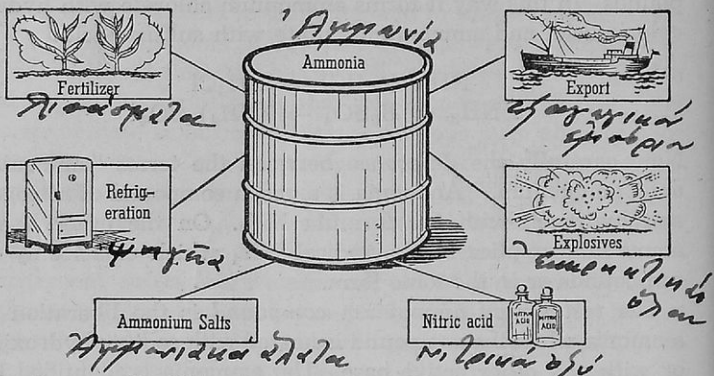
The *test for an ammonium compound* is the liberation of ammonia when the compound is heated with sodium hydroxide or with any other active base. The ammonia is identified by its characteristic pungent odor or by its ability to turn red litmus blue.

What are the many uses of ammonium compounds? Ammonium compounds may be prepared either by the direct combination of ammonia with acids or by neutralizing ammonium hydroxide. All ammon*ium* compounds contain the radical NH_4. This radical acts as a metal, so it has the *-ium* ending.

Ammonium compounds are generally classed with those of the alkali metals, lithium, sodium, potassium. Most of them are very soluble in water. But they are very different in their stability when heated.

Ammonium compounds are usually white crystalline substances and all are soluble in water. They are unstable compounds and can be decomposed by heat. This reaction usually gives ammonia and the acid from which the compound was formed. The nitrate and the nitrite are exceptions, for these two compounds do *not* give ammonia and the acid from which they were formed. Some ammonium compounds are unstable at ordinary room temperatures, particularly the hydroxide, the carbonate, and the acetate. Ammonium compounds are distinguished from sodium and potassium compounds by the ease with which they yield volatile products. When ammonium compounds are decomposed by heating, the usual products formed are gases.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



128. AMMONIA HAS MANY INDUSTRIAL USES. You know ammonia as a gas with a pungent odor. It has many uses in industry. A few of the important ones are shown here.

Ammonium salts have many uses. Large quantities of ammonium sulfate are used as fertilizers to supply nitrogen for plant food. Ammonium chloride is used as the active agent in dry cells to produce an electric current. It is also used as a flux for cleaning metal surfaces before soldering. It finds other uses in the manufacture of dyestuffs, and in calico printing. Ammonium nitrate is used in the preparation of laughing gas and many explosives. Ammonium carbonate is used in smelling salts and as a leavening agent in some bakery goods.

How is ammonia used to prepare one of the most useful acids in the world—nitric acid? Ammonia reacts with oxygen, in the presence of platinum gauze as a catalyst, to form nitric oxide (NO) and water. This is the first step in the manufacture of nitric acid by the Ostwald process which will be described in the next problem.

Readings for Pleasure and Profit

DARROW, F. L. *The Story of Chemistry.* Chap. VI, pp. 218-233, "Fixation of Nitrogen."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XIII, pp. 192-195, "Nitrogen Fixation."

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art 21, A, pp. 140-143, "Synthetic Ammonia by Catalysis."
HOLMES, HARRY N. *Out of the Test Tube.* Chap. XIV, pp. 168-176, "Fed from the Air."
ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XI, pp. 331-339, "Nitrogen Fixation."
TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXVII, pp. 415-420, "Haber and Similar Processes."

Applying in Life What You Have Learned in Chemistry

"I learned today," said Mary, "that the use of ammonia to make ice was not begun until about 1890. Where did people get their ice before that?"

Help Mary out. Find out how ice was obtained and stored. (Your grandmother or some older person can help you.) Also show how the use of ammonia in refrigeration has changed our food habits.

In ice-making plants and cold storage plants, leaks in the piping are often located by holding burning sulfur candles near the joints. Why is a leak "spotted" by the formation of white fumes?

Putting Chemistry to Work

A

(1) Why do you not collect ammonia over water as you collect oxygen or hydrogen? (2) How would you test a white solid to see if it is an ammonium salt? (3) Can you dry ammonia by passing it through concentrated sulfuric acid? Why? (4) In the reaction for the Haber process, what are the relative volumes of the combining gases and of the product? Why would you expect pressure to aid in this reaction? (Hint: See the volumes of the reacting gases and of the product.) (5) Why is a good supply of ammonia essential to our national well-being? (6) Give definite examples to show how the use of ammonia or of ammonium compounds has influenced your comfort today.

B

(7) How does any ammonium compound reacting with any active base produce ammonia? Why do these reactions go to an end? (8) What is the source of the nitrogen used in the Haber process?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

of the hydrogen? (9) How do ammonium compounds resemble sodium and potassium compounds? How do they differ? (10) What is the source of ammonia in barnyard manures? (11) Trace the changes through which ammonia passes in a refrigeration machine. Are these physical or chemical changes? (12) How could you separate a mixture of ammonia and air?

How Good Are You at Solving Problems?

(1) Express the specific weight of ammonia on the basis of air = 1; on the basis of hydrogen = 1.

(2) What is the percentage of combined nitrogen in ammonium sulfate?

(3) If you wished to prepare ammonia to fill four 250-ml bottles, what is the smallest weight of ammonium chloride needed? (Assume standard conditions and no loss of gas.)

(4) Which is the more economical to use in the preparation of ammonia, ammonium sulfate at 8¢ per pound or ammonium chloride at 12¢ per pound?

Research and Activities That You Will Enjoy

A forum: "The most important conquest of the air was not by the inventors and pilots of flying machines, but by the chemists who achieved the fixation of atmospheric nitrogen."

A demonstration: Show the class in a striking manner the great solubility of ammonia as illustrated in an ammonia fountain. Be sure to explain all points in connection with its operation.

A resumé: Read Chapter 2 in Slosson, *Creative Chemistry,* and write a brief review of it. Read or report to the class the main points of the information gained.

Problem 42

HOW IS NITRIC ACID PREPARED—WHAT ARE ITS PROPERTIES?

Very few of us realize the extent to which nitric acid enters into our daily lives. Do you know that many of the brilliant colors, which you find in the beautiful fabrics everywhere about you, are possible because nitric acid was used as the

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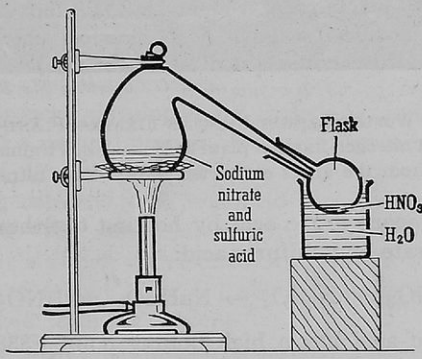
first step in the manufacture of *dyes*? When you go to the movie theater to enjoy the exploits of your favorite movie star, do you realize that your pleasure is made possible because nitric acid was used in the manufacture of the *celluloid film* which brings you the record of the story? As this year's model of the various makes of automobiles pass before you on the street, are you aware that their glossy coats contain certain compounds prepared from nitric acid? Even many of the vegetables and fruits, which give variety to your diet, are raised in truck gardens *fertilized* with nitrate fertilizers. These are a few of the ways in which nitric acid affects you every day.



129. LABORATORY PREPARATION OF NITRIC ACID. A mixture of sodium nitrate and sulfuric acid gently heated yields nitric acid.

Nitric acid is such an active compound that it is not found free in nature to any great extent. Its salts, the nitrates, are found in all fertile soils. In the dry deserts of Chile are the greatest deposits of sodium nitrate in the world. Until rather recently the world's supply of nitrates was obtained mainly from Chile. We now manufacture nitric acid by using nitrogen taken from the air.

How can you prepare nitric acid in the laboratory? The alchemists obtained nitric acid by heating alum and copper sulfate with a nitrate in a retort. Owing to its powerful corrosive action they named this acid *aqua fortis* ("strong water").

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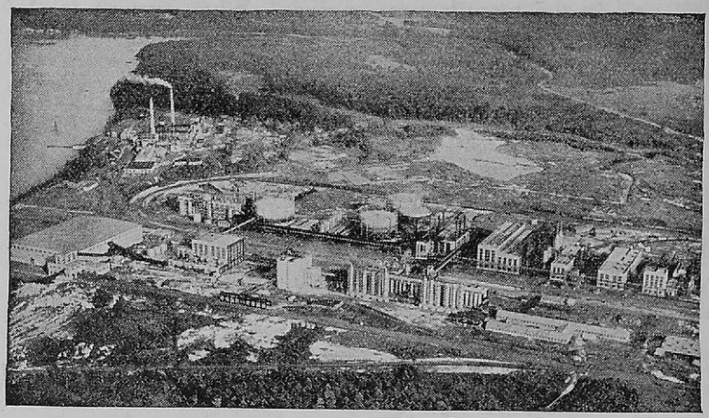

Courtesy, The Barrett Company

130. ONE OF THE WORLD'S LARGEST NITROGEN FIXATION PLANTS. An airplane view of the great nitrogen fixation plant at Hopewell, Virginia. Here nitrogen from the air is converted into sodium nitrate.

You can prepare nitric acid by heating together a mixture of sodium nitrate and sulfuric acid:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3\uparrow$$

The sulfuric acid has a high boiling point (338° C.), and the pure nitric acid boils at 86° C. It is, therefore, possible to distill the nitric acid from the mixture. In this operation the apparatus must be made entirely of glass, because cork and rubber are destroyed by the acid vapors. The acid obtained by this method has a brown color due to the presence of nitrogen dioxide (NO_2), formed by the decomposition of some of the nitric acid by heat during the distillation. To decrease this decomposition, the temperature should be kept as low as possible during the distillation.

How is nitric acid prepared by the arc process? The method described in the preceding paragraph was the only commercial method of preparing nitric acid until about 1910. Under the stress of necessity during the World War, methods were developed to make nitric acid synthetically from nitrogen of the

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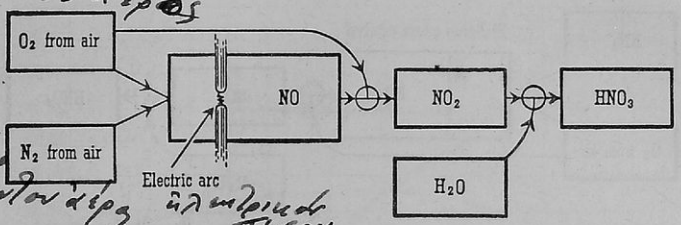

131. ARC PROCESS OF PREPARING NITRIC ACID. When air is passed through an electric arc, a small part of the nitrogen is oxidized to nitric oxide. This reacts with more oxygen to form nitrogen dioxide. Nitrogen dioxide reacts with water to form nitric acid.

air. Most of the nitric acid used in Europe and America is now produced by one of two modern methods: the arc process and the ammonia-oxidation process.

The *arc process*, developed by Birkeland and Eyde, is an adaptation of a natural process. In every lightning flash small quantities of nitrogen are oxidized. The oxides of nitrogen, thus formed, combine with water to form minute quantities of nitric acid. The industrial arc process consists of passing preheated air through an electric arc. At the high temperature of the arc (about 3000° C.) about 5 per cent of the nitrogen is oxidized to nitric oxide:

$$N_2 + O_2 \rightarrow 2\ NO\uparrow$$

The nitric oxide is cooled by cold air, whereupon it undergoes further oxidation to nitrogen dioxide:

$$2\ NO + O_2 \rightarrow 2\ NO_2\uparrow$$

The nitrogen dioxide reacts with water, forming nitric acid:

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO\uparrow$$

Since this process calls for a large expenditure of electrical energy, it is practical only where cheap electrical power is available.

How is nitric acid prepared by the ammonia-oxidation process? The ammonia-oxidation process (Ostwald process) is at present the greatest source of nitric acid. Ammonia and air are

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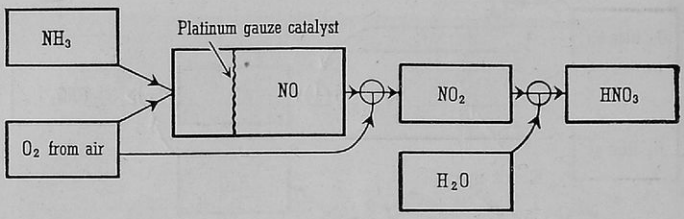

132. AMMONIA-OXIDATION PROCESS OF MAKING NITRIC ACID. When ammonia and oxygen are passed through a heated platinum gauze, nitric oxide is formed. On cooling, this combines with more oxygen to form nitrogen dioxide, which reacts with water to form nitric acid.

passed through a heated platinum gauze which acts as a catalyst. The ammonia reacts with the oxygen of the air, forming nitric oxide:

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO\uparrow + 6\ H_2O$$

The nitric oxide becomes nitrogen dioxide by contact with air and combines with water as in the arc process.

How does nitric acid resemble other acids in physical properties? Nitric acid is a colorless liquid when pure. It fumes in moist air, but it is no different from hydrochloric acid in this respect. It is moderately heavy, being about one and one-half times as heavy as water. Its low boiling point of 86° C. is worth noticing, since this property permits nitric acid to be prepared by distillation. The concentrated nitric acid of commerce is a solution of about 68 per cent acid in water, which boils at about 120° C. Like the other common acids, nitric acid is miscible with water in all proportions.

How does nitric acid resemble other acids in several chemical properties? Dilute nitric acid shows the usual properties of an acid. It has a sour taste and affects indicators as other acids do. It neutralizes bases and reacts with metallic oxides, but it *rarely produces hydrogen when it reacts with metals.* Nitric acid is quite unstable; when heated or exposed to sunlight it decomposes as follows:

$$2\ HNO_3 \rightarrow H_2O + 2\ NO_2 + [O]$$

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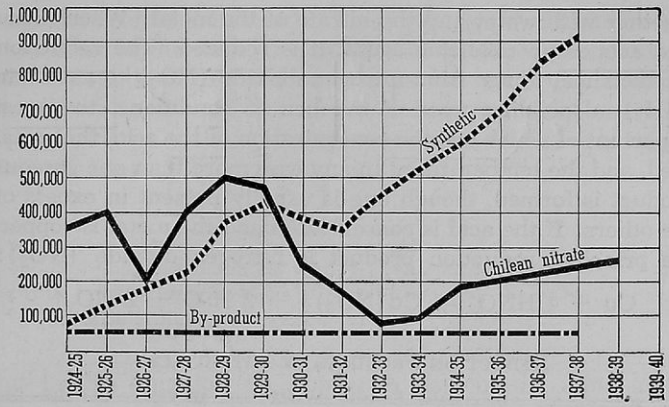

133. WORLD'S PRODUCTION OF NITROGEN COMPOUNDS IN METRIC TONS OF NITROGEN. Note the increased use of nitrogen compounds, especially within the past decade. Synthetic nitrogen compounds are increasing in importance.

What properties make nitric acid different from other acids? The ease with which nitric acid decomposes and the oxygen which it liberates when it decomposes cause nitric acid to be a vigorous oxidizing agent. Concentrated nitric acid supports very well the combustion of organic matter (wood shavings) or charcoal. The instability and the powerful oxidizing ability of nitric acid enable it to react with metals below hydrogen in the activity series.

A mixture of nitric and hydrochloric acids was used by the alchemists to dissolve gold. Since this combination of acids would thus affect the most royal of all metals, they called it *aqua regia*—"royal water." The great activity of "aqua regia" is due to the oxidation of the hydrochloric acid by the nitric acid which produces free chlorine. The free chlorine reacts with the gold:

$$3\ HCl + HNO_3 \rightarrow 2\ H_2O + NO + 3\ [Cl]$$

The *action of nitric acid on metals* liberates hydrogen only when the acid is very dilute and when the metal is very active. Because of the powerful oxidizing action of the acid, the gaseous products are usually reduction products of nitric acid,

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together with water and the nitrate of the metal. When nitric acid acts as an oxidizing agent, it is reduced. The reduction products may range from nitrogen dioxide (NO_2) to ammonia (NH_3), depending upon a number of conditions, the most important of which are the concentration of the acid, the metal used, and the temperature. In any case more than one gaseous product is formed, though one is usually present in excess of the others. If the acid is concentrated and the metal is copper, the principal reduction product is nitrogen dioxide (NO_2):

$$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2\uparrow$$

REDUCTION PRODUCTS OF NITRIC ACID

Valence of Nitrogen	Formula and Name	Valence of Nitrogen	Formula and Name
+4	NO_2 nitrogen dioxide	+1	N_2O nitrous oxide
+3	N_2O_3 nitrogen trioxide	0	N_2 nitrogen
+2	NO nitric oxide	−3	NH_3 ammonia

With dilute nitric acid of the concentration usually used in the laboratory (about one part of acid to four of water), the principal reduction product is nitric oxide (NO):

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO\uparrow$$

With a still more dilute acid, considerable quantities of nitrous oxide (N_2O) may be formed; and with an active metal such as zinc, ammonia may be the reduction product. In any case, the products are always a nitrate of the metal, a reduction product of nitric acid, and water.

How can the reaction of copper and nitric acid be explained from the standpoint of electron exchanges? When *concentrated* nitric acid reacts with copper, brown nitrogen dioxide is set free and the blue color of the cupric ion appears in the solution after dilution. This shows that the copper has been oxidized, each copper atom having given up two electrons. The valence of the nitrogen has decreased from +5 to +4; each nitrogen atom has taken on one electron as it changed

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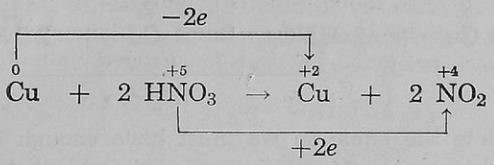
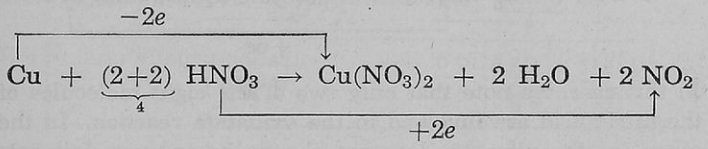
from the acid to the dioxide. Since the gain and loss of electrons must be the same, this shows that two molecules of nitric acid are required to oxidize one atom of copper. Each copper atom gives up enough electrons to reduce two nitrogen atoms. Considering only these electron exchanges in the first equation, we have:

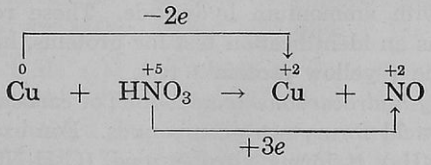


But in this equation the copper is now in the ionic form. In order to provide the copper ion with its complementary negative ions and to complete the equation, two more molecules of nitric acid must be used. The *balanced equation* then becomes:



Here two molecules of nitric acid act as an oxidizing agent, while the other two act in the usual capacity as an acid.

When dilute nitric acid reacts with copper, colorless nitric oxide is liberated and the blue color of the cupric ion is seen in the solution. The electron changes are as follows:



This indicates that the copper has gained two in valence, since each atom has given up two electrons. The nitrogen atom has gained three electrons by decreasing its valence from five to

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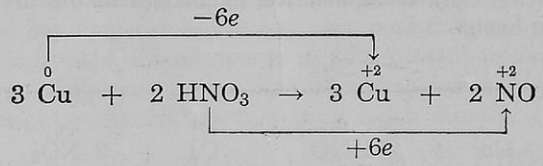
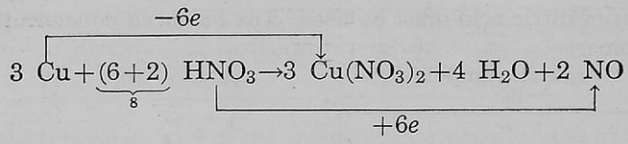
two. In order to make the electronic exchange balance, six electrons must be transferred. This means that two nitric acid molecules can oxidize three atoms of copper. These facts are shown thus:



To complete the equation we must have enough additional nitric acid to supply the three cupric ions with their negative ions. This requires six additional molecules of nitric acid. The completed equation then becomes:



In this case, we note that only two of the eight molecules of the nitric acid are involved in the oxidation reaction. In the other six the nitrogen does not change its valence, but acts in the usual capacity of an acid.

How does nitric acid form useful products by reacting with organic compounds? The behavior of nitric acid with organic matter is a valuable and interesting property. Nitric acid stains proteins yellow. The color is intensified to orange by treatment with ammonium hydroxide. These reactions are often used as an identification test for proteins, known as the xanthoproteic ("yellow protein") test.

With many hydrocarbons (compounds of carbon and hydrogen) nitric acid forms nitro-compounds. For example, with benzene (C_6H_6) it forms nitrobenzene ($C_6H_5NO_2$). Under proper conditions, toluene ($C_6H_5 \cdot CH_3$) and phenol (C_6H_5OH) are converted into trinitrotoluene TNT [$C_6H_2(NO_2)_3CH_3$] and picric acid [$C_6H_2(NO_2)_3OH$].

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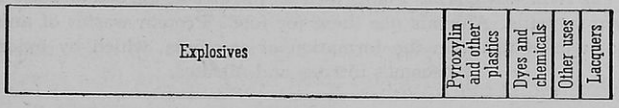
All three of these compounds are powerful explosives and starting materials for the manufacture of dyes.

With alcohols (organic compounds containing hydroxyl radicals) *esters* are produced. Esters are compounds which contain an organic radical combined with an acid radical. Their formulas resemble the formulas of salts with a hydrocarbon radical in place of the metal of the salt. Unlike salts, esters are not ionized in solution. Glycerin treated with nitric acid under the proper conditions forms glyceryl nitrate.

$$\underset{\text{glycerin}}{C_3H_5(OH)_3} + 3\ \underset{\text{acid}}{HNO_3} \rightarrow \underset{\text{("nitroglycerin")}}{C_3H_5(NO_3)_3} + 3\ \underset{\text{water}}{H_2O}$$

Concentrated sulfuric acid is added to remove the water which is a by-product. The compound glyceryl nitrate is the powerful explosive commonly called "nitroglycerin." Similarly, cellulose (cotton) is converted into cellulose nitrate, or guncotton. Large quantities of nitric acid are used in the preparation of these organic compounds just mentioned.



134. USES OF NITRIC ACID. While you may not use much nitric acid as such, nitric acid enters into the preparation of many things you use every day.

What are other uses of nitric acid? From cellulose nitrate industrial concerns prepare smokeless gunpowder, celluloid, some forms of rayon, and nitrocellulose lacquers. In preparing "cuts" for the printing of artist's illustrations, zinc and copper plates are etched with nitric acid.

The salts of nitric acid are known as nitrates—how can you test for a nitrate? All nitrates are soluble in water, so it is impossible to have a precipitation test for them as for a sulfate and a chloride. The test for the nitrate ion is performed in the following manner.

The unknown substance to be tested is put in solution and mixed with a freshly prepared solution of ferrous sulfate.

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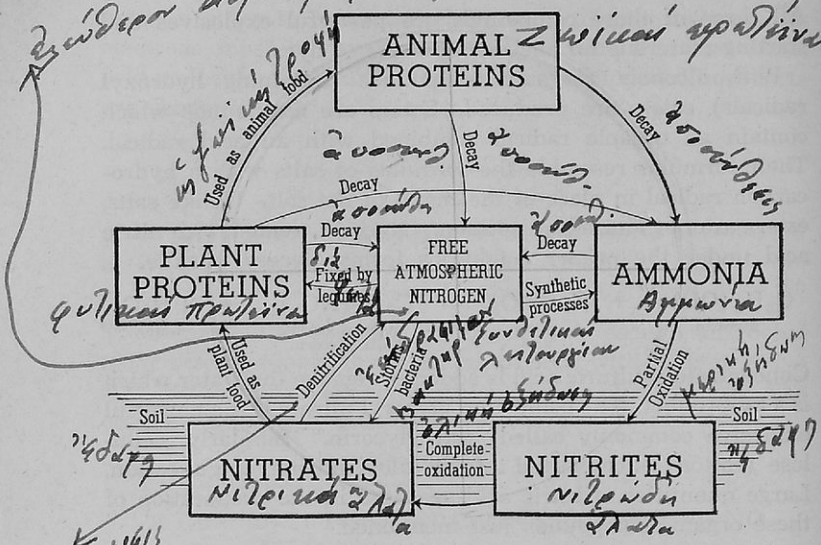

A35. THE NITROGEN CYCLE. Plants feed on nitrates in the soil and use them to form proteins. Animals use these for food. Protein wastes of animals living or dead result in the formation of ammonia, which by oxidation becomes nitrites and nitrates.

Concentrated sulfuric acid is carefully poured into this mixed solution with the test tube tilted to an angle of about forty-five degrees. The acid, being much heavier than the solution, flows to the bottom of the tube. Between the two liquids a brown layer or ring forms. The appearance of this layer is the test for a nitrate ion. Since nitrites behave similarly, it is necessary to distinguish them from nitrates by repeating the test using acetic acid instead of the sulfuric acid. Only nitrites give the brown color reaction with acetic acid.

All nitrates are decomposed by heat. When heated, the nitrates of the active metals (such as the alkali metals) lose an atom of oxygen and become nitrites:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2\uparrow$$

When they are heated, the nitrates of the heavy metals decom-

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pose and yield the metallic oxide, nitrogen dioxide, and oxygen:

$$2\ Cu(NO_3)_2 \rightarrow 2\ CuO + 4\ NO_2\uparrow + O_2\uparrow$$

Ammonium nitrate decomposes when heated, yielding nitrous oxide and water:

$$NH_4NO_3 \rightarrow N_2O\uparrow + 2\ H_2O$$

How are the oxides of nitrogen prepared and used? The oxides of nitrogen already have been mentioned as products which form when nitric acid reacts with metals. Two of them, nitric oxide and nitrogen dioxide, also have been mentioned in the preparation of nitric acid by the arc process and the ammonia-oxidation process.

There are five oxides of nitrogen as shown:

N_2O	nitrous oxide
NO	nitric oxide
N_2O_3	nitrogen trioxide
NO_2	nitrogen dioxide
N_2O_5	nitrogen pentoxide

Nitrogen trioxide and nitrogen pentoxide are the anhydrides of nitrous acid and of nitric acid, respectively. They are difficult to prepare and are unstable.

Nitrous oxide (laughing gas) is prepared in the laboratory by heating ammonium nitrate, which decomposes into nitrous oxide and water. The equation for this reaction is given above.

Nitrous oxide is a colorless gas, about one and one-half times as heavy as air ($44/29 = 1.52$). It has a slightly sweet odor and taste and is somewhat soluble in water. It supports combustion of most substances almost as well as oxygen. Nitrous oxide can be distinguished from oxygen by mixing it with colorless nitric oxide. A mixture of nitric oxide and nitrous oxide shows no change in color, while a mixture of nitric oxide and oxygen turns brown due to the formation of nitrogen dioxide.

The great importance of nitrous oxide lies in its use as an anesthetic. It is sometimes used by dentists and surgeons in

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minor operations. It was one of the first substances to be used as an anesthetic.

Nitric oxide is prepared in the laboratory by the reaction between dilute nitric acid and metals:

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO\uparrow$$

It may also be prepared by the oxidation of nitrogen in the electric arc and by the oxidation of ammonia, using platinum as a catalyst:

$$N_2 + O_2 \rightarrow 2\ NO$$
$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

Both of these reactions are used as steps in the synthetic manufacture of nitric acid.

Nitric oxide is a colorless gas, slightly heavier than air (30/29 = 1.04), and insoluble in water. It does not support the combustion of most substances, though phosphorus when burning brightly continues to burn when lowered into a jar of the gas. The most noticeable chemical characteristic is the ease with which it combines with oxygen, forming nitrogen dioxide:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Nitric oxide is produced in considerable quantities in the industrial preparation of nitric acid. In these reactions the gas is not isolated but is immediately oxidized to nitrogen dioxide.

Nitrogen dioxide can be prepared by the action of concentrated nitric acid on metals, by the oxidation of nitric oxide, or by heating the nitrates of the heavy metals:

$$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2\uparrow$$
$$2\ Cu(NO_3)_2 \rightarrow 2\ CuO + 4\ NO_2\uparrow + O_2\uparrow$$

Nitrogen dioxide is a red brown gas, about 1.6 times as heavy as air (46/29 = 1.58). It is very soluble in water. It has an unpleasant odor and is quite *poisonous*. At room temperature it reacts with water to form nitric acid as one of its products:

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

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When nitrogen dioxide is cooled, its brown color fades to a pale yellow. Molecular weight determinations show that this yellow substance has a formula N_2O_4. Two molecules of the nitrogen dioxide have united to form one molecule of the new product, *nitrogen tetroxide:*

$$\underset{\substack{\text{nitrogen dioxide}\\(\text{brown})}}{2\ NO_2} \rightleftarrows \underset{\substack{\text{nitrogen tetroxide}\\(\text{yellow})}}{N_2O_4}$$

The importance of nitrogen dioxide lies in the fact that it combines readily with water to form nitric acid. This is the final step in the synthetic production of nitric acid.

In the chamber process for the manufacture of sulfuric acid, oxides of nitrogen play an important part. Nitrogen dioxide acts as an oxidizing agent in the lead chambers, causing the sulfur dioxide to be oxidized to sulfur trioxide which then unites with water to form sulfuric acid.

Readings for Pleasure and Profit

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XIII, pp. 194-197, "Nitrogen Fixation."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 21, B, pp. 144-146, "Oxidation of Ammonia."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XIV, pp. 168-177, "Fed from the Air."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. V, pp. 176-190, "Nitric Acid"; Vol. I, Chap. XI, pp. 326-340, "Fixation of Nitrogen."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXVII, pp. 405-415, "Fixation of Atmospheric Nitrogen."

Applying in Life What You Have Learned in Chemistry

"Goin' to the movies tonight?"

If it were not for nitric acid, you probably would not go to the "movies" tonight. Show why.

Will the production curve for synthetic nitrogen compounds (Fig. 133, page 383) serve as a business barometer? Compare with the curve for sulfuric acid (Fig. 98, page 291).

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Putting Chemistry to Work

A

(1) What three possible sources are there for the ammonia used in the Ostwald process? (2) If you were given samples of three acids, sulfuric, hydrochloric, and nitric, what physical and chemical tests could you use to identify each? (3) Show how the use of nitric acid has indirectly influenced your life today. (4) When you heat a mixture of sulfuric acid and sodium nitrate in a retort, only a little nitric acid is formed at a time. How and why is it removed? Why is hydrochloric acid not used instead of sulfuric acid to prepare nitric acid? (5) Why do we not test nitric oxide with a flaming splint? (6) Five jars are filled separately with HCl, NH_3, N_2O, NO, and NO_2. How can you identify each gas? (7) "Nitrogen fixation is the changing or fastening down of the free nitrogen of the air into useful compounds." Explain. (8) Liebig, a German chemist, once said that the extinction of life on earth would come when we had used up our supply of combined nitrogen. What did he mean? Does his statement still hold true today? Explain.

B

(9) In what ways does nitric acid resemble other acids? In what ways is it different? (10) Why does nitric acid acquire a brown color when it is heated or exposed to sunlight? (11) Show by equations with explanations how ammonium nitrate can be prepared from air and water. (12) Compare and contrast the action of copper on nitric acid and on sulfuric acid. (13) When copper dissolves in nitric acid, what becomes of the copper? What gas is evolved? What compound forms when this gas comes in contact with the air? (14) What decomposition products do you expect when nitrates of metals are decomposed by heat? What nitrates do not decompose in this manner? Write equations to illustrate the decomposition of three classes of nitrates.

How Good Are You at Solving Problems?

(1) Compare the weights of the gases, N_2O, NO, and NO_2, with NH_3.

(2) What is the percentage of nitrogen in ammonium nitrate?

(3) Compare the volume relations in the reactions for the Haber process, for the arc process, and for the Ostwald process.

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(4) A student wishes to prepare 1500 ml of nitrous oxide. What is the smallest weight of ammonium nitrate he will need if the gas is collected under standard conditions? if the gas is collected over water whose temperature is 23° C. when the barometer reads 745 mm? (Disregard solubility in water.)

Research and Activities That You Will Enjoy

Haber and Ostwald: Before 1913 nitric acid was made from Chilean nitrate. About that time Haber was able to produce ammonia from the nitrogen of the air, and Ostwald devised the process of oxidizing ammonia to nitric acid. Germany then was no longer dependent on the outside world for explosives. What great war began the next year in 1914? Report a part of the life of one of these two men.

Problem 43

EXPLOSIVES—HOW IS NITROGEN TURNED LOOSE?

Nearly all explosives used in industry and in warfare contain some compound of nitrogen, usually derived from nitric acid. The first explosive to be used in warfare was black gunpowder, a mixture of potassium nitrate, sulfur, and charcoal. Its European discovery has been attributed to Roger Bacon about 1270 and to Friar Schwartz in Germany about 1325. Its first recorded use in war was at the Battle of Crecy, in 1346, when the English foot soldiers used it against the flower of the French knighthood. The French knights were thrown into confusion by the new weapon. The results of this battle showed conclusively that a common man with a gun was more than equal to a knight on a horse.

Gunpowder was the only powerful explosive in use for 500 years. During that time improvements were made in its composition and in its physical properties. It was not until near the middle of the last century that new explosives appeared. In 1845 guncotton was discovered and in 1847 nitroglycerin was first prepared. Our modern explosives are mostly derivatives of these compounds.

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What happens during an explosion? An explosion is simply a very rapid combustion which produces a large volume of gas. As in all combustions, heat is liberated. This rise in temperature increases the volume of the gas produced and makes the explosion more effective. In the explosion of ordinary black gunpowder, carbon dioxide, carbon monoxide, and nitrogen are produced as well as potassium carbonate and potassium sulfide. Temperatures as high as 2500° C. have been noted. In gunpowder the potassium nitrate acts as the oxidizing agent, supplying the oxygen for the combustion of the sulfur and the charcoal. Since the oxygen and the combustible matter are in separate molecules, the oxidation is not complete, and in the hurry of the reaction some of the carbon escapes as unburned black smoke.

A milliliter of gunpowder produces about 500 ml of gaseous products. At the temperature of the reaction (2500° C.) this volume is increased to about 5,000 ml. At an atmospheric pressure of 15 pounds to the square inch, this is equivalent to a pressure of about 75,000 pounds. This pressure is developed in about a second.

What are some of our modern explosives? When cellulose in the form of wood pulp or cotton is treated with nitric acid (with sulfuric acid present as a dehydrating agent), there is no apparent change in the material. The product is guncotton, or *cellulose nitrate*. When lighted, it burns with a flash producing neither smoke nor ash. When compressed into cartridges and fired, it produces very violent explosions. The reaction takes place in about 1/2000 of a second. The speed of the reaction seems to be due to the fact that the oxygen and the combustible material are here in the same molecule, and are, therefore, much closer together than they could possibly be in a mixture like gunpowder.

Guncotton dissolves in acetone producing a thick viscous liquid. Upon evaporation of the solvent, a horny mass is left. When this is granulated or cut into strings it forms smokeless powder. It is smokeless, because all of the products of the explosion are colorless gases.

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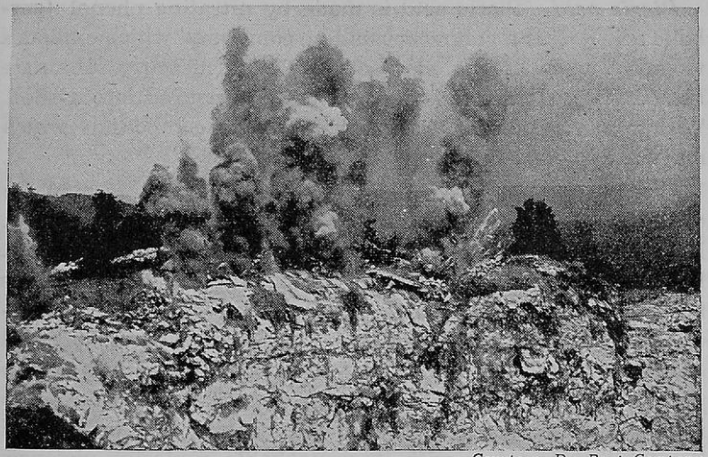

Courtesy, Du Pont Company

136. EXPLOSIVES ARE USED IN ENGINEERING. We think of explosives in connection with warfare or Fourth of July celebrations. Far more explosives are used for blasting in mines, quarries, or engineering projects than are used for warfare.

Nitroglycerin. Nitroglycerin is prepared from glycerin by treatment with a mixture of nitric and sulfuric acids. It is a thin yellowish liquid, insoluble in water but soluble in most organic solvents. It is *extremely unstable* and must be handled with great care. It freezes at 12° C. and the solid is more unsafe to handle than the liquid. The "nonfreezable" nitroglycerin is now prepared by nitrating a mixture of glycerin and ethylene glycol. In its pure state its use is limited mainly to "shooting" oil wells. Cans of it are lowered to the bottom of oil wells and fired, thus smashing the rock and promoting the flow of oil. When it is mixed with porous earth, or wood dust, and packed into sticks it forms dynamite. Mixed with nitrocellulose, nitroglycerin forms a jellylike mass known as "blasting gelatine." This is an extremely powerful explosive producing gas that has nearly 100,000 times the volume of the explosive itself. The temperature of the explosion is about 5000° C. How does this temperature compare with the temperature of the sun? (See table in appendix.)

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Picric acid. Picric acid is made by nitrating phenol (carbolic acid). It is a yellow crystalline compound which explodes violently when detonated ("set off") with mercury fulminate $Hg(CNO)_2$. It can be safely melted and poured into a shell. With some metals it forms very unstable compounds which may be exploded by the slightest shock.

Trinitrotoluene. Trinitrotoluene (TNT) is formed by treating toluene with a mixture of nitric and sulfuric acids. It is a white crystalline solid, quite stable and safe to handle. It melts at 80° C., and can be poured into shells where it is fired by mercury fulminate. On exploding it produces a mixture of CO, CO_2, N_2, H_2, and C. Its explosion is so rapid (about 1/5000 of a second) that it cannot be used in a gun to propel the shell. The enormous gas pressure is produced so rapidly that the gun would burst. Its safety in handling and its stability, together with its remarkable explosive violence, make it a suitable explosive with which to fill projectiles designed to explode when they "hit."

Ammonium nitrate. Ammonium nitrate either with or without an admixture of TNT, may be fired with mercury fulminate and is widely used as a substitute for TNT. Upon explosion, it reacts thus:

$$2\ NH_4NO_3 \rightarrow 2\ N_2 + O_2 + 4\ H_2O$$

We are apt to think of explosives only in terms of warfare, but the use of explosives in industry is very common and necessary. More than 100 million pounds of nitroglycerin are produced in America in a year, most of which go into the preparation of industrial explosives. Blasting in engineering work, in mines, and in quarries is a general practice. The farmer uses explosives to "clear" land by blasting out stumps of trees, and large quantities of nitroglycerin are used every year in the petroleum industry to "shoot" oil wells as described on page 395. Without explosives, great engineering projects such as the Panama canal, Boulder dam, and Norris dam would be almost impossible. Miners and quarry men use special types of explosives prepared especially for their use.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Readings for Pleasure and Profit

HAYNES, WM. *This Chemical Age.* Chap. XX, pp. 353-373, "Our Chemical Armory"; Chap. V, pp. 78-94, "Mars: Chemical Dictator."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. II, pp. 13-21, "Nitrogen—Preserver and Destroyer of Life."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. II, pp. 12-23, "Explosives in Peace and War."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXVI, pp. 389-405, "Explosives."

Putting Chemistry to Work

A

(1) Why is an adequate supply of nitrogen compounds essential to agriculture? to national defense? (2) Why is nitrogen fixation a relatively difficult process to achieve? What relation does this have to the fact that many nitrogen compounds are explosive? (3) "The elements nitrogen and chlorine are the Dr. Jekylls and the Mr. Hydes of chemistry." What does this statement mean? Can you justify it? (4) Stores of smokeless powder are regularly tested with litmus. Samples that turn litmus red are considered dangerous and are destroyed. Can you explain the change which occurs?

B

(5) What is an explosion? (6) What are the essential conditions for a dust explosion? (7) What are high explosives? How are they used? (8) What is a propellent explosive? How is it used?

Looking Back into Unit 9

Be sure you know the purpose of this unit. Read again the material on page 362, "Looking Ahead into Unit 9." Then study the following Summary Test.

Summary Test

1. *What should you know about the lazy element, nitrogen?*
   (a) How is nitrogen prepared—
   (1) In the laboratory? *(2)* In industry?
   (b) What are the chemical characteristics of nitrogen?
   (c) Why is nitrogen fixation such an important process?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

2. *How can you prepare and use ammonia?*
   (a) How is ammonia produced—
      (1) In nature?
      (2) In the laboratory?
      (3) In industry—
         A. By the cyanamide process?
         B. By the Haber process?
   (b) What qualities of ammonia make it useful?
   (c) How is ammonia used—
      (1) In preserving foods?
      (2) In your home?
      (3) In ammonium compounds?
3. *How is nitric acid prepared; what are its properties?*
   (a) How is nitric acid prepared—
      (1) In the laboratory?
      (2) In industry—
         A. By the arc process?
         B. By the ammonia-oxidation process?
   (b) How does nitric acid resemble other acids?
   (c) What properties of nitric acid make it different from other acids?
   (d) What compounds are formed when nitric acid reacts—
      (1) With metals?
      (2) With organic compounds?
      (3) With bases?
         A. How can you test for a nitrate?
   (e) How are the oxides of nitrogen prepared and used?
4. *What property of nitrogen makes possible its use in explosives?*
   (a) What happens during an explosion?
   (b) What are some of our modern explosives?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

You should not underestimate the importance of the nitrogen compounds. Lazy, inactive *nitrogen,* on the one hand, and such important explosives as *nitroglycerin* and TNT, on the other, illustrate an important chemical principle, namely, that *inactive elements form unstable compounds.*

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

One of the worth-while accomplishments of the chemist has been to utilize the *nitrogen* of the *air* in the formation of valuable *compounds*. You find admirable success in this in the manufacture of *ammonia* and *nitric acid* by the so-called *fixation* of *atmospheric nitrogen* processes.

Nitrogen affords us an excellent example of an element with a variable valence. Under certain conditions five oxides of nitrogen can be produced, each with its characteristic properties. Does one of our basic chemical laws still hold true (the Law of Multiple Proportions)?

Much *ammonia* is still produced as a by-product in the coking of coal. You perhaps are most familiar with the use of ammonia in *refrigeration*, as *ammonium hydroxide* for household use, and as *ammonium sulfate* for *fertilizer*.

Until less than a generation ago the only method for preparing *nitric acid* was by the action of *concentrated sulfuric acid* on *sodium nitrate* (Chile saltpeter). However, it was found that *ammonia* can be *oxidized* in the presence of catalysts thus leading the way to the formation of nitric acid. This method of preparing nitric acid is replacing the older method. Economically, the present methods of preparing nitric acid tend to make each country less dependent upon the other, since nitric acid is the starting point for many articles of commerce.

As a consumer you may not be so conscious of the benefits of *nitric acid* as you are of the benefits of ammonia. But few chemicals, if any, are more important in our economic and social life.

From the purely chemical side, you should remember that *nitric acid* is an excellent *oxidizing agent*, reacting with many metals either as a dilute or concentrated acid. Have you compared its action on metals with the action of other acids?

You are constantly being led in these advanced units to the more practical aspects of chemistry. You should practice associating the theoretical concepts with these applications. If you do not, you are letting your mind "get by" with loose habits of thinking.

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Looking Ahead into

Unit Ten

In the everyday activities of a home sometimes "things go wrong." Perhaps the fruit juice does not jell—or the salad dressing does not stay put together, or the coffee is "muddy." Similarly in the industrial world a whole batch of soap may "go sour" and not run together as it should, or in a sugar factory the sugar may not crystallize out of the sirup. Or, the weather may intensify the smoke nuisance of a city almost beyond endurance. The dust storms of the Great Plains may bring discomfort and damage to all the people of a dozen states.

A few centuries ago these ills would have been attributed to "bad luck." Now we know that these and other similar troubles can be largely prevented by applying knowledge of matter that is in the colloidal state. In this unit is shown just what the colloidal state is and how you meet it in everyday life.

Most of you have cooked food over a campfire and have soiled your hands with soot from the fire. When you tried to remove the soot with water alone, you were unsuccessful because the soot adhered to your hands more than it did to the water. By using soap with the water, you spread a film of soap molecules over the soot particles. This caused the soot particles to discontinue adhering to your hands.

Washing with soap is only one of thousands of examples of problems involving adhesion and cohesion which people daily meet and solve. The degree of these attractive forces between molecules is different for each kind of molecule. Note that the behavior of matter is greatly influenced not only by these forces but also by the size of the particles involved.

Problem 44. *What Are Colloidal Dispersions — How Can You Recognize Them?*

Problem 45. *How Are Colloidal Dispersions Prepared and Used?*

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Colloidal State: The Twilight or "In-between" Condition of Matter

Problem 44

WHAT ARE COLLOIDAL DISPERSIONS — HOW CAN YOU RECOGNIZE THEM?

Colloidal dispersions are an "in-between" condition of matter. You already have learned that true solutions are dispersions of molecules or of particles as small as molecules. For example, in a solution of sugar and water the particles dispersed in the water are sugar molecules and therefore are too small to be seen even with the most powerful microscope. Such a solution will not "settle out." A solution can stand for days or even centuries and still remain a solution if evaporation and chemical action are prevented.

On the other hand, a mixture of fine sand and water will stay mixed for a limited time only; the sand particles are too large to stay in suspension permanently.

What occurs when particles larger than most molecules and smaller than very fine sand are dispersed? You will find in this unit that the dispersion of particles of this size—larger than most molecules and smaller than fine grains of sand—forms substances which have peculiar properties. These substances are said to be in the colloidal state. They are in a sort of "in-between" or "twilight" condition of matter in that "their dispersed particles are larger than those of true solutions, but are still too small to settle out."

Today many of our most useful products are substances of this type. Even such common mixtures as soap in water, starch in water, and glue in water are colloidal dispersions rather than solutions.

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What is meant by dispersion? Any process of dividing any material again and again into smaller and smaller particles and scattering them throughout a second material is called dispersion. India ink is a dispersion of carbon particles in water, and milk is a dispersion of butterfat and casein in a solution of milk sugar and salts.

The material that is divided and scattered is often called the *disperse phase* or inner part, while the material in which the subdivided material is scattered is known as the *dispersion medium* or outer part.

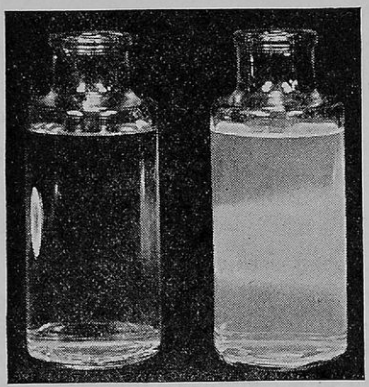
How the word "colloid" was derived. One of the earliest workers in the field of colloidal chemistry was Thomas Graham. He made some simple experiments such as you may perform in your laboratory. He noted two general classes of substances. Substances like sugar and salt, whose solutions pass through an animal membrane, he called crystalloids. They were crystalline solids. Other substances, such as soap, starch, and glue, when mixed with a liquid, did not pass through a membrane. These substances he called *colloids* from the Greek word meaning "gluelike." Later experiments showed that the colloidal state is *not a kind* of matter but a *condition* of matter obtained by dispersing particles of certain sizes. Many so-called crystalloids have been prepared in the colloidal condition, and other substances ordinarily in the colloidal state have been crystallized. It is possible that any material can be prepared in the colloidal state by the proper procedure. For this reason it is preferable to say that a substance is in the *colloidal condition* or in the colloidal state instead of calling it a "colloid," which implies a kind of matter.

WHAT CHARACTERISTICS OF COLLOIDAL DISPERSIONS ENABLE YOU TO RECOGNIZE THEM?

Colloidal dispersions show a path of light. When a narrow beam of light enters a darkened room through a small opening in a window shade, small particles of dust may be seen. Many of these particles are of colloidal size and consequently cannot be seen in a well-lighted room. In a darkened room,

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

however, they reflect the light to the eye and thus show the path of light through the room. This same effect may be observed by passing a beam of light through a liquid containing a colloidal dispersion. The small particles, that are dispersed in the liquid, act in the same manner as the dust particles; they scatter the light in all directions, thus making it possible for you to see the path of the beam of light through the mixture. This is called the *Tyndall effect*, after the British physicist who first studied it. The beam of a powerful searchlight or aërial beacon in a smoky or foggy atmosphere is another illustration of the Tyndall effect.



A strong beam of light is passed through the two bottles. The bottle on the left contains a solution. The bottle on the right contains a colloidal suspension. The colloidal particles reflect the light so the path of the beam can be traced through the bottle. This is known as the Tyndall effect. In the same manner a beam of light shows colloidal dust particles in air.

137. STRONG LIGHT REVEALS THE PRESENCE OF COLLOIDAL PARTICLES

Solutions, on the other hand, do not show the Tyndall effect since their dispersed particles are too small to scatter the light. Neither do coarse suspensions show the Tyndall effect very noticeably since a beam of light will not penetrate them to any great distance.

The ultramicroscope makes use of the Tyndall effect. An intense beam of light is passed through a colloidal dispersion contained in a small cell. A powerful microscope is focused on the colloidal dispersion which is viewed against a dark background. Although the colloidal particles are extremely small, nevertheless they are large enough to reflect the

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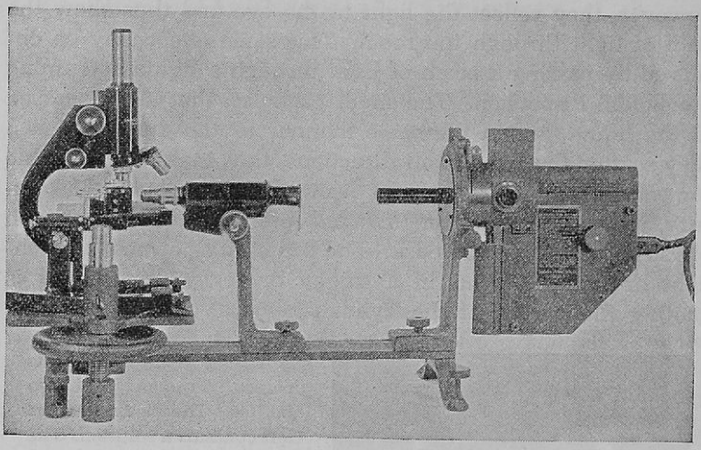

Courtesy, Bausch and Lomb

138. ULTRAMICROSCOPE. Particles in the colloidal state can be observed by the use of an ultramicroscope.

light. Consequently, tiny glistening points of light can be seen in the liquid.

Colloidal particles are continuously moving and zigzagging about—why? When colloidal dispersions are examined through an ultramicroscope, the dispersed particles appear as tiny specks of light which are in a continuous, dancing, zigzagging motion. This movement of colloidal particles is called the *Brownian movement,* after the botanist, Robert Brown, who first observed and reported it in the case of pollen dust suspended in water. The cause of this interesting effect was not understood for many years, but it is now thought that the dancing particles are being continuously bombarded by the moving molecules of water. The Brownian movement provides one of the most convincing evidences of the kinetic-molecular theory.

Colloidal particles do not settle. Colloidal particles are too small to settle readily as ordinary suspended particles do. Colloidal dispersions are similar to solutions in this respect.

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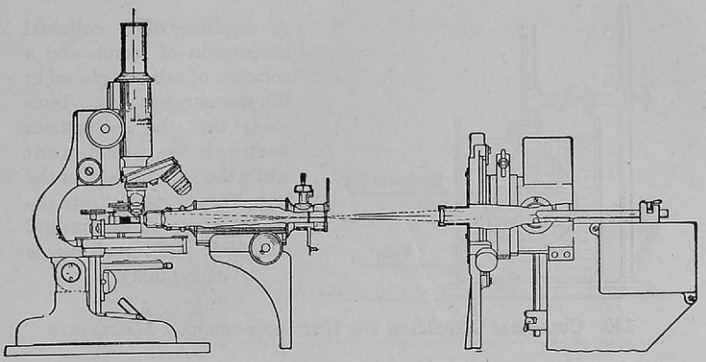


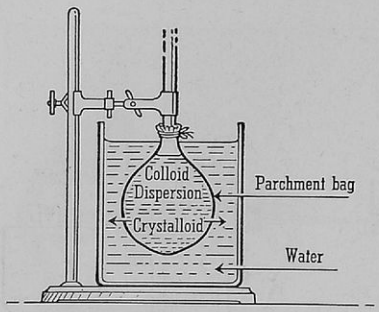
139. DIAGRAM OF ULTRAMICROSCOPE. Intense light coming from the electric arc is focused on the colloidal particles in the liquid cell. The observer may see bright dancing points of light reflected from the particles.

The particles are too small for the pull of gravity to overcome the friction on the dispersion medium. Also, the continuous bombardment of molecules against the colloidal particles helps to keep them scattered so they do not settle but remain suspended. In fact, colloidal suspensions of gold have been kept for years without any settling.

Colloidal particles pass through ordinary filters. The pores of ordinary filter paper are much too large to remove colloidal dispersions. Materials in the colloidal state may often be filtered out, however, by using an ultrafilter. This device may consist of an unglazed disk or a filter paper supporting a layer of jellylike material such as gelatin or silicic acid. Materials in solution pass through an ultrafilter while colloidal material remains behind in the layer of jelly.

Colloidal particles do not pass through the lining of an eggshell. Substances in the colloidal state will not pass through many kinds of membranes such as an animal bladder, inner lining of an eggshell, parchment, collodion film, and cellophane. The pores of these membranes are small enough to stop colloidal particles but large enough to permit solutions to pass through.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



A mixture of a colloidal suspension of starch and a solution of salt are placed in the parchment bag. Tests show that the salt passes through the parchment while the starch stays in the bag. This process of separation of true solutions and colloidal suspensions is called dialysis.

140. COLLOIDAL PARTICLES DO NOT PASS THROUGH MEMBRANES

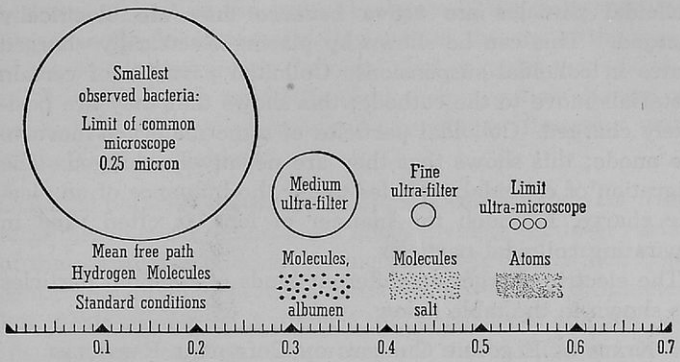
You, therefore, can separate a solution from a colloidal dispersion with a membrane. This process is called *dialysis.* It can be demonstrated by placing in distilled water a membrane bag containing colloidal starch and a solution of table salt. After a time the iodine test shows that the starch has not passed through the parchment. The silver nitrate test shows that the chloride has passed through the bag into the distilled water.

How small are colloidal particles? For expressing the dimensions of particles of colloidal size, the millimeter is much too large. Instead, a millimicron (mμ) is used. A millimicron is one millionth of a millimeter.

If you slice a dime into a thousand circular slices and then slice *each* of these into a thousand more circular slices, you have one million "slices of dime" each of which is approximately one millimicron thick.

Dispersed particles whose diameters are about 250 mμ, or slightly larger, are visible under powerful microscopes and possess the characteristics of suspensions. (Study carefully the table on page 407.) If the dispersed particles in a mixture have diameters less than 1 mμ, the mixtures exhibit the properties of solutions. Colloidal particles in general have diameters between 1 mμ and 100 mμ, although the limits are rather indefinite and blend into those of solutions on one side and of suspensions on the other.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



141. RELATIVE SIZE OF SOME VERY SMALL PARTICLES. This entire scale represents only seven-tenths of a micron or 700 millimicrons.

Scientists have been able to judge the sizes of colloidal particles by means of (a) the ultramicroscope, (b) filters with known porosity, and (c) the color of the colloidal dispersion. By decreasing the size of colloidal gold, the colors red, green, and blue are in turn produced—the colors formed depending upon the size of the dispersed particles.

CHARACTERISTICS OF DISPERSIONS AND SUSPENSIONS

0.1 mμ	1 mμ	10 mμ	100 mμ	1 μ	10 μ	100 μ	1000 μ
Solutions	Colloidal dispersions			Fine suspensions . . .			Coarse suspensions
Clear				Cloudy			
Do not settle				Settle			
Pass through ordinary filter paper				Do not pass through filter paper			
Pass through membranes	Do not pass through animal membranes						
Not visible	Visible in ultramicroscope			Visible with microscope or with naked eye			
	Show Brownian movement			No Brownian movement			

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Colloidal particles are active because they are electrically charged. This can be shown by placing electrically charged plates in colloidal suspensions. Colloidal particles of certain materials move to the cathode; this shows that they are positively charged. Colloidal particles of some materials move to the anode; this shows that they are negatively charged. The migration of colloidal particles under the influence of an electric charge, in much the manner of ions, is often used in separating colloidal particles.

The electric charges on different kinds of colloidal particles are shown in the table below.

KINDS OF ELECTRIC CHARGES ON COLLOIDAL PARTICLES

Positively charged	*Negatively charged*
Aluminum hydroxide	Clay
Ferric hydroxide	Paper
Hemoglobin	Many metals in colloidal form
	Powdered charcoal
	Silicic acid

The charges on many types of particles are probably due to the adsorption of ions from solution. If the particles adsorb positive ions more readily than negative ions, the colloidal particles become charged positively. If negative ions are more readily adsorbed, the particles become negatively charged. However, colloidal particles of the same kind carry the same kind of electrical charge (provided conditions are the same)—they are either all positive or all negative. Because like charges repel, this tends to keep the colloidal particles apart, thus making the colloidal dispersion more stable.

Lightning is caused by the discharge of the accumulation of an enormous number of electrically charged particles suspended in the atmosphere.

Why has the Mississippi river built up a big delta at its mouth? The particles of a colloidal dispersion are often precipitated by neutralizing the charges on the particles by the

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

addition of ions of the opposite charge. This is interestingly shown in the formation of deltas such as the one at the mouth of the Mississippi river. Colloidal clay particles suspended in the fresh water do not settle until their negative charges are neutralized by the positive sodium ions in the salty water of the Gulf of Mexico.

Colloidal particles adsorb gases, liquids, and solids. As a material becomes more and more finely divided, the total surface of the particles is enormously increased. A cube which is one centimeter on an edge has a surface of six square centimeters, but if this same cube is divided into particles of colloidal size, the total surface may become as much as six thousand square meters—an increase of ten million times! This great increase of surface is largely responsible for the properties shown by matter that is in the colloidal condition, because the surfaces tend to attract and hold molecules of other substances.

The tendency of particles of one substance to adhere to the surface of another material is called *adsorption.* This term should not be confused with *ab*sorption—such as the absorption of water by a sponge, or of ink by a blotter in which the liquid penetrates the solid. In *ad*sorption one material forms thin films on the surfaces of another material. These films are estimated to be only a few molecules in thickness.

Not all materials are adsorbed equally by colloidal particles. The fact that surfaces of colloidal particles are selective and adsorb some materials more readily than others enables firemen, miners, and others to use gas masks as a protection against injurious gases. The masks contain charcoal which adsorbs many objectionable and harmful gases. On the other hand, the life-giving oxygen in the air is adsorbed much less readily.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. VIII, pp. 110-127, "Colloids—The World of Neglected Dimensions."

DARROW, F. L. *The Story of Chemistry.* Chap. IX, pp. 317-328, "The Twilight Realm of Matter."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XX, p. 323-340, "Colloid Chemistry."

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XIII, pp. 222-235, "Colloids."

Applying in Life What You Have Learned in Chemistry

A study hint: To think accurately you must have ideas and a good vocabulary to express them concisely.

You cannot think without ideas; you cannot think well without facts; you cannot express your ideas to others without a good vocabulary. Words are the building blocks of thoughts, just as elements are the building blocks of all matter.

Your ability to think is determined to a large extent by the stock of meanings which you have been acquiring all your life. Only by using words which have meanings to others can you exchange ideas with them.

This is especially true in science study because many scientific terms have special or exact meanings which are understood only by those who are trained to know them. Acquiring a scientific vocabulary will enable you to express your ideas more concisely.

As you study this unit and other units, see how many of the terms used have special meanings. Learn to express your thoughts clearly by choosing your words carefully.

Putting Chemistry to Work

A

(1) In a movie theater what effect is illustrated by the shaft of light coming from the projector to the screen? Why does smoking in the balcony make this effect more pronounced. (2) Why do some precipitates pass through a filter paper when they are washed repeatedly? (3) What purpose does charcoal serve when placed in the food compartment of a refrigerator? (4) What operation will remove precipitates from a liquid but will not remove colloidal particles? (5) Tell how you would separate a mixture of gelatin and sugar in warm water. Draw a diagram to illustrate your point.

B

(6) Why is the older term *colloid* less accurate than the term *colloidal state?* (7) What reason can you give for calling the colloidal state the "twilight zone of matter"? (8) Can you explain why gravity, which causes large particles suspended in a liquid to settle, will not also cause very small particles to settle out? (9) What questions would you ask yourself in deciding whether a certain material is a solution, a colloidal dispersion, or a suspension? (10) Use milk

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

and sugar solution as examples to explain the meaning of *dispersion, disperse phase,* and *dispersion medium.*

Research and Activities That You Will Enjoy

A demonstration: Shake some litmus solution with powdered charcoal and then filter it. Repeat this procedure with copper sulfate solution. Observe and explain any difference in action.

A forum: Ask a physician to visit the class or appoint several members of the class to visit different physicians to justify this statement by the famous surgeon, W. J. Mayo, "The colloidal field today represents the most promising realm of medical research."

Special reports: (a) How mirrors are silvered. (b) How cohesion aids in fire-polishing glass. (c) How colloidal dispersions are related to the swelling which follows certain types of injury.

Problem 45

HOW ARE COLLOIDAL DISPERSIONS PREPARED AND USED?

The colloidal state of matter is important to you in many ways. The tissues of your body are largely colloidal. Your blood is in colloidal state and all your food passes through this condition while it is being prepared for assimilation in the body. Even life itself has its beginnings in colloidal protoplasm.

Nature uses "wind and wave" and temperature to form small particles. Nature causes the formation of small particles in many different ways. The weathering of rocks breaks them into smaller pieces. The rains wash rocks and soil and make particles small enough to remain suspended as in muddy water. Waves grind fine particles from pebbles and roll them upon the shores. Winds carry the particles far and wide. Rivers wash them back down to the sea. Nature is continuously carrying on these activities.

Man also divides materials into small particles by crushing, rolling, and grinding, but his methods are much faster than those of nature.

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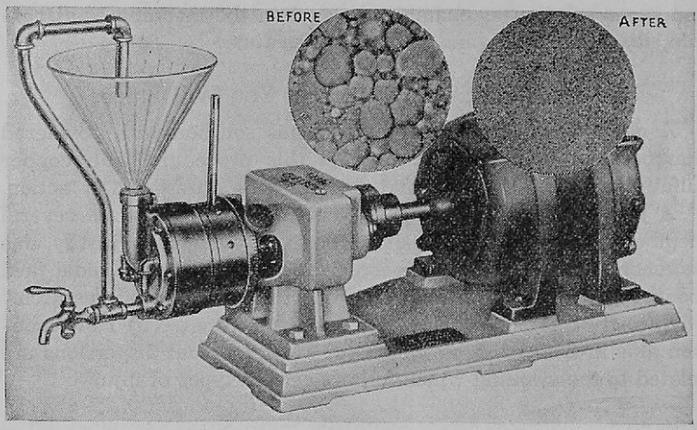

Courtesy, U. S. Colloid Mill Corporation

142. A COLLOID MILL. Particles of colloidal size are made by grinding substances in a liquid in this specially designed mill. A comparison of the particle size before and after passing through the mill is shown above.

The paint on your school building was put into the colloidal state by dispersion. Since the colloidal state is a borderland between coarse dispersions and solutions, you can prepare colloidal dispersions by either one of two general methods. You can start with coarse or solid matter and subdivide it until the colloidal state is reached, or you can start with particles of molecular size and build them up until they reach colloidal size. The first plan was used to prepare the paint on your school building. This plan is often known as the *dispersion* method (sometimes called peptization), while the second plan is usually called the condensation (or coagulation) method. These two approaches to the colloidal state are shown in the following diagram.

Dispersion Methods →		← Condensation Methods
Matter in mass	Colloidal dispersions	True solutions
Particles larger than 1000 mμ	Particles between 100 mμ and 1mμ	Particles less than 0.1 mμ

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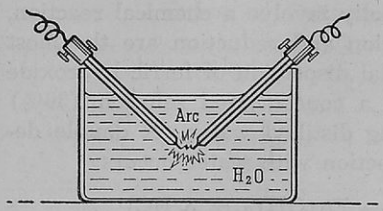

Gold, silver, platinum, and other metals may be prepared in colloidal condition by passing an electric arc between wires of the pure metals under water. The arc tears particles of metal from the metal wires.

143. BREDIG'S ARC METHOD OF PREPARING COLLOIDAL METALS

Colloid mills are sometimes used to prepare and disperse particles of colloidal size. In a colloid mill (Fig. 142) particles in suspension are passed between revolving surfaces that are very close together.

Once a colloidal dispersion is formed, the dispersed material frequently tends to go back into larger particles. To prevent this, some special substance may be added to the mixture. This substance may be a *protective colloid* which keeps the dispersed particles apart by forming a protective coating over them. Gum arabic is used to make carbon particles stay dispersed in India ink. Gelatin acts as a protective colloid in ice cream to make it smooth. A colloidal dispersion of graphite in water (aquadag) or in oil (oildag) is prepared and made permanent by "grinding" a suspension of graphite in the presence of tannin. Gelatin, glue, and agar require no peptizing agent or "grinding" since they are readily dispersed by water.

Colloidal dispersions of certain metals, such as gold and silver, may be prepared by electrical dispersion (Bredig's arc method). When an electric arc is produced between two metal electrodes *under water,* the metal disintegrates and forms a colloidal dispersion.

Some substances are put into the colloidal state by condensation. Condensation methods (coagulation) start with molecules and cause them to collect into particles of colloidal dimensions. The process must stop when colloidal particles are reached, otherwise the particles become so large that a precipitate is formed. Protective colloids are often employed to prevent the formation of larger particles.

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Condensation methods usually involve a chemical reaction, of which double decomposition and reduction are the most common. A dark red colloidal dispersion of ferric hydroxide may be formed by pouring a concentrated solution (30%) of ferric chloride into boiling distilled water. A double decomposition (hydrolysis) reaction with water occurs:

$$FeCl_3 + 3\ HOH \rightarrow Fe(OH)_3 + 3\ HCl$$

Ferric hydroxide is insoluble and usually precipitates when it is formed in solution. In this case, however, by the time particles of colloidal size form, they have acquired positive charges which prevent further coagulation. These colloidal particles will remain dispersed if their electric charge is not neutralized. However, the addition of negative ions (by adding a solution of a sulfate or a phosphate) neutralizes the charges on the positive colloidal particles and precipitates them.

HOW ARE COLLOIDAL DISPERSIONS USED?

The colloidal state is not limited to solids and liquids. Since the three states of matter—gases, liquids, and solids—may be dispersed in each other in pairs, there are nine combinations possible. Eight of these combinations may give rise to colloidal dispersions. A colloidal dispersion of one gas in another is obviously impossible because this represents a molecular dispersion—a "true" solution.

The table on page 415 shows these eight types of colloidal systems as classified by the German chemist, Ostwald. Foams, fogs, emulsions, smokes, and solid suspensions in a liquid are perhaps the most interesting colloidal dispersions. Many colloidal materials are complex mixtures and are exceedingly difficult to classify.

Your mother sometimes serves cake covered with a delicious colloidal dispersion: whipped cream—it is a gas dispersed in a liquid. Typical foams are produced when cream is whipped and when egg white is beaten. Minute bubbles of air are thus forced into the liquid. Foams are often made quite stable by the presence of other colloids. Firefoam (Foamite) for ex-

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TYPES OF COLLOIDAL DISPERSIONS

Dispersed Material	*Dispersion Medium*		
	Dispersed in **Gas**	*Dispersed in* **Liquid**	*Dispersed in a* **Solid**
Gases (bubbles)	Colloidal state not possible. Gases form *molecular* mixtures.	*Foams* Whipped cream Beaten egg whites Fire foam Ice-cream soda	*Solid foams* Plaster Pumice Meerschaum Adsorbed gases
Liquids (droplets)	*Fogs* Mists Clouds Sprays	*Emulsions* Mayonnaise Milk Insecticides Blood	*No general name* Water in paraffin Butter Cheese
Solids (grains, films)	*Smokes* Fumes Ammonium chloride "smoke" Dust	*Sols, Gels* Jelly Hot chocolate Muddy water Paint	*No general name* Colored glass Some alloys Porcelain Paper

tinguishing oil fires is essentially a colloidal dispersion of carbon dioxide gas in water. (See page 440.) Through the use of licorice, the bubbles of carbon dioxide are bound together into a stiff stable foam.

Foaming causes liquids to boil over easily, as may be seen when milk, cereals, and other similar foods are cooked. Since such foods are more likely to scorch, they are frequently cooked in double boilers.

Foams often present serious difficulties in industrial processes. In such cases it is necessary to find methods of preventing or destroying them. For example, when water foams in steam boilers, it is carried over with the steam, producing hammering effects in the engines or throwing turbines out of balance. To remedy this condition, the amount of dispersed and suspended materials in the water must be regulated.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Aviators try to avoid colloidal dispersion in the atmosphere: fog—it is liquid dispersed in a gas. This type of colloidal dispersion is especially interesting from the standpoint of weather and aviation. Minute droplets of water suspended in air constitute a fog. The droplets probably condense on particles of suspended solids, such as dust particles.

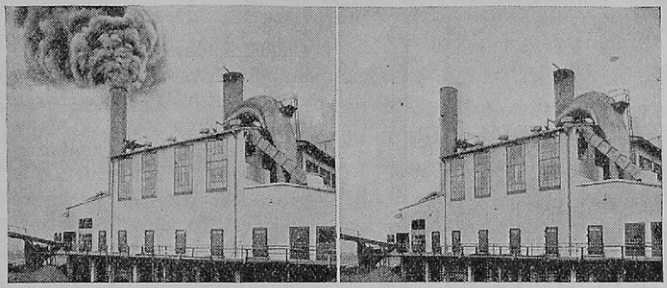
The mayonnaise on your salad is an emulsion—it is a liquid dispersed in another liquid. You know, of course, how mayonnaise adds zest and zip to your salad. It adds flavor to your meal and its smooth creaminess makes it one of the most popular salad dressings in use. Mayonnaise dressing is an emulsion—a mixture of olive oil and vinegar. However, if you try to make mayonnaise by vigorously shaking together olive oil and vinegar, you find that droplets of the olive oil remain suspended in the vinegar for a short time only. Quite soon after you stop shaking the mixture, the oil droplets run together and separate out as a layer of oil. An "emulsion" formed by such shaking is not permanent. To prepare a stable, permanent emulsion, you must add a third substance called an *emulsifier* or emulsifying agent, which may itself be a colloid. The emulsifier used in mayonnaise is egg yolk. This emulsifier forms protecting layers around the droplets and keeps them from coming together.

Soap is an emulsifying agent for kerosene and water. The value of soap in cleaning is largely due to its ability to form an emulsion between water and oils and grease (dirt).

Why is butter churned from sour cream instead of sweet cream? Another typical example of an emulsion is milk which contains droplets of butterfat in a water solution of milk sugar and salts. The casein in the milk acts as the emulsifier. When milk or cream "sours," the milk sugar changes to lactic acid due to bacterial action, and the casein is precipitated. The emulsion is no longer stable and the butterfat can then be separated more easily from the whey. This is the reason why butter is churned from "sour" cream more easily than from sweet cream. Butter itself is an emulsion of water in butterfat.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Although many emulsions contain particles larger than colloidal dimensions, they often show many of the properties of colloidal systems. This is especially true with fine emulsions which approach closely to the true colloidal condition.



Courtesy, Western Precipitation Corporation

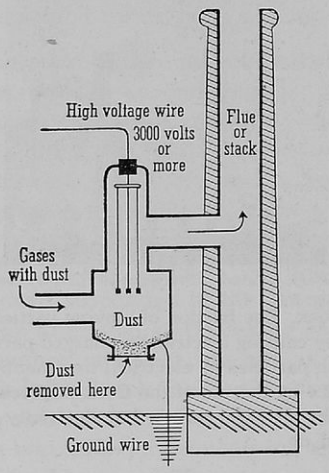
144. THE COTTRELL PRECIPITATOR AT WORK. The friction of moving particles detaches electrons from atoms, thereby causing electrically charged particles. The Cottrell process removes such particles by electrical treatment. A factory can decrease its smoke nuisance by the use of the Cottrell process. This illustration shows conditions before and after the electricity is turned on.

Many of our chimneys spout out smoke which is a colloidal dispersion of a solid in gas. Ordinary dark-colored smoke consists mainly of minute particles of unburned carbon suspended in the air. Even after the larger particles have settled, there remains a colloidal blue haze which forms a very stable system. The blue haze of forest fires, that hangs in the air for weeks without settling, often lends charm to Indian summer. The beautiful color effects of sunsets are produced by colloidal particles of smoke and dust.

In many communities smoke and fumes are nuisances. They also often represent a loss of valuable by-products. In order to recover valuable substances from smokes and fumes and to decrease the smoke nuisance, F. G. Cottrell, an American chemist, devised a method of electrically precipitating the suspended particles. The *Cottrell electrical precipitator* is based on the fact that the suspended solids, even though their size

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

may exceed colloidal dimensions, are electrically charged. The escaping smokes and fumes are passed between two electrodes (usually a plate and a wire) which are highly charged with electricity. If the suspended particles have a negative charge, they are attracted to the positive electrode.



Colloidal particles in smoke and flue dust are electrically charged. A high voltage charge is passed into wires or plates suspended in the precipitating chamber. The outer surface is grounded. Whether the smoke and dust particles are charged positively or negatively they are discharged by contact with the oppositely charged surfaces and removed as dust. A factory can decrease its smoke nuisance in this manner. Dust particles other than those in smoke can also be precipitated in this manner.

145. HOW THE COTTRELL PRECIPITATOR WORKS

If the suspended particles have a positive charge, they are attracted to the negative electrode. At the electrodes the dispersed particles are discharged, and they at once collect into larger particles and precipitate.

The gelatin dessert you had at lunch was a solid dispersed in a liquid. You perhaps enjoy the pleasing taste and flavor of the gelatin desserts served in your home or in your school lunchroom. You may know, too, that a very small package of the powdered gelatin makes a large bowl of the gelatin dessert.

In warm water gelatin, jellies, and many similar substances form colloidal dispersions called *sols,* or suspensoids. Before your gelatin dessert cooled, it was a sol. It is possible to prepare a sol with gold and with many other substances.

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A gold sol consists of colloidal particles of gold suspended in water.

When your gelatin dessert is warm it is a sol. As it cools, the suspended particles collect into thin films which inclose most of the water. In this way the dessert takes the form of a semisolid, which is now known as a *gel* or an emulsoid. A gel is a colloidal system which is more or less rigid; it possesses somewhat the properties of a solid. Other examples of gels are cold molded jelly and coagulated egg white.

The substance which forms the gel in fruit juices is pectin. Some fruits contain little or no pectin, so it is impossible to make jelly from their juices. To overcome this deficiency, pectin from some other source is added. In this way it is possible to make jelly from the juice of many fruits which in their natural state would not gel.

Colloidal dispersions in liquids are common and useful and often exhibit interesting qualities. Many finely divided solids that have been dispersed in a liquid appear to have an attraction for the liquid. They adsorb the liquid thus becoming *hydrated* (in the case of water), or solvated. Examples of these "water-loving" colloids are gelatin, glue, egg white, starch, and gums. Most foods are of this type. Foods easily and naturally form colloidal dispersions with water without the use of colloidal mills or without the use of any special methods for preparing dispersions. In general, foods are *reversible* and pass easily from a gel to a sol.

On the other hand, colloidal dispersions of metals and inorganic compounds, such as sulfides and hydroxides, do not have an attraction for their liquid medium. They are known as "liquid-hating" colloids. They are artificial (man-made) and require special methods in their preparation. They are easily precipitated.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. VIII, pp. 110-127, "Colloids—The World of Neglected Dimensions."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XX, pp. 323-340, "Colloid Chemistry."

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HOWE, H. E. *Chemistry in Industry.* Vol. II, Chap. X, pp. 171-189, "Glues and Gelatins."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. I, p. 90, "Cottrell Precipitator"; Vol. II, Chap. L, pp. 1429-1444, "Glues and Gelatins."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XIII, pp. 222-235, "Colloids."

Applying in Life What You Have Learned in Chemistry

In what way does the addition of gelatin to ice cream or babies' milk make it more easily digested? (Hint: Remember that casein in milk forms a curd before it is digested.)

Richard got stung! He was really stung by a wasp, and did he know it?

His father suggested that the immediate application of a thick paste of baking soda might ease the pain. What justification can you see for placing baking soda on a bee or wasp sting? (Hint: The swelling is caused by formic acid which causes proteins to absorb water.)

Mandy certainly knew how to make good coffee. It was always clear, too.

Now Mandy had a way of her own that many modern housewives might not approve. When making coffee, she placed egg shells in the coffeepot!

What happens when egg white is added to cloudy coffee?

Gerald Randall thought he had a "swell" idea. The crank-case oil in his car had become very dirty. He decided he would remove the "carbon" and renew the oil for use again by filtering the oil.

He was disappointed, however, when he found that the oil was still dirty after it came through the filter. What fact had he failed to take into account?

He then wondered if the oil could be clarified by using some adsorbing agent. What do you think of this?

Putting Chemistry to Work

A

(1) Denatured alcohol may contain a small amount of benzine, which is an oil like gasoline. Why does this alcohol turn cloudy

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

when water is added? (2) From the standpoint of electric charge, show why aluminum hydroxide is useful in removing suspended clay particles from water. (3) How could the smoke nuisance in a manufacturing district be reduced? (4) In preparing photographic films and paper, solutions of silver nitrate and sodium bromide are mixed in the presence of gelatin. Can you explain why silver bromide does not separate out as a precipitate? (5) What substance causes the colloidal dispersion in certain fruit juices to form a gel when cooked with sugar and then cooled? How can jelly be made from fruit juices that do not contain this substance? (6) What explanation can you offer for erasing pencil marks from paper with "art gum"? (7) Can you see any reason, aside from taste, for adding lemon juice or cream to tea? Offer a possible explanation.

B

(8) How would you distinguish between solutions, colloidal dispersions, and suspensions for a person who had not studied chemistry? (9) Classify each of the following colloidal dispersions according to the table on page 415: (a) soapsuds; (b) sea foam candy; (c) soap bubbles; (d) invisible dust in air; (e) sodium chloride in alcohol; (f) ammonia and hydrogen chloride fumes (ammonium chloride); (g) blue tobacco smoke; (h) ordinary house paint; (i) fruit jelly. (10) How can you account for the beautiful colors of (a) a sunset; (b) the summer sky; (c) bluebird feathers; (d) opals? (11) From your knowledge of colloidal dispersions give a reason for each of the following: (a) the formation of deltas; (b) the use of gums in making certain inks; (c) the use of egg yolk in making mayonnaise dressing.

Research and Activities That You Will Enjoy

A model: Build a model of a Cottrell precipitator to illustrate the principles involved.

A report: By asking a chemical engineer or by outside reading, learn how ores are concentrated by the flotation process. Report your findings to the class.

A display: Beautiful "gardens" may be grown in silicic acid gel. Prepare several of these and show them to the class. Good ones to try are the "lead tree," mercuric iodide, copper chromate. (Refer

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to Holmes, *Laboratory Manual of Colloid Chemistry,* or to "Lead Trees Grown in Silica Jells," by Brewington, in *J. Chem. Ed.,* 6: 2228-30, Dec., 1929.)

Looking Back into Unit 10

Be sure you know the purpose of this unit. Read again the material on page 400, "Looking Ahead into Unit 10." Then study the following Summary Test.

Summary Test

1. *What are colloidal dispersions; how can you recognize them?*
   (a) How are colloidal dispersions an "in-between" condition of matter?
      (1) What is meant by dispersion?
      (2) How was the word "colloid" derived?
   (b) What characteristics of colloidal dispersons enable you to recognize them?
      (1) What does the Tyndall effect show you about colloidal dispersions?
      (2) What does the Brownian movement show you about colloidal particles?
      (3) Why do colloidal particles not settle out?
      (4) Why do colloidal particles pass through ordinary filters?
      (5) How can you separate colloidal dispersions from solutions by dialysis?
      (6) What effects result from the electric charge on colloidal particles?
      (7) What uses are made of the ability of colloidal particles to adsorb other substances?

2. *How are colloidal dispersions made and used?*
   (a) How are small particles formed in nature?
   (b) How are colloidal particles formed—
      (1) By dispersion methods?
      (2) By condensation methods?
   (c) How are colloidal dispersions used?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

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Closing the Unit

Here you have a study of *particles* that are in the *"in-between"* state. They are neither individual molecules which you cannot see; nor are they large suspended particles which you *can* see in muddy water with the naked eye. Chemists think of a *solution* as a *molecular dispersion,* the *solute* being incapable of separating out and settling from the solvent. At the other extreme is a *suspension* whose *solid particles* settle rather quickly upon standing. Between these extremes is the *colloidal dispersion,* in which *particles* may exist in a great range of sizes; some settling upon standing for some time, others remaining dispersed for years.

You find that the constant motion of *colloidal particles,* seen under the *ultramicroscope* and known as the *Brownian movement,* strengthens the *kinetic-molecular theory.* You find the size of colloidal particles entering into the explanation of *dialysis* and *osmosis,* in which *true solutions* are able to pass through *membranes* while *colloidal dispersions* do not pass through. These processes are vitally related to the maintenance of life in plants and animals and in your own body.

Because *colloidal particles* possess either *positive* or *negative electrical charges,* an exposure to ions of opposite charge may precipitate the colloidal material. So you find river water depositing deltas when it reaches salt water. One of the best industrial applications of this process is the *Cottrell electrical precipitator* which is doing effective work in eliminating the smoke nuisance. One of our large electrical companies is applying the idea to especially constructed hospital rooms for relief of extreme cases of hay fever and other respiratory ailments.

Colloidal dispersions may be brought into being by *chemical* means as well as by physical means. However, colloidal dispersions are based on certain *physical* conditions rather than on definite chemical reactions.

Since the study of *colloidal dispersions* is a science of *particles,* you should have gained from your study a concept of the enormous *surface area* they present. This *adsorption* power of colloids is one of their most distinctive properties. Are you familiar now with some new units of measurement—the *micron* and the *millimicron?*

Colloids and *you!* Look about you and see how much of this branch of the study of chemistry and its application affect your life both by direct and indirect means.

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Looking Ahead into

Unit Eleven

What would you think of a person who made a statement like the following one? "I need ashes for my garden and carbon dioxide for my trees, so I'll have to buy ten more tons of coal." That certainly would be a very foolish statement.

You know that you buy coal for the heat that is released when the carbon and other elements in the coal burn by combining with oxygen from the air. Coal is a sort of carrier of energy, but this energy is not released as heat energy until the carbon burns, thereby transforming the stored-up chemical energy into heat energy. Carbon is a typical source of energy.

But the element carbon in its different garbs has many other uses also. Perhaps no other element shows such different and striking allotropic forms. How different are a lump of coal and a sparkling, brilliant diamond! But they are brothers chemically because they both are largely carbon. Someone has aptly said that a diamond is simply a lump of coal that stuck to its job! Can you explain?

Then, too, the oxides of carbon are useful and important. It may seem strange that the product of the complete burning of carbon should serve such different uses as putting out fires and putting the tingle into your soft drinks. But such is the case with carbon dioxide. It may seem strange also that a gas as treacherous as carbon monoxide should be a useful fuel.

You will find much of interest and practical value in the following problems.

Problem 46. *How Are Different Forms of Carbon Produced and Used?*

Problem 47. *How Do the Oxides of Carbon Affect Our Lives; How Are They Produced?*

Problem 48. *How Can You Use Fuels Most Efficiently?*

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Carbon and Fuels: Carbon—A Typical Source of Energy

Problem 46

HOW ARE DIFFERENT FORMS OF CARBON PRODUCED AND USED?

The coal that you burn in your furnace contains carbon and other materials—how was coal produced? Coal did not just happen. Its origin goes back millions of years to a time when great sections of the earth were covered with very dense vegetation. Although some of this growth was removed by slow oxidation and decay, much of it collected in deep layers and was submerged under water and sediment. Pressure and chemical changes slowly converted these deposits of vegetable matter to peat and then to lignite. Both of these products are now used in some localities as fuel. A continuation of this *carbonization process* produced soft (bituminous) coal and then, under continued pressure and heat, hard (anthracite) coal. Coal, as you can see, is the result of a long natural process.

AVERAGE COMPOSITION OF SOFT AND HARD COAL
(Actual analyses vary greatly)

	Bituminous	*Anthracite*
Water	9.94%	3.33%
Ash	8.84	9.12
Volatile matter	15.04	6.2
Carbon	66.18	81.35

The United States produces and uses about six times as much soft coal as hard coal. The world's yearly production

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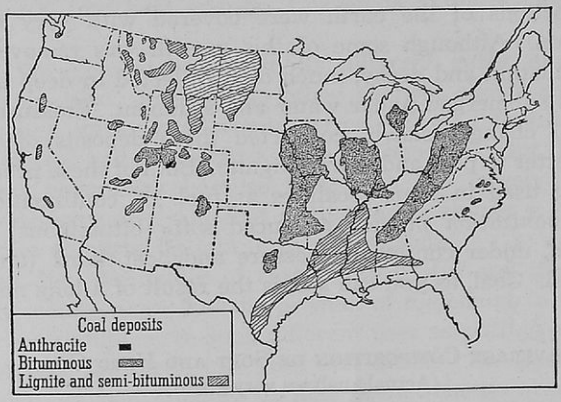
of coal is well above a billion tons, almost half of which is produced in this country.

The table on the previous page and the one on this page show interesting comparisons between soft and hard coal and estimations of our supply of each.

COMPARISON OF SOFT AND HARD COAL

Supply	*Bituminous* (soft)	*Anthracite* (hard)
Estimated U. S. supply (in tons)	3,422 billion	22½ billion
Used to date	22 billion	7 billion
Supply may last	3,500 years	100 years



146. COAL DEPOSITS OF THE UNITED STATES

Coke contains less volatile matter than coal and therefore burns with less smoke in an ordinary furnace—how is coke prepared and what are its by-products? The need for an efficient fuel and reducing agent has caused many industrial plants to produce and use coke instead of coal. The developments of the coke and iron industries are closely related. At first wood was used to reduce iron ore (oxides) to iron; then charcoal was

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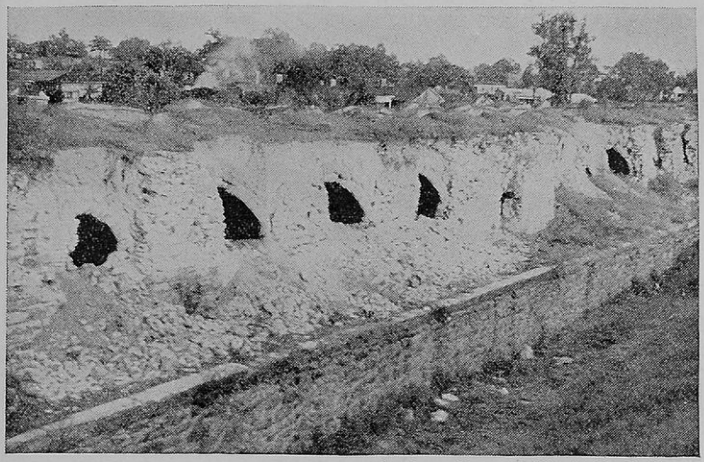

Courtesy, Carnegie-Illinois Steel Corp.

147. BEEHIVE COKE OVENS. In ovens of this type, coke is the only product. All volatile products such as gas, tar, ammonia, and hydrocarbons are lost. This type of oven is going out of use.

found to be more satisfactory. As the forests disappeared, furnace men turned to coal and finally to coke as the cheapest and most satisfactory reducing agent. Coke is formed when coal is heated in the absence of air. In this process, called *destructive distillation,* the volatile materials are driven off from the coal, leaving a porous mass containing a high percentage of carbon.

Originally, coke was made by incompletely burning coal in conical piles, covered with dirt. Openings were left at the base and at the top. Since there was a limited supply of air available, coke was formed. Later brick beehive ovens (so-called from their shape, Fig. 147) were used, but it was found that valuable materials were being wasted. As uses were found for these "by-products," coke ovens were designed to save them.

In the modern manufacture of coke, crushed coal is passed into the top of long, flat, rectangular, bricked-in ovens, as large as 40 feet long, 14 feet high, and about a foot thick.

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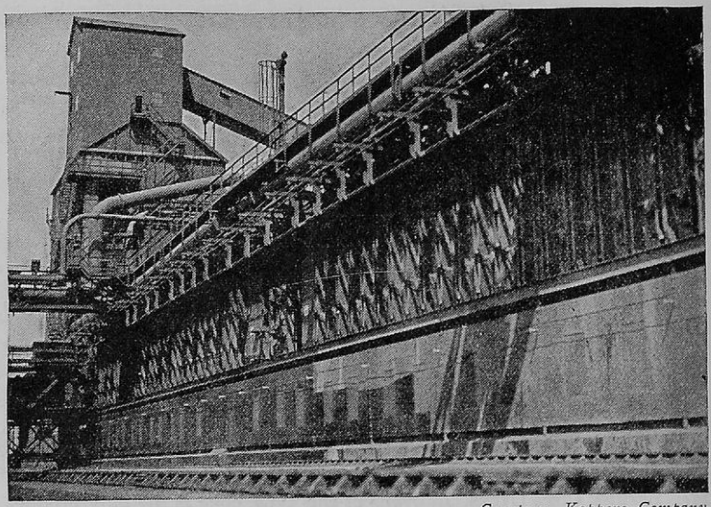

Courtesy, Koppers Company

148. BY-PRODUCT COKE PLANT. In this type of coke plant all valuable volatile products are saved. By-product plants are rapidly replacing the wasteful beehive ovens.

As many as fifty-two of these single ovens may be arranged side by side in batteries. (See Fig. 148.) Between each pair of ovens is a gas compartment, in which coal gas is burned to produce the heat necessary to coke the coal. This coal gas is a by-product of the process. As the coal is heated, a mixture of volatile materials such as coal gas, ammonia, oils, and tar, leaves the ovens at the top near one end. These materials are conveyed to the by-product plant for further treatment and separation. After the coal has been coked in an oven for several hours (from 11 to 31, depending on the demand), the doors are removed from each end of the oven and the hot coke is pushed out into a waiting car. The coke is then taken to a "quenching tower" where it is cooled by a spray of water. It is then ready for use.

At the by-product plant the distillate (that is, the mixture of coal gas, ammonia, oils, tar, etc.) is treated to recover several valuable products. The following table shows the variety

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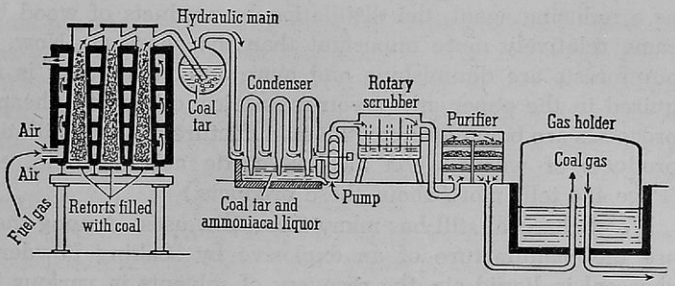

149. PLANT FOR MAKING COAL GAS. Coal gas is made by heating coal in retorts. After the removal of all condensable products, hydrogen sulfide is removed in the purifier, and the coal gas passes into the gas holder for storage.

of the most important "first" products obtained from one ton of coal.

One ton of coal yields	10,000 to 12,000	cu. ft. coal gas
	1,400 to 1,500	lbs. coke
	6 to 9	gal. coal tar
	5 to 6	lbs. ammonia
	2 to 3	gal. light oil

Coal gas is used as a fuel both in industrial plants and in many homes (city gas). Tar also may be used as a fuel, although much of it becomes the source of many useful and valuable synthetic products such as dyes and medicines. Ammonia is usually converted to ammonium sulfate, vast amounts of which are used for fertilizers. The light oils are separated by fractional distillation into such materials as benzene, toluene, and phenol—all useful starting materials for a wide variety of important products. Perhaps you may now question the economy of burning coal in our homes and thus wasting all of these important by-products.

What products may be obtained by heating wood? When wood was more plentiful, much charcoal was used as a reducing agent. Charcoal was then the chief product obtained by the destructive distillation of wood. As coke replaced charcoal

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as a reducing agent, the distillation by-products of wood became relatively more important than the charcoal. Now, as our forests are diminishing and more and more wood is required in the paper and rayon industries, other and cheaper processes are being used for the manufacture of the distillation products of wood—wood alcohol, acetic acid, acetone, etc. (Page 484 tells more about these products.)

Wood charcoal still has many important uses. Among them are the manufacture of an explosive by soaking powdered charcoal in liquid air, the recovery of solvents in various industries, and the removal of objectionable colors and odors.

How is activated charcoal used? In Unit 10 (page 409) you learned why many finely divided materials have the ability to condense and hold certain gaseous and liquid substances on their surfaces. This process is known as *adsorption.* Due to its very porous nature, charcoal has much surface and therefore is a good adsorbing agent. Its surface, and consequently its adsorbing ability, may be increased even more by a process known as *activation.* While the details of this process are more or less a trade secret, it is known that activated charcoal is prepared by heating charcoal at a high temperature in the presence of steam or certain chemical substances. It is believed that this treatment removes tarry materials which clog the pores of the charcoal.

Charcoal from many sources is used in gas masks to adsorb poisonous or otherwise objectionable gases. In recent years the use of activated charcoal has been extended to many industries, such as the clarification of oils, extracts, and sirups.

Sugar is made white by bone black—what is bone black? When bones and other animal refuse are heated in the absence of air, there finally remains a porous material which is known as animal charcoal, or bone black. Animal charcoal contains a high percentage of mineral matter, mainly calcium phosphate, and only about 10 per cent carbon. Nevertheless, this form of impure carbon possesses an adsorbing ability and is used as a decolorizer, chiefly in the refining of sugar and oils.

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India ink and black paints are made from gas black—how are gas black and lamp black obtained? When natural gas is partially burned in a very limited supply of air, an excellent form of finely divided carbon known as *gas black* is produced. The escaping particles (carbon dust or soot) are collected on a revolving disk, (which is cooled with cold water), and then scraped off into bags. Large amounts of this carbon black are used in printer's ink, India ink, black paints, auto tires, electrodes, and arc carbons. *Lamp black* is obtained in a similar manner from the burning of oils. In either process only a small percentage of the carbon in the fuels is recovered.

Diamonds are "white carbon"—how are diamonds produced? It is believed that diamonds are formed under great heat and pressure by the crystallization of carbon dissolved in molten materials. A diamond is a pure, hard, compact form of carbon with a density of 3.5. This is greater than the density of other forms of the element.

Tiny diamonds have been made by man. In 1893 Henri Moissan, a French chemist, reported his success in producing very tiny diamonds by an artificial process. He dissolved very pure sugar charcoal in molten iron and then cooled it suddenly by plunging the mass into cold water. This brought about great internal pressure which caused some of the carbon to crystallize. When acid dissolved away the iron, some microscopic crystals of diamonds were seen along with much graphite. Very little success has resulted from later attempts to produce synthetic diamonds of any size.

Diamonds and graphite are crystalline forms of carbon. Coke, charcoal, and lamp black, described previously, are amorphous forms of carbon. They have no definite molecular structure and are therefore noncrystalline. Crystalline carbon, however, is found in nature in the form of diamonds and graphite. It can be proved that both of these substances are carbon by completely burning them. In either case carbon dioxide is the only product formed by the burning. These types of carbon—diamonds, graphite, and the various kinds of amorphous carbon—are the *allotropic forms of carbon.*

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What is it that makes a diamond more valuable than a piece of glass? There are mainly two properties that make a diamond more valuable than other substances. (1) A diamond is the hardest substance known. (2) A diamond has a very high *index of refraction.* This means that when rays of light enter a diamond they often are "trapped" or reflected back and forth on the inside of the diamond before they escape. This is the reason that properly cut diamonds make the most brilliant jewels known.

Small amounts of impurities (probably metallic oxides) give diamonds various colors. Black and poorly colored diamonds are still used extensively for cutting, grinding, and polishing hard surfaces; however, artificial abrasives (grinding materials) such as silicon carbide and aluminum oxide are important products that are now used considerably.

The rarity and hence the high cost of diamonds is largely artificial, due to a careful control of the supply. Diamonds are fairly abundant in deposits in Brazil and Africa. The Kimberly mines in South Africa are among the best known.

The "lead" in your writing pencil is not lead; it is a mixture of clay and crystallized carbon, called graphite—how is graphite produced? Another crystalline form of carbon is *graphite.* This word comes from a Greek word meaning "to write." Mixed with clay in varying amounts, it forms the "lead" in pencils.

Graphite has many other uses. Since it is soft and "greasy," it is used as a lubricant. For this purpose it generally is suspended in a colloidal form in oil (oildag) or in water (waterdag). (*Dag* is a trade name for deflocculated Acheson graphite.) (See page 413.)

Graphite withstands high temperatures; it therefore is used in crucibles that serve many purposes. It conducts electricity well enough to be used for electrodes. In powdered form it is spread over cheap nonconducting surfaces, where copper or other metallic plating and electrotyping is to be done. It is used also in stove polish, rust-prevention paints, and compounds for boiler repair.

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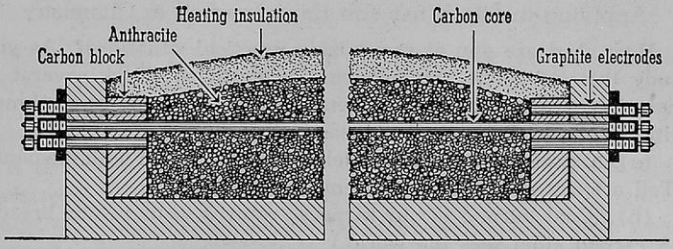

150. GRAPHITE FURNACE. Anthracite coal or coke is heated in a resistance furnace to a temperature of nearly 3500° C. It is converted to graphite as it cools.

Graphite is found embedded in natural deposits of rocky material, chiefly in Ceylon, Russia, and Czechoslovakia. This rocky mixture must be crushed in order to free the graphite. Today graphite is more often made artificially by heating anthracite coal (hard coal) or coke in an electric furnace from which air is excluded. This process was invented by Acheson, who first made carborundum. By heating the coal or coke at the high temperature of 3500° C. for 24 to 30 hours, excellent crystals of graphite are formed.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. VI, pp. 98-117, "Carbon Fuels."

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XXIII, pp. 281-287, "Carbon."

DARROW, F. L. *The Story of Chemistry.* Chap. IV, pp. 152-194, "Chemistry and Power."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XXI, pp. 341-348, "Forms of Carbon."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 23, pp. 158-165, "The Romance of Carbon."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XVIII, pp. 210-222, "Fuels and Smoke."

REED, A. MAXWELL. *America's Treasures.* Chaps. IX-XII, pp. 139-183, "Men Discover the Use of Coal."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. III, pp. 24-34, "Fuel for Tomorrow."

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Applying in Life What You Have Learned in Chemistry

How good are you at recognizing practical situations? As you study this unit, note the following suggestions. Work several of them into "Applying in Life" items. Try for originality combined with accuracy. Present your ideas to the class.

(a) A strange case of a Dr. Jekyll and Mr. Hyde with elements. (Tell a story about these elements in parallel.)

(b) "Coal burned in our furnaces returns to us in our bread." (A carbon atom sees the world.)

(c) Many so-called "diamonds" are simply cut glass.

(d) Admiral Byrd's experience with carbon monoxide. (See *The National Geographic Magazine*, Oct., 1935.)

(e) A lighted candle is sometimes lowered into a well to test the purity of the air in it.

(f) Write a reward notice for the apprehension of a dangerous chemical sneak thief, carbon monoxide.

Putting Chemistry to Work

A

(**1**) For what purpose does a physician sometimes prescribe charcoal tablets? Ask a doctor. (**2**) Is the heat of an arc lamp caused by the burning of the carbon electrodes? Explain. (**3**) Why may the destructive distillation of wood eventually become of very little industrial importance? (**4**) Suggest advantages for the use of coke as a fuel in the home. (**5**) Account for the fact that ammonium sulfate may be considered a by-product from the coke plant. (**6**) How could you distinguish between bituminous and anthracite coal? (**7**) Why does the future production of industrial carbon offer a promising problem to the young industrial chemist?

B

(**8**) What products, formerly wasted, are now saved by using by-product coke ovens? (**9**) Coal has been referred to as "fossil sunlight." Is this figure of speech appropriate? (**10**) Suggest reasons why hard coal and coke burn in a similar manner. (**11**) What contributions to industrial science has E. G. Acheson made? (**12**) A student says: "Coke is made by burning coal in the absence of air." Criticize and correct this statement. (**13**) What adsorbing agents have you now studied? What practical applications have they? (**14**) What point was missed by the student who defined destructive distillation as the "decomposition of an organic substance by means of heat"?

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Research and Activities That You Will Enjoy

An argument: If large artificial diamonds ever become possible, should they be permitted to flood the market and make the present diamonds worthless or should the supply of artificial diamonds be strictly controlled?

A demonstration: Show your class the great adsorbing ability of charcoal by pushing a small previously heated piece of it into a large test tube of ammonia inverted over mercury. Explain what happens and point out the application to gas masks.

A report: After outside reading, tell the class the most interesting things you have learned about diamonds.

Howard Acheson invented a method of making an almost pure graphite. He also prepared carborundum in an electric furnace from coal. Give a report of his achievements and the uses of graphite in industry.

Problem 47

HOW DO THE OXIDES OF CARBON AFFECT OUR LIVES; HOW ARE THEY PRODUCED?

In 1754 a Scottish scientist by the name of Joseph Black heated some magnesium carbonate and discovered a "new" gas—carbon dioxide. Much later, Lavoisier proved that this gas was a compound of carbon and oxygen. Priestley discovered its value in the making of beverages and is indirectly responsible for the beginnings of the soft-drink industry in America. Priestley also first identified carbon monoxide as the gas burning in the blue flame over a furnace fire.

As friend or foe, the oxides of carbon are playing an important role in the chemistry of this modern age.

Carbon dioxide is by no means a new friend to you. You have learned that it is breathed out of your lungs, that plants use it in the manufacture of their food, and that it is produced in all ordinary oxidation processes. These facts are indicated in the diagram of the carbon cycle (Fig. 151). All "carbon roads" lead back to atmospheric carbon dioxide.

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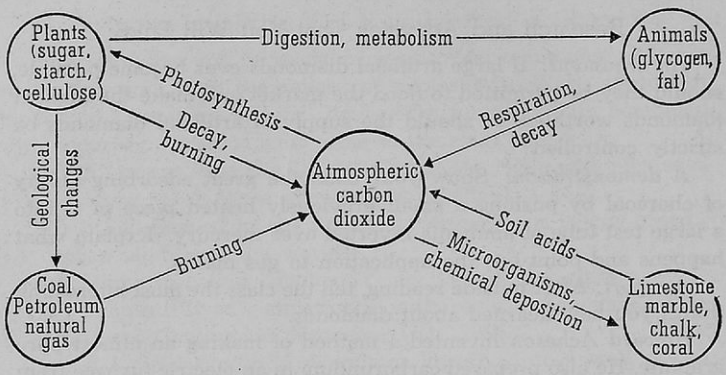

151. THE CARBON DIOXIDE CYCLE. Carbon dioxide is used by plants to build starch and sugar. Animals use these for food. Through oxidation and decay of animal tissues, carbon dioxide is formed.

Carbon dioxide is the most common oxide of carbon—how is it produced? When any carbon-bearing fuel burns completely, carbon dioxide is formed. This does not produce very pure carbon dioxide, but it is a cheap commercial source of the gas. Some carbon dioxide is recovered from flue gases by dissolving it in a sodium carbonate solution and then heating the solution to free the pure carbon dioxide.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2\ NaHCO_3$$

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\uparrow$$

Carbon dioxide is also a by-product from many other commercial processes, from which it may be collected and used. Thus when limestone ($CaCO_3$) is heated to produce quick lime (calcium oxide, CaO), carbon dioxide is released:

$$CaCO_3 \text{ (heated)} \rightarrow CaO + CO_2\uparrow$$

Or when glucose ferments under the catalytic influence of yeast, carbon dioxide is produced along with the alcohol:

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2\uparrow$$

In a few scattered places carbon dioxide may be obtained from

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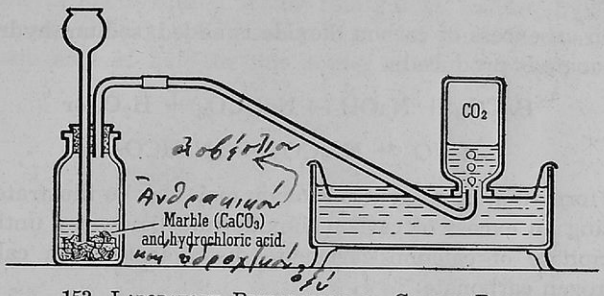
natural waters. When the pressure on the water is released, the gas escapes. The decay of plant and animal materials is continuously liberating carbon dioxide into the air.



152. LABORATORY PREPARATION OF CARBON DIOXIDE

In the laboratory a convenient source of carbon dioxide is the action of hydrochloric acid on calcium carbonate, either in the form of marble chips, limestone, or chalk (Fig 152):

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$

This is a general method; *any strong acid and any carbonate may be used.*

What are the qualities of carbon dioxide? As a pure gas, carbon dioxide is odorless and colorless. It is only moderately soluble in water, one volume of water at 15° C. dissolving approximately 1 volume of this gas. Carbon dioxide is about one and one-half times as heavy as air (44/29 = 1.52). One liter at standard pressure and temperature weighs 1.96 grams.

Carbon dioxide neither burns nor supports ordinary combustion. Its presence is proved by its characteristic reaction with limewater to produce a white precipitate of calcium carbonate:

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

Dissolved in water, carbon dioxide forms unstable carbonic acid:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

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Carbonic acid neutralizes bases to form carbonates, for example:

$$H_2CO_3 + 2\ NaOH \rightarrow Na_2CO_3 + 2\ H_2O$$

When an excess of carbon dioxide is added, sodium hydrogen carbonate is produced:

$$H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O, \text{ or}$$

$$H_2CO_3 + Na_2CO_3 \rightarrow 2\ NaHCO_3$$

The formation of an acid carbonate may also be illustrated by passing an excess of carbon dioxide into limewater until the precipitate of calcium carbonate dissolves to form calcium hydrogen carbonate:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + 2\ H_2O$$

$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2$$

The last reaction is reversible, as illustrated by heating or evaporating the calcium hydrogen carbonate solution:

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$$

Two interesting applications of this action of carbon dioxide are shown in the formation of hard water and in the cave formations in limestone regions.

Carbon dioxide puts the bubbles and the "tang" in your soda-fountain drinks. Large quantities of carbon dioxide are used in carbonated drinks. Although carbon dioxide is only moderately soluble in water, its solubility is appreciably increased when the gas is placed under a pressure of three or four atmospheres. *Henry's law* applies: The weight of a moderately soluble gas dissolved in a liquid is proportional to the pressure applied. When the pressure is reduced by removing the cap from a bottle or by drawing the "soda water" from a fountain, some of the carbon dioxide escapes with effervescence. The carbonic acid which remains gives to the drink a slightly sour, tingling taste.

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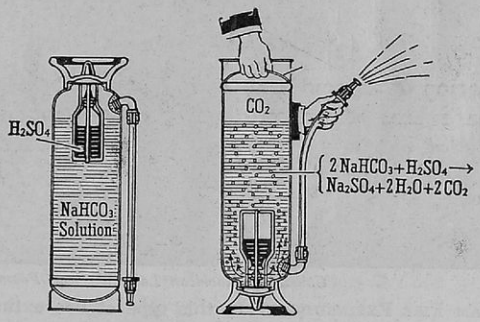
Carbon dioxide is a very good fire fighter. Carbon dioxide is heavier than air and will not burn or support combustion. It is therefore valuable in smothering fires. For this purpose a tank is filled with a water solution of sodium hydrogen carbonate (baking soda) and a bottle of crude concentrated sulfuric acid is held in the holder at the top (Fig. 153).



153. FIRE EXTINGUISHER. Sulfuric acid and sodium bicarbonate produce carbon dioxide. The pressure which the carbon dioxide exerts makes this gas more soluble in the solution; this pressure is used to force the liquid out of the tank.

When the tank is inverted, the stopper is either broken or it falls out, and the sulfuric acid and sodium hydrogen carbonate react to produce carbon dioxide, according to the equation:

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

The pressure of the gas forces on to the fire a stream of water heavily charged with the gas.

The *Foamite* or firefoam type of fire extinguisher is especially valuable for fighting oil fires. In this type of extinguisher the carbon dioxide is held in a foamy mass by tough colloidal films. The materials used in this extinguisher consist of a mixed solution of sodium hydrogen carbonate and licorice to which is added an aluminum sulfate solution when the tank

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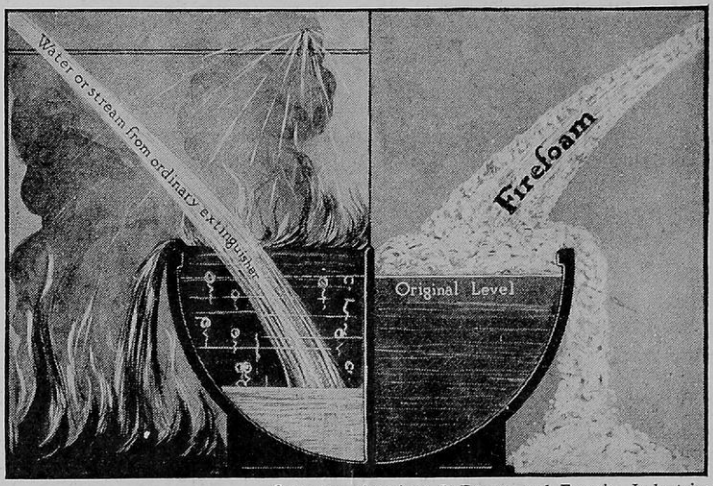


Courtesy, American LaFrance and Foamite Industries

154. FIREFOAM FIRE EXTINGUISHER. In this type of fire extinguisher the carbon dioxide forms a tough blanket of foam which floats on top of oil fires. How does this tend to put out fires of this type?

is inverted at the time of the fire. The aluminum sulfate reacts with water (hydrolyzes) to form sulfuric acid:

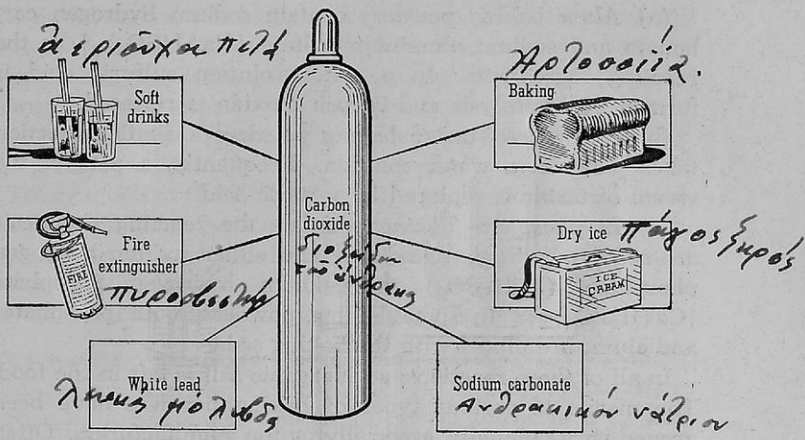
$$Al_2(SO_4)_3 + 6\ HOH \rightarrow 2\ Al(OH)_3 + 3\ H_2SO_4$$

The sulfuric acid in turn reacts with the sodium hydrogen carbonate, releasing carbon dioxide. The aluminum hydroxide and licorice form colloidal films which inclose the carbon dioxide in a mass of bubbles.

There are two advantages to this type of extinguisher. The light firefoam floats on top of liquids such as gasoline and oil and soon excludes air. In small fires in the home, it has little effect on fabrics and furniture since the acid formed is used up in the reaction and the harmless residue can be cleaned up easily.

Carbon dioxide makes it possible for you to have "soft" bread for dinner. The harmless properties of carbon dioxide and the ease with which it may be liberated make it the most acceptable gas for making bread and other baked goods rise.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής



155. SOME USES OF CARBON DIOXIDE. Products involving the use of carbon dioxide are common in your everyday life.

In breadmaking, yeast plants cause sugar to ferment and produce carbon dioxide and alcohol. The carbon dioxide causes the bread to rise and the alcohol is vaporized by the heat of baking.

Carbon dioxide used in baking is also produced by the use of various chemicals. In each case, sodium hydrogen carbonate, commonly called baking soda, is used. An acid is allowed to react with the sodium hydrogen carbonate to produce carbon dioxide. Sour milk contains lactic acid, and may be used with baking soda. Likewise, acid-reacting cream of tartar ($KHC_4H_4O_6$), when added to sodium hydrogen carbonate in the presence of water, liberates carbon dioxide:

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow$$

Commercial baking powders are often a more convenient source of carbon dioxide. Dry baking soda is mixed with an acid-reacting salt which releases carbon dioxide when water is added. Starch or flour is frequently added to baking powders to absorb moisture and keep the mixture dry. The three common types of baking powders are listed on the following page.

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(a) *Alum baking powders* contain sodium hydrogen carbonate and sodium aluminum sulfate [$NaAl(SO_4)_2$] as the reacting ingredients. In a water solution sulfuric acid is formed by hydrolysis and carbon dioxide is released.

(b) *In cream-of-tartar baking powders* a similar reaction takes place in a water solution. Frequently, a part of the cream of tartar is replaced by tartaric acid.

(c) *In phosphate baking powders* the reacting chemicals are sodium hydrogen carbonate and either sodium hydrogen phosphate (NaH_2PO_4) or calcium hydrogen phosphate [$Ca(H_2PO_4)_2$]. In some baking powders, both phosphates and alums are mixed with the baking soda.

In all of these reactions, an inorganic salt is left in the food. The merits of various types of baking powders have been argued very pointedly, especially by the manufacturers. Often these attacks concern the residue which remains after the carbon dioxide has served its purpose. It would seem that final judgment should be withheld until more information is available. It can be said fairly, however, that the more expensive baking powders contain tartrates, and that the cheaper ones are phosphate-alum baking powders.

Ammonium hydrogen carbonate (NH_4HCO_3) is used for certain classes of baked goods, especially crackers, and has the advantage of completely decomposing and leaving no residue:

$$NH_4HCO_3 \rightarrow NH_3\uparrow + H_2O + CO_2\uparrow$$

Frozen carbon dioxide ("dry ice") often preserves foods for you; it is very cold. Prior to 1925, solid carbon dioxide was a laboratory curiosity and had no practical uses. Recently, as much as eight thousand tons of "dry ice" have been produced in one month. Since carbon dioxide is a by-product or "waste product" in so many industrial processes, the gas is comparatively cheap.

In the manufacture of "dry ice," carbon dioxide gas is freed from impurities, and then liquefaction is brought about by compressing the gas and removing the resulting heat.

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The liquid carbon dioxide is then further cooled and permitted to expand into the "snow press." Here the pressure is slightly higher than one atmosphere. Fifty per cent of the liquid changes to solid carbon dioxide. The carbon dioxide snow is then pressed into cakes about ten inches on a side, weighing about fifty pounds.

Today much of the "dry ice" that is produced in the United States is used by the ice-cream industry (Fig. 155), and in the refrigeration of perishable foods that have been quickly frozen instead of canned. Many new uses are developing, as refrigeration equipment for handling it is perfected.

Why is carbon monoxide a treacherous poison? Carbon monoxide is an odorless, nonirritating gas which forms when carbon or a compound containing carbon burns in a limited supply of air:

$$2\ C + O_2 \rightarrow 2\ CO$$

$$2\ CH_4 + 3\ O_2 \rightarrow 2\ CO + 4\ H_2O$$

It combines with the hemoglobin of the red blood cells about 250 times as readily as oxygen, and quickly forms a very stable compound. After carbon monoxide has combined with the hemoglobin, the blood can no longer carry oxygen. Exposure to carbon monoxide in an unventilated room may cause death or may permanently injure the brain or other organs. Despite public warnings and an educational campaign by safety organizations, many deaths result each year from this most treacherous of gases. In a dilution of only one part of carbon monoxide to 200 parts of air, death occurs in about two minutes, while in a ratio of 1 to 500, collapse results in less than one hour.

Three common sources of this poisonous gas are from the exhaust of the automobile engine, from leaky gas mains, and from defective furnaces and flues. Since the greatest enemy of carbon monoxide is the circulation of fresh air, ventilation of the home, garage, and other places where carbon monoxide is found is essential. Long tunnels used by automobile traffic at Pittsburgh and New York City are equipped with devices

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which record the concentration of carbon monoxide and automatically set fans in motion for its removal.

Putting a public enemy to work—carbon monoxide. Carbon monoxide is an excellent fuel. It burns with a blue flame, and a great deal of heat is given off.

$$CO + \overset{\frac{1}{2}\,O_2}{[O]} \rightarrow CO_2 + 68{,}000 \text{ calories}$$

In many industrial processes, the air supply is so controlled that carbon monoxide instead of carbon dioxide is formed in the process. This carbon monoxide is then used as fuel in some other part of the plant.

Since carbon monoxide is easily oxidized, it acts as a good reducing agent. Many ores are reduced by coke, in which case carbon monoxide as well as the coke takes part in the reduction. Typical reactions in the making of iron in blast furnaces illustrate this:

(1) $C + O_2 \rightarrow CO_2$

(2) $C + CO_2 \rightarrow 2\ CO$

(3) $Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$

Coke burns to form carbon dioxide which is reduced by more coke to form carbon monoxide, which in turn reduces the iron oxide ore. The carbon dioxide formed is further reduced by coke to produce a flue gas, rich in carbon monoxide, thus making blast furnace gas a good fuel.

How can you prepare carbon monoxide for study? In the laboratory pure carbon monoxide can be prepared by gently heating oxalic acid crystals in the presence of concentrated sulfuric acid as a dehydrating agent. Both carbon monoxide and carbon dioxide are produced, but the carbon dioxide can be removed by passing the mixture through a sodium hydroxide solution:

$$H_2C_2O_4 \xrightarrow{+H_2SO_4} H_2O + CO\uparrow + CO_2\uparrow$$

$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

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Formic acid may also be dehydrated with concentrated sulfuric acid to produce pure carbon monoxide:

$$HCOOH \rightarrow H_2O + CO$$

Quantities of carbon monoxide are now being combined directly with hydrogen to make synthetic wood alcohol, or methanol. This is done in the presence of a suitable catalyst. (See page 484.) Another product is the poisonous gas, *phosgene* ($COCl_2$), a compound of carbon monoxide and chlorine.

Readings for Pleasure and Profit

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XXI, pp. 352-359, "Oxides of Carbon."

Putting Chemistry to Work

A

(1) Why does a blanket or rug thrown over burning clothing extinguish flames? (2) How do you account for the formation of carbon monoxide in a gasoline engine? (3) To what is the "tingle" in soft drinks due? (4) How do you think "soda water" got its name? (5) In what ways is the older soda-acid type of fire extinguisher better than the Foamite type? (6) Both hydrogen and carbon monoxide burn with a pale blue flame. How could you distinguish between these gases? (7) What property of carbon dioxide is utilized in making "soda water"? (8) Why may carbon monoxide properly burned be a better fuel than carbon improperly burned? (9) Although CO_2 is not poisonous, animals die when placed in the gas. Why? (10) What is an easy way to show the presence of carbon in a compound?

B

(11) How do you account for the formation of carbon monoxide when coal is burned in a stove? when a gas flame strikes a pan of cold water? (12) Explain the difference between an unstable acid and a weak acid. Name an acid which has both of these properties. (13) Why do we speak of carbon as an inactive element, when it combines with most of the other elements? (14) Explain: When carbon dioxide is passed into limewater, the limewater first turns cloudy and then clears. Write two equations. (15) Give evidence that sulfur dioxide may act as a reducing agent while carbon dioxide may not. Why should this be so? (16) Name the reducing

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agents that you have studied thus far in your work and indicate by equations their reactions with hot copper oxide. (17) Suppose you were given bottles filled separately with ammonia, nitrous oxide, sulfur dioxide, hydrogen, oxygen, nitrogen, chlorine, carbon dioxide, and carbon monoxide. What means would you use to identify each gas? (18) Write equations to show how carbon dioxide may be formed from each of the following: charcoal, methane (CH_4), calcium carbonate by heating, calcium carbonate with an acid, sodium hydrogen carbonate, and acetylene (C_2H_2). (19) Design an apparatus and outline directions for the preparation and collection of pure carbon monoxide from oxalic acid ($H_2C_2O_4$).

How Good Are You at Solving Problems?

(1) By using gram-molecular volume, determine the weight per liter (S.T.P.) of each of the oxides of carbon.

(2) An average home, using coal as a fuel, burns about 10 tons of coal annually. If you assume that the coal is 80 per cent carbon, how many tons of *air* are required for the complete combustion of the carbon? How many tons of carbon dioxide are added to the atmosphere?

(3) Which releases the greater quantity of carbon dioxide, sodium carbonate or sodium bicarbonate, when equal weights are treated with an excess of an acid? What is the difference in volume?

(4) If a gram-molecular weight of solid carbon dioxide were allowed to evaporate into a closed liter vessel containing air at S.T.P., what pressure would be exerted on the walls of the vessel?

(5) What weight of carbon dioxide will be contained in the same volume as that which contains 4 grams of oxygen, volumes being measured at S.T.P.?

(6) How many liters of oxygen are required to burn completely 30 liters of acetylene (C_2H_2), volume being measured under the same conditions? How many liters of carbon dioxide will be formed?

Research and Activities That You Will Enjoy

A safety council: Organize a small group of students to draw up a safety-practice sheet for carbon monoxide. List all the cases you can where one might be exposed to dangers from the gas and offer recommendations for eliminating or decreasing the dangers.

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A guest speaker: Invite your family physician to explain to your class the physiological effects of carbon monoxide; or visit him and ask about the effects of the gas, why artificial respiration is of little use in cases of carbon monoxide poisoning, and about the methylene blue antidote treatment.

A discussion: "Carbon monoxide is one of the most dangerous, one of the most treacherous, and one of the most useful of the gases studied in chemistry."

Problem 48

HOW CAN YOU USE FUELS MOST EFFICIENTLY?

If you lived on an island in the warm southern waters of the Pacific, you would not need to think much about keeping warm; the sun's heat would probably be sufficient. In the temperate zone people require "artificial" heat in their homes and in industry. This heat is released by the chemical action of the burning of fuels.

What is a fuel? A fuel is a substance which burns readily, but not too fast. It liberates a large amount of heat. Generally speaking, fuels are composed of carbon or carbon compounds containing hydrogen. Free hydrogen is an excellent fuel, but it is highly flammable and too expensive. The following table lists several common fuels, grouped according to the physical state in which they are commonly purchased by industry or the public.

Solid Fuels	*Liquid Fuels*	*Gaseous Fuels*
Coal	Gasoline	Natural gas (methane)
Coke	Kerosene	Coal gas (a mixture)
Lignite	Benzene (from coal tar)	Water gas ($CO+H_2$)
Peat	Furnace oils	Producer gas ($CO+N_2$)
Wood	Alcohol	Hydrogen
Charcoal	Animal fats	Acetylene
Petroleum coke		

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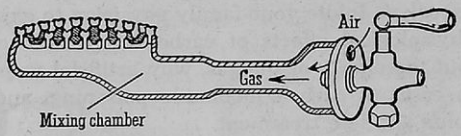

156. BURNER USED ON A GAS RANGE. Can you show how this burner resembles your Bunsen burner?

Why do some fuels produce flame when they burn? Most fuels burn with a flame, although a few such as charcoal and coke merely glow without much flame. *A flame is produced only by the burning of gas.* If a solid fuel burns with a flame, it is a sign that the solid is forming gas—it is this gas which is producing the flame. When no gas is formed, no flame is produced, although the combustion may be active as illustrated by the burning (glowing) of iron.

Getting a true picture of the gas flame on your Bunsen burner or your mother's gas range. The Bunsen burner is a simple device for mixing air with fuel gas so it will burn completely and liberate a great amount of heat. The character of the flame is determined largely by the amount of air that is mixed with the gas. A burner on your kitchen gas stove (Fig. 156) is merely a collection of many small Bunsen burners. You perhaps know that if the air openings are too small, the flame becomes yellow because of incomplete combustion, and the utensils soon become covered with soot. The grid burner (Fig. 157b) is a modified Bunsen burner that produces greater heat.

The mixture of gas and air is pushed through the burner by the gas and atmospheric pressure. When heated to its kindling temperature, the gas burns producing a pale, blue flame with a conelike appearance. The flame really consists of at least *two* cones, one being inside the other. A wood splinter held in the inner cone does not ignite readily. This shows that the gas in the inner cone is not burning yet; a Bunsen flame is therefore "hollow." A little higher up in the inner cone, the gas (if it is natural gas) is decomposed by the heat into carbon and hydrogen. Both of these elements are reducing agents;

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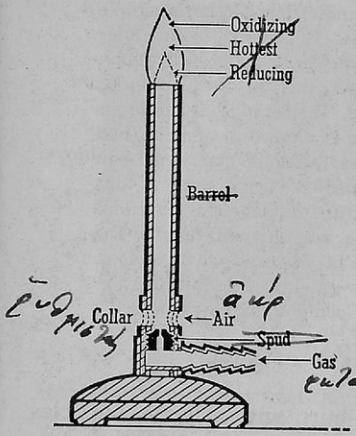
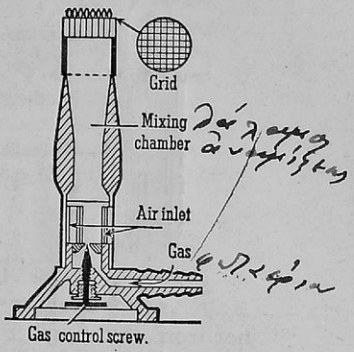


157a. LABORATORY BURNER. The Bunsen burner admits gas through a small opening in the spud. The gas, thoroughly mixed with air, burns at the top of the barrel. The collar permits the regulation of the quantity of air.



157b. LABORATORY BURNER. The Meeker type of burner is similar to the Bunsen burner except that it has a grid at the top. This breaks up the large inner cone and increases the area of the greatest heat. A needle valve can control the gas.

that is, they will withdraw oxygen from oxides. For example, when hot gases from the inner cone of a flame are directed against lead oxide by means of a blowpipe, the lead oxide is reduced to lead. Consequently, the inner cone is known as the *reducing flame.*

The outer cone of a flame is surrounded by plenty of atmospheric oxygen, so the burning is complete. The products formed by the burning are carbon dioxide and water vapor. The high temperature and the excess oxygen make the outer cone an *oxidizing flame.* Metals may be oxidized in this cone.

Some people still read by flames—how can you get a luminous flame suitable for reading? If you ever have been near a steel mill at night or if you have celebrated with Fourth of July iron "sparklers," you have noticed the brilliant illumination of

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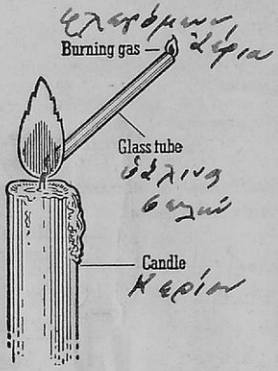

A candle flame is not a simple flame. It consists of an outer mantle of a pale blue color. Below this is the luminous cone. Inside of this luminous cone is a mixture of unburned gases. A small glass tube can be used to bring some of this mixture outside the luminous cone, where it will burn at the end of the tube when ignited. The gases in this mixture are compounds of carbon.

158. INNERMOST ZONE OF A FLAME

hot iron. Although iron does not burn with a flame, particles of iron may become white hot and luminous. When the air holes of a Bunsen burner are open, the flame is almost colorless and practically nonluminous. But when you sprinkle powdered iron, chalk dust, or powdered carbon into this nonluminous flame, the foreign particles become incandescent (white hot) and emit a bright light. A luminous flame also is produced by a Bunsen burner when the air supply is partially shut off. White hot particles of unburned carbon make the flame luminous. The presence of these carbon particles can be shown by holding in the flame a cold object, such as an evaporating dish. A black deposit of carbon (soot) collects on the dish.

The luminosity of gas flames, and consequently their suitability for reading purposes, has been greatly improved by heating solid objects to white heat (incandescence). The *Welsbach burner* (in an ordinary gas light) is such a device (Fig. 159). It consists of a mantle, composed of a mixture of 99 per cent thorium oxide and 1 per cent cerium oxide, which becomes white hot from the burning gas. This mantle gives off a steady soft light which is more agreeable and intense than would result from the burning gas alone. Of course, the use of electricity in lighting has practically replaced this method in most communities.

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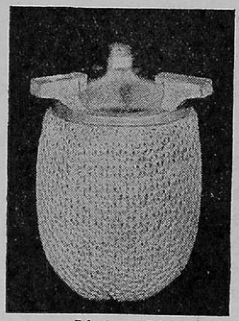

This gas mantle is composed of a mixture of 99% of thorium oxide and 1% of cerium oxide. In a Bunsen flame the Welsbach mantle becomes incandescent at a comparatively low temperature. Burning gas provides illumination by heating the mantle until it gives off light. This gas mantle, consisting of these brittle oxides, is very fragile.

Lindsay Light Co.

159. WELSBACH GAS MANTLE

How much heat are you getting for your money? When you buy a fuel, you are interested in buying *heat*, although the convenience of some fuels (such as their cleanliness, the small amount of ash produced, and ease of transportation) is an important item. Amount of heat is expressed in calories or in British thermal units (*B.T.U.*). (See page 101 for definitions of these units if you do not remember them.) The measurement of heat is accomplished by using a *calorimeter* ("measurer of heat"). The heat value of fuels, such as coal, is determined in a bomb, or combustion, calorimeter. (See Fig. 160.) A small known weight of powdered coal is completely oxidized and all the heat liberated by this burning is measured by noting the rise in the temperature of a known weight of water.

Before you buy coal or coke, why don't you find out how many *B.T.U.* of heat you can get from each ton? You can make a similar inquiry concerning other types of fuels. Today wise purchasers are buying "with their eyes open."

How can you get the most heat from a fuel? In order to get the greatest amount of heat, it is necessary to obtain complete combustion of the fuel.

You get the most heat from a fuel when it is completely burned. The complete burning of 12 grams of carbon (a gram-atomic weight) releases 94,390 calories of heat. This

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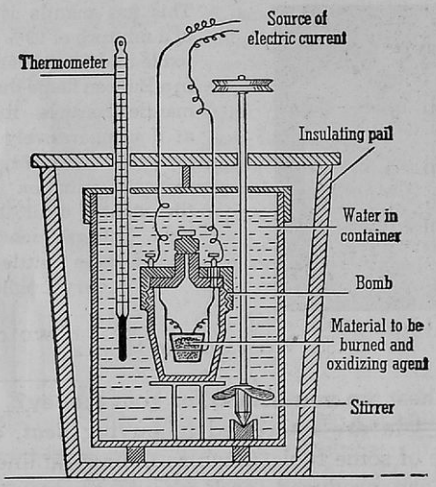

160. BOMB CALORIMETER. This device is used to test the heat value of fuels. The fuel is completely burned in an atmosphere of oxygen under pressure. All of the heat evolved is collected in a known volume of water. From the increase in the temperature of this water, the heat value of the fuel is determined.

accompanies the formation of a gram-molecular weight of carbon dioxide as shown by the *thermal equation:*

$$C + O_2 \rightarrow CO_2 + 94{,}390 \text{ calories of heat}$$

The 94,390 calories is the *heat of formation* of carbon dioxide. When an insufficient amount of air or oxygen is present, carbon monoxide is formed. (The following equation, using a half molecule of oxygen, is given for comparison.)

$$C + \underset{\frac{1}{2}\,O_2}{[O]} \rightarrow CO + 26{,}430 \text{ calories of heat}$$

The formation of this product of incomplete combustion, carbon monoxide, represents a great loss of heat. From the above thermal equations you can see that incomplete combustion may result in as high as a 70 per cent loss of heat. In actual practice, of course, the loss never reaches this figure, because

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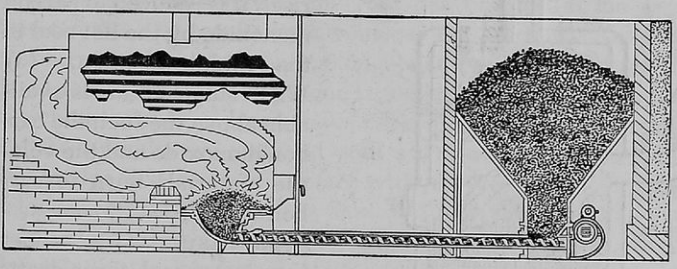
much of the carbon monoxide is burned in the outer part of the flame before it goes up the flue. If the furnace is regulated and fired properly, a greater amount of the combustible material is completely burned and more heat is obtained from the fuel.

The hydrogen in fuels always burns completely to form water vapor, thus releasing 68,380 calories of heat for every two grams of hydrogen.

$$H_2 + \underset{\frac{1}{2}\,O_2}{[O]} \rightarrow H_2O + 68{,}380 \text{ calories of heat}$$

The heat values of a few other fuels are shown on page 470.



161. AUTOMATIC STOKER. Coal is fed to the firebox mechanically through a pipe from the coalbin. A thermostat controls the speed with which the coal moves. The coal is fed through the bottom of the firebox so that it is coked and the gaseous products are burned and do not pass off in the smoke.

Smoke from your furnace indicates that it is "losing heat." The escape of smoke from chimneys is often a wasteful nuisance. It indicates a loss of heat. This loss of heat is due to the escape of unburned carbon and volatile materials and is very common in the use of soft coal.

A great many industries are preventing much of this waste by the use of automatic stokers and forced drafts (Fig. 161). Good stokers add fresh fuel no faster than it can be burned completely; they supply a sufficient amount of air to all the burning fuel. Usually the fuel is pushed in from the bottom of the furnace. In some instances, low-grade coal is powdered

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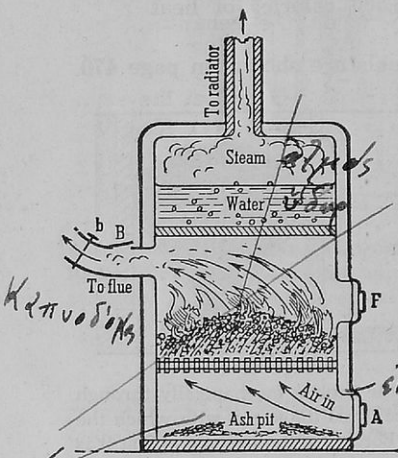
and blown into the furnace to obtain complete combustion. Forced drafts make possible a sufficient supply of air.

Smoke may be prevented from escaping into the air by the use of the Cottrell precipitator.

How can you regulate a furnace in order to save money on fuel? The complete burning of coal in a surface-fired furnace is thought of as taking place in three steps. (1) The fuel in the lower part of the furnace burns in an ample supply of air to form carbon dioxide. (2) As this carbon dioxide rises, it is reduced to carbon monoxide by the hot coal in the middle section. (3) When sufficient air is available above the fuel, the carbon monoxide and the volatile materials burn to carbon dioxide.



162. STEAM-HEATING FURNACE

To insure the proper burning of coal, three drafts are used. The bottom, or ashpit, damper (*A* in Fig. 162) regulates the amount of air which rises *through* the burning coal (step 1). The front, or firebox, damper (*F*) permits air to pass *above* the firebed (step 3). The back, or flue, damper (*B*) regulates the rate the gaseous materials leave the furnace. If *A* is open and the other dampers are closed, the combustion of the fuel will be rapid but incomplete. Opening *F* and *B* makes the combustion more complete. For a slowly burning fire, *B* and *F* should be open. While burning soft coal, *F* should be open most of the time. When fresh soft coal is to be added, the live coals should be pushed a little to one side to make room for it. *F* should then be closed for a short time and then reopened. These arrangements permit more complete com-

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bustion of the volatile matter that leaves the coal as it is heated.

Why should fuel supplies be conserved? There has been a great deal of waste in the burning of fuels. In the earlier days there was no thought of fuel conservation. Realizing that fuel supplies, when once used, are forever lost, engineers have devised many efficient types of burners and feed controls. The aim of such devices is to get from all grades of fuel the greatest heat energy content they possess. Conservation of our solid, liquid, and gaseous fuels should become a national policy. Even now we look on the generation just passed as being very wasteful.

How can you save money on your gas bill and at the same time get the best results from your gas range? (1) Keep the gas burners *clean* and the openings clear. (2) Don't turn the flame too high. When the flame is too high, insufficient oxygen may be available and poisonous carbon monoxide may result. The best results are obtained with a well-regulated *low* flame whose tips just come in contact with the vessel that is being heated. (3) Avoid a yellow flame. If the flame is yellow or sooty, more air should be admitted to the gas-mixer. A yellow flame indicates incomplete combustion.

How can you keep your car from burning more gasoline than it should burn? The carburetor of a car vaporizes gasoline and mixes it with air. The gasoline vapor cannot burn properly in the cylinders unless there is enough air (oxygen) in the fuel mixture. Hence to save gasoline: (1) The carburetor should be adjusted for mixing the proper amount of air with the gasoline vapor. Cleaning the carbureter may also be necessary now and then. (2) If you have a "hand" choke, remember that pulling out the choke cuts down on the percentage of oxygen mixed with the gasoline vapor. This can easily cause incomplete combustion and waste. Hand chokes are for use when starting a car, *not* when running it. (3) Poorly fitting valves and piston rings allow part of the burning gas to "leak out" of the cylinders. This is a waste of power and gasoline.

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These are the main parts of a car that should be watched in order to save gasoline. However, other things are important. Tires that are too low cause more friction and thus make it necessary to use more gasoline. Driving at too high a speed is not only dangerous but wasteful. No car gets the most out of gasoline when it is driven at high speeds. This is partly due to increased wind resistance and partly to increased internal friction.

Bearings and rolling surfaces that are properly greased run with less friction and therefore necessitate a smaller consumption of gasoline.

Readings for Pleasure and Profit

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XVIII, pp. 210-222, "Fuels and Smoke."

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. V, pp. 99-132, "Wheels and Wings."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XVIII, pp. 272-279, "Luminosity of Flames."

Applying in Life What You Have Learned in Chemistry

"For goodness sake, Richard," called his mother, "do something to the furnace; it's cold up here."

Wishing to make the fire burn faster, Richard opened the front coal door of the furnace so as to obtain a good draft.

What would you have done? Tell why.

Suppose that a burner on your mother's kitchen gas stove is poorly regulated and gives a smoky flame. How could the difficulty be remedied?

Putting Chemistry to Work

A

(1) How would you prove the statement that the products of the combustion of most fuels are carbon dioxide and water vapor? (2) What arrangement in a Bunsen burner makes it possible to burn city gas without smoke? (3) A certain city estimated its annual property loss due to smoke at $8,000,000. How may this loss be decreased? (4) What makes it possible for you to read by a kerosene lamp? by a gasoline lamp? by a "gas" light? (5) Why is the

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choke used in starting an automobile? Why is this device used more in winter than in summer? Why will fuel be wasted if the choke is left on? (**6**) What is meant by the *calorific value of fuels?* How is it measured? (**7**) How can you use a Bunsen burner to free a metal from its oxide or to produce an oxide from the metal? (**8**) Is electricity a fuel? Justify your answer. (**9**) What effect do you think the installation of air conditioning equipment in homes and public buildings will have upon the conservation of fuels? Explain your answer.

B

(**10**) What is a *thermal equation?* Point out several facts that are shown by a thermal equation. (**11**) City gas burns with a smoky flame unless air is mixed with it. What is smoke? How could you prove your answer? (**12**) What volumes of oxygen and of air are required to burn completely 500 cu. ft. of methane (CH_4)? What volume of carbon dioxide is formed? (All volumes are measured under the same conditions.) (**13**) In how many different ways can you increase the intensity of the heat from the burning of a given volume of fuel gas? (**14**) Arrange the following fuels in the order of their heat-energy content, basing the order first on the burning of one gram-molecular weight of each fuel and next on the burning of 100 grams of each: acetylene (C_2H_2), benzene (C_6H_6), gasoline (use C_8H_{18}), methane (CH_4), hydrogen, and carbon. Explain any difference in the two lists. (See page 780, Table XVI.)

Looking Back into Unit 11

Be sure you know the purpose of this unit. Read again the material on page 424, "Looking Ahead into Unit 11." Then study the following Summary Test.

Summary Test

1. *How are different forms of carbon produced and used?*
   (a) How were different types of coal formed?
   (b) What valuable products can be obtained from coal by destructive distillation?
   (c) How are other kinds of amorphous carbon useful?
   (d) What are diamonds?
      (1) How were they produced?
      (2) What makes diamonds valuable?
   (e) How is graphite produced and used?

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2. *How do the oxides of carbon affect our lives?*
   (a) How is the most common oxide of carbon produced?
   (b) What qualities of carbon dioxide distinguish it from other substances? What are its properties?
   (c) How is carbon dioxide useful—
      (1) In carbonated drinks?
      (2) In putting out fires?
      (3) As a leavening agent?
      (4) In the ice cream industry?
   (d) How is carbon monoxide—
      (1) A treacherous poison?
      (2) Useful in industry?
   (e) What three sources of carbon monoxide threaten careless users?
   (f) How can you prepare carbon monoxide?
3. *How can you use fuels most effectively?*
   (a) What is a fuel?
      (1) What is a flame?
      (2) What is the true picture of a Bunsen flame?
      (3) How can you get a luminous flame?
   (b) How can you determine the heat value of fuels?
   (c) How can you get the most heat from a fuel?
   (d) How can you save money by regulating—
      (1) Your furnace?
      (2) Your gas range?
      (3) Your automobile?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

In this unit are brought together many facts about *carbon, carbon dioxide, carbon monoxide,* and *fuels.* Here you deal with chemistry on a very practical level. *Diamonds* serve as jewels and abrasives; *graphite* furnishes you with "lead" pencils, crucibles, and lubricants; *coal* and *coke* are used for fuel; *charcoal,* for gas masks and the adsorption of gases, colors, and odors; *gas black,* for ink, auto tires, and electrodes; and *bone black,* for removing objectionable colors from sugar.

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Spence

ONE OF AMERICA'S RICHEST OIL FIELDS. This field is near Long Beach, Calif.

Carbon dioxide serves you in many ways. It is a "first aid" for *putting out fires;* it gives "tingle" to *soft drinks;* when in the form of dry ice, it *refrigerates your food;* it is the basic *food* of *plants;* and it brings about what we call "lightness" in many of *baked foodstuffs.* Unfortunately, it also sometimes *hardens water supplies. Carbon monoxide* is a chemical compound that is both useful and dangerous. It either treacherously *poisons* us without warning or it efficiently serves us as an excellent *fuel* or as the most commonly used *reducing agent* for freeing metals from their ores.

You use *fuels* mainly for the *heat energy* they produce. You should learn how to *burn* fuels in the most *efficient* and *economical* manner. In most cases the fuels that you use from *Nature's storehouse* cannot be replaced. They should therefore be properly *conserved.*

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Looking Ahead into

Unit Twelve

Until a little over a hundred years ago, chemists believed that only nature could produce "organic compounds" of carbon. Would you be interested to know how one simple experiment started changing this idea?

In 1828 the German chemist Wöhler showed that the inorganic compound ammonium cyanate (NH_4CNO) by heating can be changed into urea [$(NH_2)_2CO$], a typical organic compound. He showed that organic compounds can be produced by chemists in the laboratory as well as by living beings. In this way he destroyed once and for all the sharp distinction between organic and inorganic chemistry. It then became more accurate to identify organic chemistry (such as you will study in this unit) as the chemistry of the carbon compounds rather than as the chemistry of living things.

Since Wöhler's eye-opening experiment, chemists have prepared over 300,000 compounds of carbon! No need for alarm; you will study only a few of them. It is doubtful if any phase of chemistry more closely touches your everyday life, as you will see when you proceed with the following problems.

Problem 49. *What Useful Hydrocarbon Products Do Petroleum and Similar Materials Give You?*

Problem 50. *How Do Chemists Picture Hydrocarbon Molecules—How Do Hydrocarbons React?*

Problem 51. *How Are Alcohols Related to Hydrocarbons? How Are Alcohols Used?*

Problem 52. *How Are Other Valuable Products Obtained from Alcohols?*

Problem 53. *What Are Esters; How Do They Serve Us?*

Problem 54. *What Important Things Should You Know about Carbohydrates?*

Problem 55. *How Is Paper Made from Cellulose?*

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Organic Compounds: Hydrogen and Carbon Compounds and Their Useful Relatives

Problem 49

WHAT USEFUL HYDROCARBON PRODUCTS DO PETROLEUM AND SIMILAR MATERIALS GIVE YOU?

The first petroleum well was drilled near Titusville, Pennsylvania, in 1859 by Colonel Drake. Since that time more than 20 billion barrels have been produced from wells in the United States, Venezuela, Russia, Mexico, Persia, and other countries. The United States alone produces nearly a billion barrels a year. The petroleum industry today ranks second to the steel industry in production and value, and first in the tonnage shipped by railroads. The discovery of petroleum ushered in a "new mechanical age" in which the automobile, the airplane, and the stationary gas engine have played important parts. Petroleum has served both as a source of fuel and of lubricating oils for these engines.

What is petroleum? Petroleum (Latin: *petra,* stone and *oleum,* oil) is a complex mixture of liquid, gaseous, and solid *hydrocarbons,* all compounds of carbon and hydrogen. The hydrocarbons in petroleum belong in the main to the methane series of saturated hydrocarbons in which the number of hydrogen atoms is two more than twice the number of carbon atoms. Thus the general formula for the methane series of hydrocarbons is written C_nH_{2n+2}, in which n represents the number of carbon atoms. Methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and octane (C_8H_{18}) are typical examples. The following table lists the boiling points of a few hydrocarbons in the methane series.

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METHANE SERIES OF HYDROCARBONS

Name of Hydrocarbon	*Formula*	*Boiling Point, C.*	
Methane	CH_4	−164	Gases
Ethane	C_2H_6	−86	
Propane	C_3H_8	−44.5	
Butane	C_4H_{10}	+0.6	
Pentane	C_5H_{12}	+36.2	Liquids
Hexane	C_6H_{14}	68.9	
Heptane	C_7H_{16}	98.4	
Octane	C_8H_{18}	125.8	
⋮	⋮	⋮	
Hexadecane	$C_{16}H_{34}$ (melts at 18° C.)	287.5	Solids
⋮	⋮	⋮	
Hexacontane	$C_{60}H_{122}$ (melts at 102° C.)		
⋮	⋮		
General formula	C_nH_{2n+2}		

After the Drake oil well was drilled, an extended effort was made to teach people to use petroleum products. After several years, lighting with kerosene lamps and the use of gasoline for cooking were developed, but at first gasoline was an objectionable and unusable nuisance. With the coming of the gas motor and the almost simultaneous development of electricity for lighting, the demand changed from kerosene to gasoline, and the industry did not know what to do with the kerosene. The motor age brought a great demand not only for gasoline but for lubricating oils as well. At the present time a great variety of petroleum products are widely used.

Petroleum furnishes the gasoline that "runs" your car—what other important products does petroleum furnish? The fractional distillation of crude petroleum produces a wide range of distillates, some of which are listed in the table on this page. You perhaps noticed that gasoline is not listed in the table. However, gasoline *is* a petroleum product but it has no definite formula, because it is a mixture of various hydrocarbons

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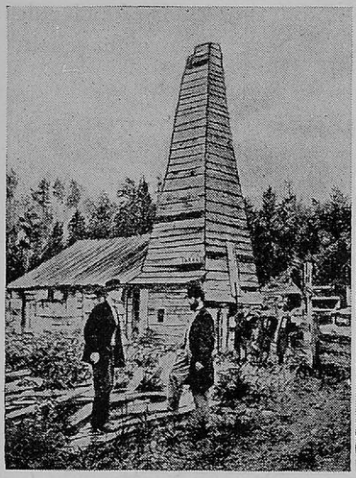

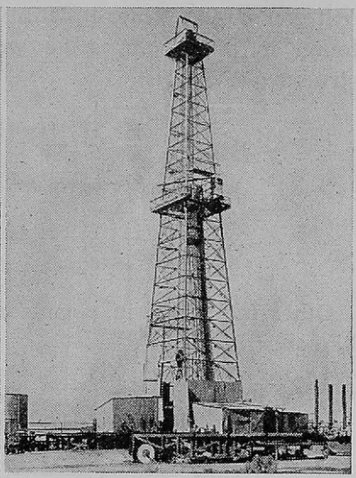

Underwood and Underwood

163. COLONEL DRAKE'S OIL WELL. 164. A DEEP OIL WELL OF TODAY.

Colonel Drake's oil well was the first well drilled in the United States for oil. It was sunk at Titusville, Pennsylvania, in 1859 and was only 67 feet deep. The modern oil well at the right is 9,700 feet deep. It is at Semitropic, California.

mainly those of the methane series coming between C_4H_{10} and $C_{13}H_{28}$ and having a boiling point less than 225°C.

Crude petroleum does not always occur where the refined products are to be used. It is brought to the surface by drilling to the necessary depths, which may be as great as 10,000 feet. Frequently the presence of natural gas with the petroleum produces enough pressure to force the "oil" to the surface and to continue its flow for some time. Much of the crude petroleum is sent by a network of pipe lines to refining plants located reasonably near where the petroleum products are to be used.

At the refineries the crude petroleum undergoes fractional distillation in steel stills. (See page 466.) Some of these stills are as much as 42 feet long and 15 feet in diameter with a capacity of 1,200 barrels. Either coal or oil is used as a fuel.

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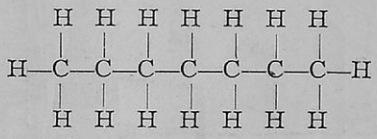
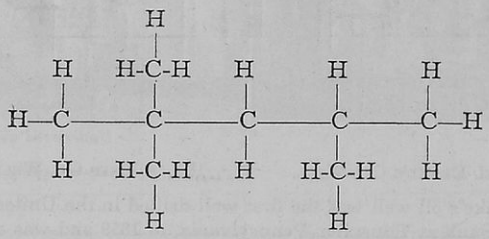
If you were to draw a picture of different kinds of molecules found in petroleum, some would have a "straight chain" structure, like this:



heptane, a "straight chain" and a poor gasoline

Other molecules in petroleum have a branched structure, like this:



iso-octane, a "branched structure" and a good gasoline

The hydrocarbons which have a straight-chain structure produce a pounding or a "knock" in the motor of your car. The hydrocarbons which have a branched structure produce very little knock in motors. Heptane, a straight-chain compound produces a violent knock; iso-octane, a branched chain, shows very little tendency to produce knock.

Iso-octane was once considered the "perfect gasoline." Even today gasolines are given an *octane rating* which indicates how they perform. A 90-octane gasoline has the same knocking tendency as a mixture composed of 90 parts of iso-octane and 10 parts of heptane. Similarly, an 85-octane gasoline has the same knocking tendency as a mixture composed of 85 parts of iso-octane and 15 parts of heptane. Recent developments have made it possible to produce an aviation gasoline which is better than pure iso-octane. It has an octane rating of considerably more than 105. Triptane, 2, 2, 3—trimethylbu-

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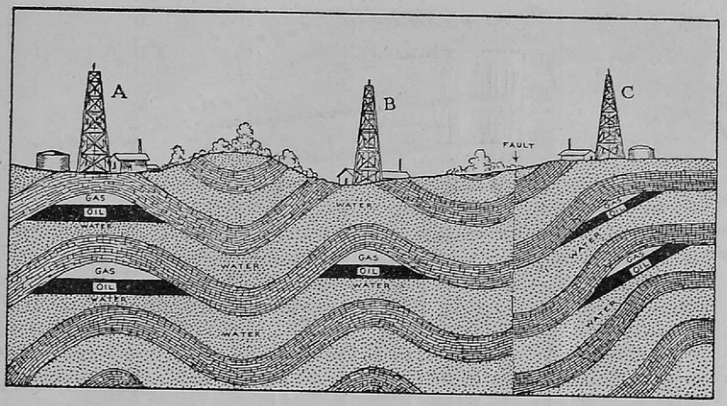

165. ROCK STRATA IN OIL FIELDS. From a study of rock strata geologists can now give information as to where oil wells should be sunk. Note carefully the conditions which are favorable for the well-driller.

tane, is now produced in experimental quantities at a cost somewhat below one dollar a gallon. With tetraethyllead it gives four times the power as 100-octane gasoline with a 25% gain in fuel economy.

The "cracking" process and the hydrogenation of petroleum produce much more gasoline from a barrel of crude oil than was formerly obtained. The increasing number of automobiles has brought about a rapid rise in the use of gasoline. Fig. 168 shows how science, through the chemist, has kept up with this demand.

Kerosene is one of the products of petroleum. It is a mixture of hydrocarbons having molecules that are *larger* than the molecules in gasoline.

One of the first steps to increase the gasoline yield of petroleum was to break down the large molecules in kerosene, such as $C_{12}H_{26}$, into the simpler molecules composing gasoline, near the range of octane, C_8H_{18}. The term "cracking" has been applied to this process. It consists of heating the heavier hydrocarbons under pressure which splits their molecules into lighter ones. By noting Fig. 168 you will see that it has been

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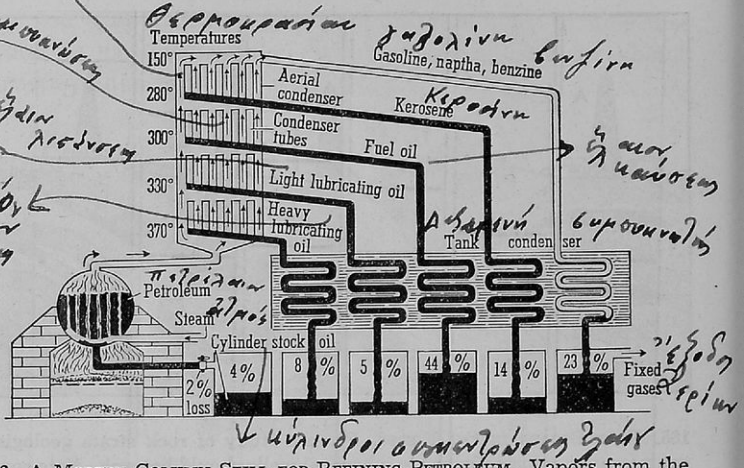

166. A MODERN COLUMN STILL FOR REFINING PETROLEUM. Vapors from the boiler enter the column. The more volatile rise to the top. Less volatile portions condense at different heights in the column and are thus separated into various products.

possible to lower the percentage yield of kerosene from 48.3 per cent in 1904 to 6 per cent in 1934, an amount probably sufficient to supply the present demand for kerosene. At the same time, the gasoline yield increased from 10.3 per cent to 43.4 per cent.

In recent years another process, known as hydrogenation, has increased the gasoline yield. In this process, hydrogen is added to the oil molecules, in the presence of a catalyst. The nature of the oil molecules is changed to such an extent that practically a 100 per cent yield of motor fuel is now possible from crude petroleum.

The gasoline supply has been increased by still another method in which the simple molecules of *gaseous* hydrocarbons, such as methane (CH_4), ethane (C_2H_6), and butane (C_4H_{10}), are combined (or "polymerized") into larger molecules that form liquids. These liquids vaporize at temperatures that make possible their use as a motor fuel. You possibly have seen advertisements concerning "poly" *gasoline*.

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Courtesy, Standard Oil Company

167. THE LARGEST OIL REFINERY IN THE WORLD. An airplane view of part of the great Standard Oil refinery at Whiting, Indiana.

The use of alcohol as a fuel for automobiles is receiving some consideration and is a mechanical possibility, but so long as the present supply of gasoline holds out, the necessary changes in motors for the burning of alcohol most likely will not be made. However, in time alcohol may become a very satisfactory motor fuel in this country.

NATURAL AND ARTIFICIAL GASES

Natural gas is a mixture of hydrocarbons. The term "natural" as applied to the gas in the earth probably was originally used to distinguish it from artificial gases. Natural gas in different parts of the country varies considerably in composition, but a main component is usually methane (CH_4). Sometimes methane is called *marsh gas,* because it is formed during the decay of vegetable matter under water and consequently is found bubbling from the water in marshy places.

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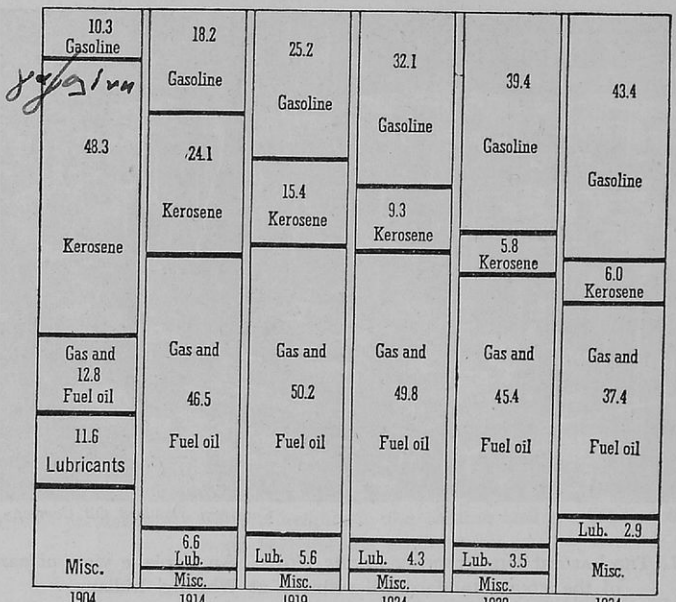

From National Petroleum News, Feb. 5, 1936

168. PERCENTAGE YIELD FROM A BARREL OF CRUDE OIL. In 1904 there was little demand for gasoline but kerosene was much in demand. The development of the automobile, airplane, and other gasoline motors has greatly increased the demand for gasoline. Chemists have responded to this need and by 1939 the possible yield of gasoline had risen to between 60 and 70 per cent. Formerly laws forbade the adulteration of kerosene with gasoline; such laws are no longer needed.

Other hydrocarbons of the methane series, such as ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}), are also often found in natural gas. The boiling points of propane and butane make them objectionable in transporting gas in pipes, since they quite easily condense to liquid. They therefore are removed from natural gas. Liquefied propane and butane ("bottled" gas) are sold to some extent for use in country homes where natural or city gas is not available. This liquefied product is also used to enrich water gas.

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How is natural gas used? Natural gas in many sections of the country also contains some of the liquid hydrocarbons, pentane and hexane, which are removed to make "natural gasoline" or *casing-head gasoline* as it is often called. More than 25 billion gallons of this "natural gasoline" have been produced since 1911 when its removal from natural gas was first started. It is very volatile and mixes well with other gasolines to improve them—especially in the starting of motors. Its removal from the natural gas yields an improved gas which has little tendency to liquefy in the pipe lines.

Many sections of the United States use natural gas as fuel for cooking or for heating. Vast amounts of it are also burned in a limited supply of air to form industrial carbon black.

How are industrial gases prepared? When natural gas is not available in sufficient quantity, three kinds of manufactured gases may be produced either for industrial purposes or for home consumption as fuel for cooking and heating. These gases are coal gas, water gas, and producer gas.

Water gas is produced by first passing air through burning coke (or anthracite coal) until the coke is white hot. Then the supply of air is cut off and steam is passed through. The steam cools the hot coke. Air and steam are passed through intermittently and the following reaction takes place:

$$C + H_2O \rightarrow CO + H_2 - 29{,}100 \text{ calories}$$

Water gas is a mixture of carbon monoxide and hydrogen. Both of these gases are excellent fuels and burn with an intensely hot flame which is nearly colorless. The large amount of poisonous carbon monoxide in this gas makes a slight pipe leak a very serious matter.

Gas for domestic consumption must give satisfactory illumination. Enriching water gas with unsaturated carbon compounds increases its illuminating power and makes the gas suitable for both heating and lighting.

Producer gas is an industrial gas that is cheaper than water gas. It is made by passing a limited supply of air through burning low-grade bituminous coal or coke. Carbon monoxide

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is thus formed. This carbon monoxide and atmospheric nitrogen, which passes through the fuel unchanged, are the main components of producer gas. It is a fuel with a very low heat value, but it is cheap and easily produced. Generally, it is burned immediately by the industry producing it.

THE WEIGHT COMPOSITIONS AND HEAT VALUES (IN B.T.U.) OF SEVERAL FUEL GASES[1]

Components	*Producer Gas*	*Blue Water Gas*	*Coke Oven Gas*	*Coal Gas*	*Sandusky, Ohio Nat. Gas*
CO_2	5.7	3.5	2.6	1.1	0.2
CO	22.0	43.4	6.1	9.0	....
C_2H_6	....	....	....	....	12.5
C_2H_4	0.4	....	5.2	6.6	....
H_2	10.5	51.8	47.9	47.0	....
CH_4	2.6	....	33.9	34.0	83.5
N_2	58.8	1.3	3.7	2.3	3.8
O_2	....	....	0.6	....	....
C_3H_8	....	....	....	....	....
B.T.U. PER CU. FT.	128	285	538	560	946

How is acetylene made and used? Acetylene is another important industrial gas that is not used to any great extent as an ordinary fuel, but it is used with oxygen for welding and cutting certain metals, particularly steel. Fig. 23 shows an oxyacetylene blowpipe, or torch, which is used for this purpose.

Acetylene is prepared by the action of water on calcium carbide:

$$CaC_2 + 2\ H_2O \rightarrow C_2H_2\uparrow + Ca(OH)_2$$

In ordinary air this gas burns with a very luminous, sooty flame. Special burners are needed to produce a flame for lighting purposes. With sufficient oxygen, acetylene burns

[1] Taken from Chemical Rubber Handbook by Hodgman and Lange.

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with an intense white light, producing a large amount of heat:

$$C_2H_2 + 5\ [O] \rightarrow 2\ CO_2 + H_2O + 310{,}000 \text{ calories}$$

Acetylene is soluble in acetone and is shipped under pressure in tanks filled with acetone. Acetylene is the starting material for a great variety of important synthetic products, including synthetic (artificial) rubber.

Readings for Pleasure and Profit

Beery, Pauline. *Stuff.* Chap. VI, pp. 117-126, "Petroleum Products."

Clarke, Beverly L. *Marvels of Modern Chemistry.* Chap. XXIII, pp. 287-291, "Liquid and Gaseous Fuels"; Chap. XXV, pp. 319-322, "Increasing Gasoline Supply."

Haynes, Wm. *This Chemical Age.* Chap. XIII, pp. 226-244, "Chemists in Spite of Themselves."

Holmes, H. N. *Out of the Test Tube.* Chap. XVIII, pp. 210-220, "Fuels and Smoke."

Howe, H. E. *Chemistry in Industry.* Vol. I, Chap. XVII, pp. 294-311, "The Petroleum Industry"; Vol. II, Chap. XII, pp. 204-220, "Lubricants."

Reed, A. Maxwell. *America's Treasures.* Chaps. XIII-XV, pp. 184-213, "Discovery of Petroleum."

Rogers, Allen. *Manual of Industrial Chemistry.* Vol. I, Chap. XIV, pp. 529-577, "Petroleum Industry"; Vol. I, Chap. XV, pp. 578-647, "City Gas"; Vol. I, Chap. XIX, pp. 736-771, "Industrial Gases."

Tilden, Sir William. *Chemical Discovery and Invention in the 20th Century.* Chap. XIX, pp. 280-296, "Petrol."

Applying in Life What You Have Learned in Chemistry

Johnny was late. The furnace wouldn't burn. He threw in some kerosene and shut the door. A little later he opened the door again. . . . Now Johnny isn't going any place because he's resting in a hospital recovering from severe burns. . . . At that, he's lucky. . . . What happened?

An analysis showed that 52.5 per cent of a sample of gasoline distilled over at a temperature of 150° C. Is this good gasoline? On what do you base your answer?

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Putting Chemistry to Work

A

(1) What properties of gasoline make it useful in automobiles but very dangerous in homes? (2) Why does water gas have a higher calorific value than producer gas? (3) How would you distinguish methane and hydrogen? (4) Burning oil wells have been extinguished by a blast of dynamite. Can you suggest what happens? (5) What physical property of butane makes it useful in high-altitude aviation? (6) Why would you expect water gas to be somewhat more dangerous to inhale than coal gas or natural gas? (See composition.) (7) Why must sulfur compounds be removed from petroleum products?

B

(8) Why can no definite formulas be given to petroleum, gasoline, and kerosene? (9) Why does a study of petroleum products involve an understanding of fractional distillation? (10) What is the most valuable petroleum product? How is the amount of this product obtainable from petroleum increased? (11) Arrange the following products in the order in which they distill over in the process of refining petroleum: benzine, fuel oil, kerosene, paraffin, gasoline, lubricating oil, vaseline. (12) The following terms are used frequently by a petroleum chemist: cracking, casing-head gasoline, ethyl, high-test, natural gasoline, and octane rating. What does each of these terms mean to you? (13) Account for the high temperature obtained by the use of an oxyacetylene flame.

Research and Activities That You Will Enjoy

A model: After examining all the diagrams of coal gas plants you can find and, if possible, talking with an industrial chemist, build a model plant and explain it to the class.

A forum: What methods should be employed to prevent the exploitation of natural resources?

A report: Write to the Bureau of Mines, Washington, D. C., for pamphlets on mine explosions and report to the class the information which interests you most.

A chart: Prepare a chart showing the main products obtained by the fractional distillation of petroleum.

An explanation: Find out about the "octane rating" of gasoline and report your findings to the class.

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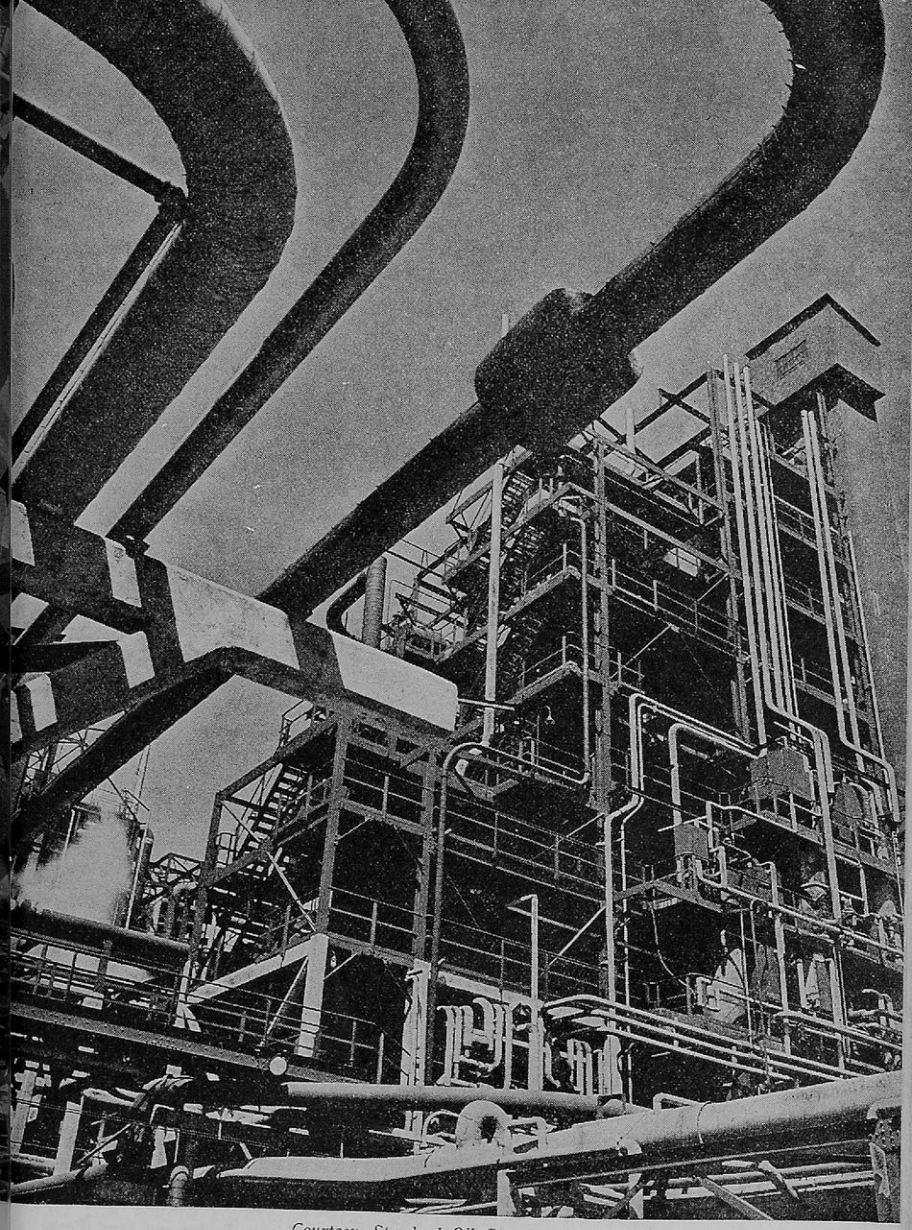

Courtesy, Standard Oil Company; Photo, Torkel Korling

PART OF A UNIT IN WHICH GASOLINE IS MADE. This maze of pipes, girders, and concrete is part of the Whiting, Indiana, refinery of Standard Oil Company (Indiana). Many such units make up the modern, large refinery.

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Courtesy, Chicago Bridge and Iron Works

TANKS FOR AVIATION GASOLINE. These spherical tanks for storage of aviation gasoline are designed to stand high pressure.

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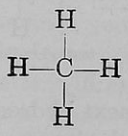
Problem 50

HOW DO CHEMISTS PICTURE HYDROCARBON MOLECULES—HOW DO HYDROCARBONS REACT?

The modern architect and contractor build different styles of skyscrapers by putting limestone, steel, bricks, tiles, and other materials together in various combinations. Likewise, the modern chemist after much effort in the laboratory has learned to build the invisible molecules of various useful compounds by combining elements in many different ways. Some of these accomplishments at first seem almost beyond the grasp of the imagination. This is especially true of the chemical "manipulation" of the compounds of carbon and hydrogen which are known as hydrocarbons. As you have just seen in your study of petroleum and natural and artificial gases, some hydrocarbons are gases, others are liquids, and still others are solids. Hydrocarbons constitute a very important group of chemical compounds.

How are the simplest hydrocarbons constructed? The contractor uses blueprints to show the structural plans of buildings; the organic chemist often uses structural formulas (bond formulas) to picture how elements are put together to form molecules. The correct molecular formula of methane, the simplest hydrocarbon, is CH_4. This formula agrees with our previous ideas of valence since the valence of the carbon atom is 4 and the valence of each of the four hydrogen atoms is 1. The methane molecule may also be represented by the following bond formula:



In the above formula each line represents a valence bond. Since this compound is a nonelectrolyte, the valence electrons

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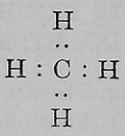
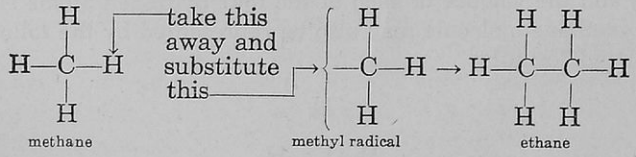
are shared and therefore the bond formula is sometimes written:



In the above formula the dots represent electrons, each pair of which is shared by one hydrogen atom and the carbon atom. In this way each hydrogen atom completes its valence shell of two electrons and the carbon atom completes its valence shell of eight electrons.

How are other simple hydrocarbons related to methane? From the ordinary valence standpoint you might think that only one compound of carbon and hydrogen is possible. However, more than 2,000 hydrocarbons are definitely known. The formation of this large number of compounds is possible because the carbon atoms "hitch together" in chains. Correct experimental data give the formulas C_2H_6 for ethane, C_3H_8 for propane, C_4H_{10} for butane, and so on. How can these formulas be pictured?

It requires but little use of the imagination to see that by removing one hydrogen atom from a molecule of *methane* and substituting a methyl radical (CH_3), an ethane molecule (C_2H_6) is formed:



In a similar manner the next hydrocarbon (propane) can be pictured by replacing one hydrogen atom of the *ethane* molecule with a carbon atom to which are attached three hydrogen atoms. Thus, propane (C_3H_8) is shown as a string of three

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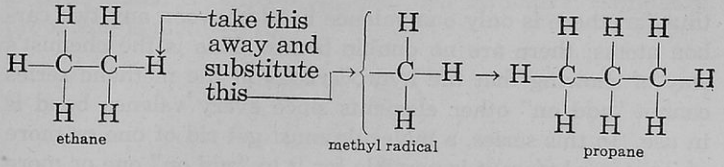
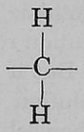
carbon atoms, making a sort of backbone with the hydrogen atoms attached like ribs on either side.



In a similar manner you now ought to be able to write the structural formulas of butane (C_4H_{10}), pentane (C_5H_{12}), and octane (C_8H_{18}).

When you write structural formulas, you must always be certain that each carbon atom has *four* bonds (or "lines") since the valence of carbon is 4, and that each hydrogen atom has only *one* bond since the valence of hydrogen is one.

How is a homologous series of hydrocarbons constructed? No doubt you already have observed that each hydrocarbon pictured thus far differs from the previous one by the group CH_2 or:



Such a series of compounds in which each differs from the next always by the same group of elements is called a homologous series (alike in structure). Since the first compound in this series is methane, the entire group of these hydrocarbons is known as the methane series. (See the table on page 462.)

A little thought will convince you that the *general formula* of the methane series of hydrocarbons is C_nH_{2n+2}, in which n is the number of carbon atoms in each molecule. Thus in the ethane formula (C_2H_6) n is 2 and (2n + 2) is 6. Using this general formula, write the formula of the hydrocarbon in this series containing four carbon atoms (butane); containing ten carbon atoms (decane); containing eighteen carbon atoms.

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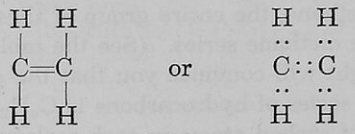
Another interesting thing you will note is that the carbon atoms are attached one after another, -C-C-C-, in a "chain" effect. Also in each of the structural formulas you have studied thus far, there is only *one* valence bond between any two carbon atoms; there are no double bonds. This is the chemist's way of showing that the hydrocarbons in the methane series cannot "add on" other elements since every valence bond is in use. In this series, a molecule must get rid of one or more of its atoms before it is possible for it to "add on" one or more atoms of other elements. Such hydrocarbons are "saturated"; there are no unused valence bonds. The methane series, therefore, is known as a *saturated chain series* of hydrocarbons. At least one atom must be lost by the molecule before another atom or radical can be taken on.

How are typical unsaturated hydrocarbons constructed? When you write the structural formulas for hydrocarbons, you must always be careful to make them agree with all the known experimental facts. With this in mind, note the structural formula for ethylene below. This formula agrees with the valence of carbon which has four valence bonds.

The ethylene series. If ethane (C_2H_6) is shaken with a little bromine water, the solution remains colored; ethane does *not* add on bromine atoms. But if ethylene (C_2H_4) is treated in a similar manner, its solution becomes colorless, showing that bromine atoms attach themselves to molecules of ethylene. Ethylene is an *unsaturated* hydrocarbon, and to show this fact a so-called *double bond* is shown between the carbon atoms, thus:



ethylene

Each carbon atom is now represented with four bonds.

Ethylene is a "chain" hydrocarbon. It is the first member of a series called the *ethylene* (or ethene) *series.* In this

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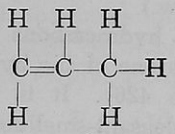
series each hydrocarbon differs from the one next in the series by CH_2, so the second member of the ethylene series is C_3H_6 which is called propylene. The structural formula of propylene is pictured as:



propylene

The general formula of the ethylene series is C_nH_{2n}. These hydrocarbons with double bonds are called *olefins* ("to make oil") because oily substances are formed when they combine with the halogens.

Ethylene is prepared in the laboratory by dehydrating grain alcohol (C_2H_5OH) with sulfuric acid:

$$C_2H_5OH \xrightarrow{+H_2SO_4} C_2H_4 + H_2O$$

An interesting use of ethylene gas is as an artificial ripener for citrus fruits and bananas. You no doubt know that these fruits frequently are picked green and ripened during transit to market or sometime before they are sold. When the fruits are exposed to air containing a small amount of ethylene, the ripening process is hastened.

A mixture of ethylene and oxygen is used as a general anesthetic in surgery, and is believed to have several advantages over ether. It acts quickly and the patient recovers consciousness more quickly without the usual nausea. Ethylene is less irritating to the lungs. Its main disadvantage is that an ethylene-oxygen mixture is very explosive, so it must be used with great care.

The acetylene series. Acetylene (ethine) has the formula C_2H_2. This gas is also an unsaturated hydrocarbon. In its structural formula a *triple* bond is used to show that there are three valence bonds between the carbon atoms. This arrangement gives the following structural formula.

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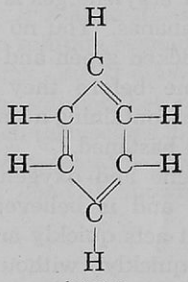
acetylene

Acetylene is the first member of an unsaturated chain series of hydrocarbons with the general formula C_nH_{2n-2}. The preparation and uses of acetylene were discussed on page 470. (Review them now.)

How are typical "ring" hydrocarbons constructed?—The benzene series. Benzene is one of the by-products in the manufacture of coke (page 426). It is obtained by fractional distillation. It is a pleasant-smelling, colorless liquid that boils at 80° C. By comparing its formula (C_6H_6) with those of the saturated hydrocarbons (methane series), you will see that benzene is not a saturated hydrocarbon. But it does not "add on" elements nearly as eagerly as ethylene and acetylene do. This suggests that benzene is not a chain hydrocarbon. Furthermore, no satisfactory graphic formula of the chain type could be proposed. (Try it to convince yourself.) Chemists were much concerned over the structural formula of the benzene molecule until 1865 when Kekulé, a German chemist, suggested a "ring" structure to look like this:



benzene

Since this convenient formula agrees with the facts better than any other, it is still used today and is known as the "benzene ring," often pictured without the symbols as:



"benzene ring" without symbols

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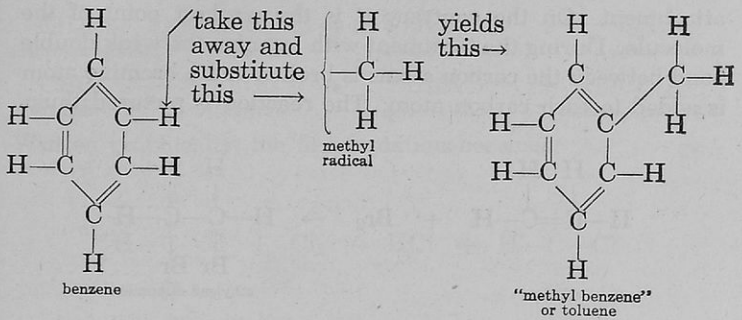
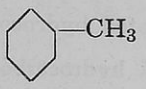
This structural ring formula has helped chemists to understand better the production of many synthetic organic compounds such as dyes and medicines.

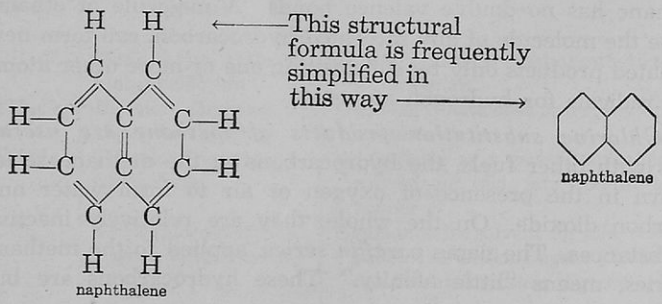
Toluene ($C_6H_5CH_3$), from which TNT is made (page 396), is the second member of the benzene series of ring hydrocarbons. You will be able to picture toluene more easily if you think of it as "methyl benzene" or as benzene with one hydrogen atom replaced by the methyl group:



The structural formula for toluene is sometimes simplified like this → The general formula of the benzene series is C_nH_{2n-6}.



Naphthalene ($C_{10}H_8$) is the first member of another series of ring hydrocarbons and is made up of two benzene rings. It is well known through its use as moth balls. Its graphic formula is pictured as:



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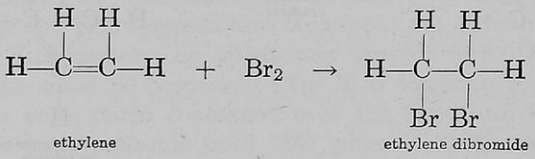
HOW DO HYDROCARBONS REACT?

Unsaturated hydrocarbons "add on" elements. You have seen that when ethylene is shaken with bromine water, the solution becomes colorless because the bromine combines with the ethylene. The unsaturated ethylene molecule (C_2H_4) has a double valence bond between the two carbon atoms. Only one valence bond, however, is needed between the carbon atoms. The so-called double valence bond does not make a stronger attachment. On the contrary it is the weakest point of the molecule. During the treatment with bromine the weak double bond between the carbon atoms is broken and a bromine atom is added to each carbon atom. The reaction is pictured thus:



Unsaturated hydrocarbons form *addition products.*

Saturated hydrocarbons can form only substitution products. You can see that the product formed by the previous reaction is ethane with two of its hydrogen atoms *replaced* by bromine atoms. However, this compound can be formed from ethane *only by substitution,* and not by the addition of bromine atoms. This is because ethane is a saturated hydrocarbon; ethane has no double valence bonds. A molecule of ethane, like the molecule of any saturated hydrocarbon, can form new related products only by substituting one or more other atoms or radicals for hydrogen atoms.

Chlorine substitution products of methane are useful. As with other fuels, the hydrocarbons in the methane series burn in the presence of oxygen or air to form water and carbon dioxide. On the whole, they are relatively inactive substances. The name *paraffin series,* applied to the methane series, means "little affinity." These hydrocarbons are but

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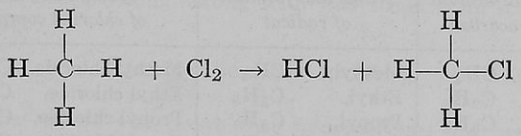
little affected by strong acids or bases. However, the simpler hydrocarbons, such as methane, react with chlorine in the sunlight to form hydrogen chloride and one or more chlorine substitution products as shown:

CH_4	+	Cl_2	→	HCl	+	CH_3Cl
methane		chlorine		hydrogen chloride		methyl chloride
CH_3Cl	+	Cl_2	→	HCl	+	CH_2Cl_2
methyl chloride		chlorine		hydrogen chloride		methylene chloride
CH_2Cl_2	+	Cl_2	→	HCl	+	$CHCl_3$
methylene chloride		chlorine		hydrogen chloride		chloroform
$CHCl_3$	+	Cl_2	→	HCl	+	CCl_4
chloroform		chlorine		hydrogen chloride		carbon tetrachloride

Written graphically, the first equation becomes:



In a similar manner, you should now be able to write the graphic equations for the other three reactions. Examine the following table which shows in condensed form the formulas, names, and uses of these four chlorine substitution products of methane.

FOUR CHLORINE SUBSTITUTION PRODUCTS OF METHANE

Formula	*Names*	*Uses*
CH_3Cl	Mono-chloro-methane Methyl chloride	In medicine as a local anesthetic; as a refrigerant
CH_2Cl_2	Di-chloro-methane Methylene chloride	Local anesthetic used as a spray upon the skin
$CHCl_3$	Tri-chloro-methane Chloroform	In medicine as a general anesthetic; solvent for oils, fats, iodine, and rubber
CCl_4	Tetra-chloro-methane Carbon tetrachloride	Nonflammable solvent for oils, resins, rubber; as cleaning agent (*Carbona*) and fire extinguisher (*Pyrene*)

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Hydrocarbons form radicals by losing hydrogen atoms. A great variety of substitution products of hydrocarbons is possible. Formulas for the simplest of the chlorine substitution products are C_2H_5Cl from ethane, C_3H_7Cl from propane, C_4H_9Cl from butane, and $C_5H_{11}Cl$ from pentane. Note in each case that the hydrocarbon has lost one hydrogen atom to form a radical which unites with the chlorine atom. These radicals are generally named from the hydrocarbon by changing the *-ane* in its name to *-yl*. Thus, meth*ane* (CH_4) forms the meth*yl* radical (CH_3), eth*ane* (C_2H_6) forms the eth*yl* radical (C_2H_5), and so on. These alkyl radicals all have a valence of one. Study the following summary until you have mastered it.

Name and formula of hydrocarbon	*Name and formula of radical*	*Name and formula of chlorine compound*
Methane, CH_4	Methyl, CH_3	Methyl chloride, CH_3Cl
Ethane, C_2H_6	Ethyl, C_2H_5	Ethyl chloride, C_2H_5Cl
Propane, C_3H_8	Propyl, C_3H_7	Propyl chloride, C_3H_7Cl
Butane, C_4H_{10}	Butyl, C_4H_9	Butyl chloride, C_4H_9Cl
Pentane, C_5H_{12}	Amyl, C_5H_{11}	Amyl chloride, $C_5H_{11}Cl$

Frequently, it is convenient to represent *any* of these radicals by the letter "R." Thus *R-Cl* represents any of the chlorides in the table.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XXIV, pp. 295-304, "Carbon Chains."

DARROW, F. L. *The Story of Chemistry.* Chap. II, pp. 50-63, "Benzene Ring and Molecular Structure."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XXII, pp. 362-372, "Hydrocarbons."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XI, p. 350, "Chloroform and Iodoform"; Vol. II, Chap. XXVI, pp. 827-845, "Coal Tar and Its Products."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XI, pp. 192-199, "Architecture of Molecules."

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Applying in Life What You Have Learned in Chemistry

A young boy was sent by his mother to a filling station to get some "cleaning" gasoline.

The station attendant explained that all their gasoline had "ethyl" in it. He refused to fill the can.

The boy insisted with, "Why not? It's gasoline, isn't it?"

What would you tell the boy?

A recent "movie" was showing some of the difficulties under which doctors in the 1890's had to work.

A certain scene showed a doctor performing an emergency operation in a private home at night. Chloroform was used as an anesthetic. Much was made of the fact that the doctor had to work almost in the dark since the kerosene lamp could not be brought near the anesthetic.

Do you see anything wrong with this scene from a chemical standpoint?

Putting Chemistry to Work

A

(1) How would you prove that hydrocarbons are nonelectrolytes? (2) Give two very different uses of carbon tetrachloride and point out the property on which each use depends. (3) Give three sources of hydrocarbons. What type of hydrocarbon is obtained from each source? (4) In what respects is the work of the "chemical architect" similar to the architect of modern buildings? In what ways has the "chemical architect" aided the modern architect? (5) At one time coal tar was thrown away as useless material. Why is it so valuable now? (6) Point out differences and similarities between ben*zine* and ben*zene*.

B

(7) Distinguish clearly between saturated and unsaturated hydrocarbons; between substitution products and addition products of hydrocarbons. Use illustrations. (8) Why is hexane known as a saturated *chain* hydrocarbon while benzene is known as a *ring* hydrocarbon? Show how the structural formulas of these two hydrocarbons are different. (9) The "ethyl" in ethyl gasoline is tetraethyl lead. What is its formula? See if you can learn why it is added to gasoline. (10) Why is ethylene bromide also added to ethyl gasoline? (Review page 331.)

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Research and Activities That You Will Enjoy

An exhibit: It is interesting and helpful in understanding the structure of carbon compounds to build model molecules from stiff wire and colored wooden balls to represent different kinds of atoms. These helpful ideas can be carried all the way through the study of related carbon compounds.

A reported interview: Ask your physician about the different anesthetics used in hospitals. Bring back to your class a summary of what you learn from the interview.

A report: Tell the class about the work of the early organic chemists in unraveling the mysteries of the structure of carbon compounds. (A good reference is Deming, *In the Realm of Carbon.*)

Problem 51

HOW ARE ALCOHOLS RELATED TO HYDROCARBONS? HOW ARE ALCOHOLS USED?

You, no doubt, are already familiar with the names, "wood alcohol" and "grain alcohol." These products belong to a large and useful group of related organic compounds known as *alcohols.* Since they all contain the hydroxyl group (OH), alcohols might be called "organic hydroxides" although their solutions contain no hydroxyl ions and therefore do not show basic properties. In this problem you will see how the alcohols are related to the hydrocarbons.

How is "wood" alcohol related to the hydrocarbon methane? "Wood" alcohol is methyl alcohol or *methanol* (CH_3OH). It is the simplest alcohol and is obtained by the destructive distillation of wood. Formerly, this was the usual source of it. Now large amounts are made by the catalytic union of hydrogen and carbon monoxide:

$$2\ H_2 + CO \rightarrow CH_3OH$$

This method of producing synthetic methyl alcohol or methanol has served to lower the price and also to conserve a diminish-

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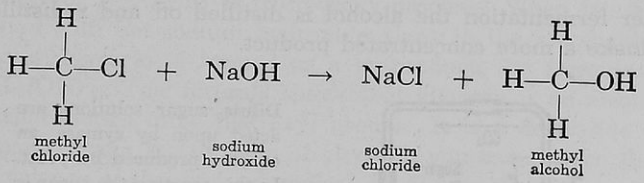
ing supply of wood for other important uses which are today drawing heavily on our forests.

Methanol is a colorless flammable liquid which boils at 65° C. It is miscible with water in all proportions. Methanol is exceedingly poisonous even in the vapor state. When breathed or taken internally it affects the optic nerve, often causing blindness. Large amounts are fatal.

The relation of methyl alcohol to methane is shown by the way in which it may be prepared in the laboratory. When methyl chloride is treated with sodium hydroxide, methyl alcohol is formed:

$$CH_3Cl + NaOH \rightarrow NaCl + CH_3OH$$



You will recall how methyl chloride was prepared from methane. The relation of these three compounds may be shown briefly as:

$$\underset{\text{methane}}{CH_4} \xrightarrow{+Cl_2} \underset{\text{methyl chloride}}{CH_3Cl} \xrightarrow{+NaOH} \underset{\text{methyl alcohol}}{CH_3OH}$$

How is "grain" alcohol related to the hydrocarbon, ethane? "Grain" alcohol is ethyl alcohol or *ethanol* (C_2H_5OH). It is related to ethane through ethyl chloride:

$$C_2H_6 + Cl_2 \rightarrow HCl + \underset{\text{ethyl chloride}}{C_2H_5Cl}$$

$$C_2H_5Cl + NaOH \rightarrow NaCl + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

Note that ethyl alcohol is a substitution product of ethane in which one hydrogen atom is replaced by the hydroxyl group. These relations may be written briefly as follows.

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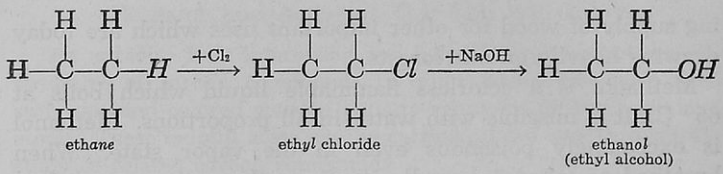
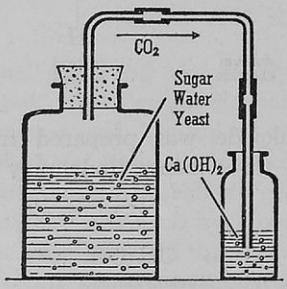


Ethyl alcohol today, as in ancient times, is prepared by the fermentation of the sugars in grains, fruits, and other plant products. The sugars are acted upon by yeast plants which secrete an enzyme called *zymase*. This enzyme acts as a catalytic agent which decomposes the sugar into carbon dioxide and ethyl alcohol.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2\uparrow$$

After fermentation the alcohol is distilled off and redistilled to make a more concentrated product.



Dilute sugar solutions are acted upon by zymase, an enzyme produced by yeast. In this reaction the sugar is converted into alcohol and carbon dioxide. When the concentration of the alcohol reaches about 16 per cent, the reaction stops. Alcohol can then be separated from this solution by distillation.

169. FERMENTATION OF SUGAR TO MAKE ETHYL ALCOHOL

Denatured alcohol is "impure" ethyl alcohol. Because ethyl alcohol is always associated with intoxicating beverages, its use has become a social problem. Many governments place high taxes on it. However, it is indispensable to industry. To avoid the government taxes—prohibitive for industrial use—it has been necessary to add certain substances to ethyl alcohol which will make it unfit for beverage purposes. Such alcohol is said to be denatured. The substance added as a denaturant is usually poisonous. It must be a substance that cannot be

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

easily removed and that will not interfere with the industrial uses of the ethyl alcohol. Methyl alcohol is a commonly used denaturant. Users of denatured alcohol are not required to pay the high taxes levied against pure ethyl alcohol. The industrial demand for alcohol is well over 100 million gallons per year.

Alcohols may be considered as substitution products of hydrocarbons. *All* alcohols contain the hydroxyl (OH) radical and all may be considered as hydroxyl derivatives of hydrocarbons. Thus propyl alcohol (C_3H_7OH) is related to propane; butyl alcohol (C_4H_9OH), to butane; amyl alcohol ($C_5H_{11}OH$), to pentane; and so on. The general formula of all the alcohols is *R-OH*.

Glycerol (glycerin) is tri-hydroxy-propane. When fats are treated with hot sodium hydroxide (lye) in the soapmaking process, glycerin is formed as a by-product. Its formula is $C_3H_5(OH)_3$. This formula shows that glycerin is an alcohol which contains three hydroxyl groups. It is a derivative of propane. From the formula of glycerol, you can deduce that the valence of the glyceryl radical (C_3H_5) is three.

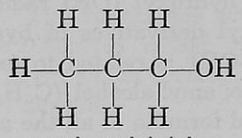
Glycerin is a colorless, sirupy, sweet liquid which is miscible with water and with ethyl alcohol. It is used in the manufacture of printer's ink, hand lotions, and glyceryl nitrate ("nitroglycerin").

Phenol ("carbolic acid") is hydroxy-benzene. Phenol (C_6H_5OH) is the simplest hydroxy derivative of the ring hydrocarbon, benzene. It is obtained along with other by-products in the manufacture of coke. Phenol is valuable as a disinfectant and in the manufacture of drugs, dyes, and synthetic plastics, such as *bakelite*.

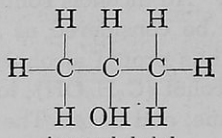
How can different compounds have the same formula? Two propyl alcohols are known. Each has *the same* "empirical" (molecular) formula (C_3H_8O). But these alcohols have different boiling points and different chemical properties. By studying certain chemical reactions, it was found that in one of these propyl alcohols the hydroxyl group was attached to

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

a carbon atom *at the end* of the molecule, while in the other propyl alcohol the hydroxyl was attached to the carbon atom *in the middle* of the molecule. You see that these two compounds have the same empirical formula but *different structural formulas.* Such compounds are called *isomers,* and the prefix *iso-* is used to distinguish them. The structural formulas of normal propyl alcohol and of isopropyl alcohol are:

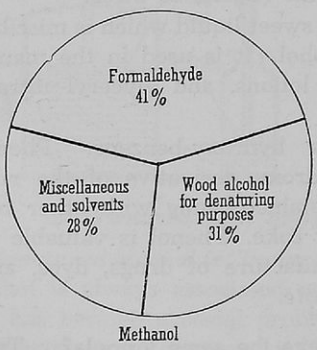


normal propyl alcohol
(a primary alcohol)



isopropyl alcohol
(a secondary alcohol)

Notice that isopropyl alcohol is a *secondary alcohol*—an alcohol in which the particular carbon atom that is attached to the hydroxyl (OH) is also attached to *two* other *carbon* atoms. In other words the primary alcohol contains the group CH_2OH while the secondary alcohol contains CHOH.



Methanol (methyl alcohol, or wood alcohol) has many uses. By gentle oxidation it is converted into formaldehyde. Formaldehyde is used as a preservative and as a starting point for the production of plastics, such as bakelite. Methanol is a common solvent for gums and lacs to form "spirit varnishes," such as shellac. It is the most common denaturant in denatured alcohol.

170. CONSUMPTION OF METHANOL

Alcohols are used in "antifreeze" mixtures. Why? The use of the automobile in cold weather has made it necessary to lower the freezing point of the water used in the radiator. A com-

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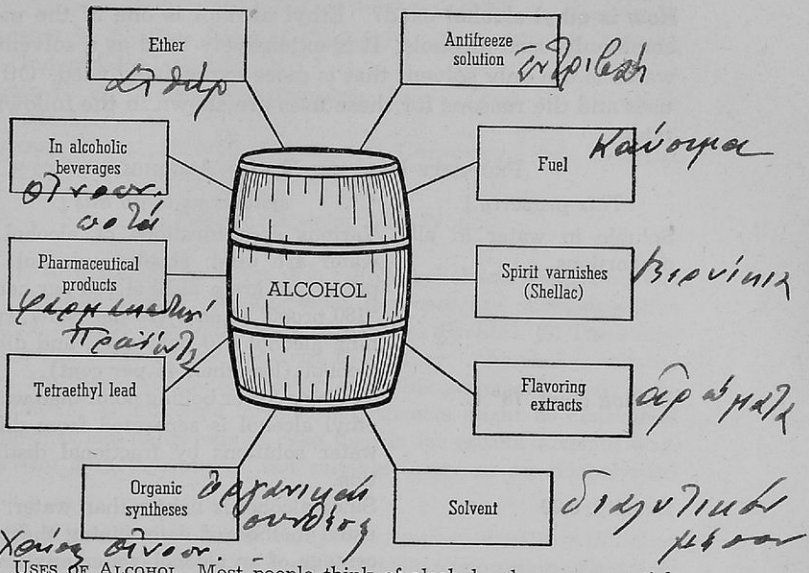

171. USES OF ALCOHOL. Most people think of alcohol only as a potential public enemy, but these uses indicate its value in industry.

mon "antifreeze" is industrial, or denatured, alcohol. Since its boiling point (78° C.) is lower than that of water, its continued effectiveness is lessened through evaporation.

An alcohol with two hydroxyl groups has come into rather common use under the trade name of "Prestone." Its chemical name is ethylene glycol and its formula is $C_2H_4(OH)_2$. It is made by treating ethylene chloride with a base. The higher boiling point of ethylene glycol (197° C.) prevents its loss through evaporation. It is miscible with water in all proportions and is noncorrosive. If leaks do not develop in the radiator, the solution may be used for several years. Ethylene glycol is also used in making a nonfreezing dynamite.

How is methyl alcohol used? Methanol is a good solvent for many resins and gums. Consequently, it is used widely in the preparation of varnishes and shellacs. It is also used as a fuel and as a denaturant for industrial alcohol.

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How is ethyl alcohol used? Ethyl alcohol is one of the most commonly used alcohols. It is extensively used as a solvent—water is the only solvent that is more extensively used. Other uses and the reasons for these uses are shown in the following table.

PROPERTY-USES OF ETHYL ALCOHOL

This property ↓	*enables us to do this* ↓
Soluble in water in all proportions	Various concentrations of alcohol in water are used; absolute alcohol (99 per cent), grain alcohol (95 per cent), "180 proof" alcohol (90 per cent), rubbing alcohol (70 per cent), and dilute alcohol (less than 45 per cent).
Boiling point, 78° C.	Having a lower boiling point than water, ethyl alcohol is separated from dilute water solutions by fractional distillation.
Density, 0.79	Since alcohol is lighter than water, the usual method of determining the percentage of an alcohol-water mixture is by determining its density.
Freezing point, —112° C. Mixtures of alcohol and water have a lower freezing point than pure water	Since alcohol is noncorrosive, it is used in "antifreeze" solutions for auto radiators.
Dissolves a wide variety of substances; a good solvent	Used in pharmacy as a solvent in the preparation of tinctures, essences, and extracts.
Burns in air or oxygen, producing carbon dioxide and water, and liberating 327,600 calories of heat per gram-molecular weight	Alcohol is used as a convenient fuel on a small scale in chafing dishes and in a semisolid form *(sterno)*. A mixture of anhydrous ethyl alcohol and gasoline is coming into use as a motor fuel.
Coagulates albumin (a protein material) and arrests growth of bacteria	Used as a preservative of biological specimens. Also acts as a preservative in many "patent" medicines.
Dehydrating agent	Taken internally alcohol acts as a poison; withdraws water from tissues, and lowers body resistance to disease.

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Readings for Pleasure and Profit

DARROW, F. L. *The Story of Chemistry.* Chap. XII, pp. 436-444, "Industrial Alcohol."

HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. III, pp. 34-53, "Alcohol."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. II, Chap. XXXIV, pp. 1020-1033, "Glycerin."

Putting Chemistry to Work

A

(1) How could you distinguish ethyl alcohol and methyl alcohol by physical means? (2) For what purposes are substances like methyl alcohol and benzine added to ethyl alcohol? (3) The statement was made by one motorist to another: "Alcohol is not the best antifreeze for autos." Why does this statement need to be qualified? (4) Methanol in flavoring extracts might be considered somewhat less dangerous in cake than in ice cream. Explain why. (5) Why is methyl alcohol not suitable to use as an alcohol rub?

B

(6) When alcohol burns completely, carbon dioxide and water are formed. What does this show about the composition of alcohol? (7) Why would ethyl hydroxide not be a good name for ethanol? (8) When alcohol for auto radiators is marked "188 proof," what is meant? (9) What inconsistency and what justification is there for calling phenol "carbolic acid"? (10) Why is the formula for an alcohol easily recognized? Of what class of inorganic compounds does it remind you? In what respects have you found it to be different? (11) Match the following by choosing one from each of the three lists:

(a) CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_6;

(b) CH_3OH, $C_2H_4(OH)_2$, C_4H_9OH, C_2H_5OH, $C_3H_5(OH)_3$, C_6H_5OH, $C_5H_{11}OH$;

(c) Amyl alcohol, butyl alcohol, ethanol, ethylene glycol, glycerol, methanol, phenol.

Research and Activities That You Will Enjoy

An interpretation: Ask an organic chemist what is meant by *combustion analyses* and what facts concerning carbon compounds are learned by these procedures. Also ask him to explain the relation among empirical formulas, rational formulas, and structural

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formulas of carbon compounds. Explain to the class what you learn.

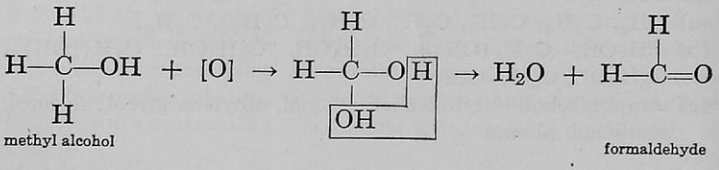
A demonstration: After outside preparation, show the class how you would distinguish between methyl alcohol and ethyl alcohol by chemical tests. Point out the importance of these tests.

A field trip: If possible, visit a pharmaceutical plant (manufacturers of drugs) to learn the importance of alcohol in the manufacture of chemicals used for medicines. Or, present to the class your summary of "The Role of Alcohol" in Fuller, *The Story of Drugs*, or in other similar books on the manufacture and use of drugs.

Problem 52

HOW ARE OTHER VALUABLE PRODUCTS OBTAINED FROM ALCOHOLS?

Methyl alcohol, gently oxidized, produces formaldehyde. When a hot spiral of copper wire is thrust into methyl alcohol, a gas with a pungent odor is formed. This gas is formaldehyde. It is produced by the *gentle oxidation* (not burning) of the methyl alcohol. The same product is obtained when a mixture of methyl alcohol vapor and air is passed through heated copper or platinum gauze, or when methyl alcohol is treated with a moderately active oxidizing agent. This reaction is more easily understood when it is represented by structural formulas:



methyl alcohol

formaldehyde

We may first consider that the atom of oxygen "adds on" to an atom of hydrogen to form the second hydroxyl group. But *two* hydroxyl groups do not stay attached to the *same* carbon atom; instead, water "breaks off." This leaves an

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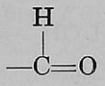
oxygen atom attached to the carbon atom by means of a double bond.

Formaldehyde is the first member of a series of compounds known as *aldehydes*, a word which means "oxidized *al*cohols *dehyd*rated." The characteristic group that identifies the aldehydes is the CHO group:

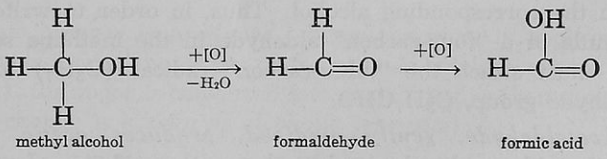


The general formula of aldehydes, therefore, is *R–CHO*.

Formaldehyde is largely used as a 40 per cent solution known as *formalin*. It is an excellent preservative, but its poisonous nature prevents its legal use in foods. Formalin is a disinfectant which is used in embalming fluids.

Formaldehyde is also used in making plastic substances such as *bakelite*, which is a synthetic resin made by heating and pressing a mixture of phenol and formaldehyde. Bakelite and similar products find wide uses in phonograph records, combs, billiard balls, electrical insulating material, and telephone receivers.

Formaldehyde, gently oxidized, produces formic acid. The simplest organic acid is formic acid (HCOOH), which is present in ants, bees, and other insects. The relation of formic acid to methyl alcohol is shown by the gentle oxidization of formaldehyde:



Here is a general summary of the oxidation products of hydrocarbons—it is important. In this problem and in the previous one, you have seen how a hydrocarbon may be changed by substitution and oxidation into different classes of related

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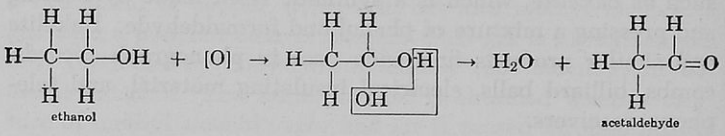
products. The story is reviewed here with general formulas. Ethane is used as an example. (Note the systematic naming of these products.)

R–*H*	→	R–*Cl*	→	R–*OH*	→	R–*CHO*	→	R–*COOH*
hydrocarbon		chlorine substitution product		alcohol		aldehyde		acid

C_2H_6	$\xrightarrow{+Cl_2}$	C_2H_5Cl	$\xrightarrow{+NaOH}$	C_2H_5OH	$\xrightarrow{+[O]}$	CH_3CHO	$\xrightarrow{+[O]}$	CH_3COOH
eth*ane*		eth*yl* chloride (monochloroethane)		eth*anol* (ethyl alcohol)		eth*anal* (acetaldehyde)		eth*anoic* acid (acetic acid)

Ethyl alcohol, gently oxidized, produces acetaldehyde. The above summary will be very helpful in giving you a complete and connected picture of the oxidation products of hydrocarbons. You will find it to your advantage also to study the oxidation of ethyl alcohol as it forms the second aldehyde in the methane series:



From its formula you can see that acetaldehyde (CH_3CHO) is a "two-carbon" aldehyde, related through ethyl alcohol to ethane. But one of the carbon atoms in acetaldehyde is included in the aldehyde group CHO, so the radical attached to the aldehyde group (CH_3) *contains one less carbon atom* than the corresponding alcohol. Thus, in order to write the formula of a "four-carbon" aldehyde in the methane series, you must attach the "three-carbon" radical (C_3H_7) to the aldehyde group, C_3H_7CHO.

Acetaldehyde, gently oxidized, produces acetic acid. Acetic acid may be obtained by the gentle oxidation of acetaldehyde. This reaction not only shows that acetaldehyde is the intermediate oxidation product between ethyl alcohol and acetic acid, but it also gives a clearer picture of the molecular structure of acetic acid. Note the following diagram.

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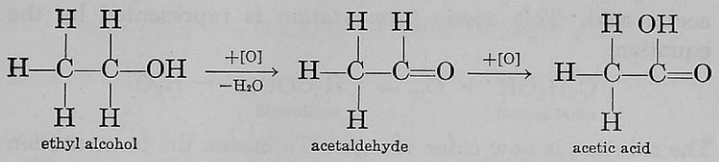

The above formula for acetic acid shows that the characteristic group for organic acids is COOH, so the general formula becomes *R–COOH*. It should be noted again that here, as with acetaldehyde, the radical (R) contains one less carbon atom than the acid itself since one carbon atom is always found in the carboxyl (COOH) group. Thus the organic acid corresponding to butane is C_3H_7COOH, butyric acid.

Although organic acids ionize only slightly, salts of some of them are well known. For example, in acetic acid the last hydrogen atom written in the formula (CH_3COOH) is the replaceable ("acid") hydrogen, so the formula for sodium acetate becomes CH_3COONa. Therefore the *acid radical* is written by omitting the replaceable hydrogen atom from the acid.

Acetic acid is the most important organic acid industrially. Formerly the chief commercial source was as a by-product in the destructive distillation of wood, but recently it is synthesized from acetylene. Acetic acid acts as a solvent for many organic substances, and large quantities of it are used in the preparation of cellulose acetate which is used in making nonflammable motion picture film, cellophane, and one type of rayon.

How vinegar is produced. When the sugar in apple juice ferments due to the action of the organic catalyst zymase (in yeast), the sugar is converted into alcohol and carbon dioxide. This change is known as *alcoholic fermentation:*

$$\underset{\text{sugar}}{C_6H_{12}O_6} \rightarrow 2\ \underset{\text{ethyl alcohol}}{C_2H_5OH} + 2\ CO_2\uparrow$$

The solution containing from 4 to 8 per cent of alcohol is called "hard" cider. In the presence of certain bacteria ("mother of vinegar") and oxygen, the alcohol is oxidized to

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acetic acid. This *acetic fermentation* is represented by the equation:

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + O_2 \rightarrow \underset{\text{acetic acid}}{CH_3COOH} + H_2O$$

The solution is now cider vinegar. To hasten the fermentation process, a large wooden container is filled loosely with beechwood shavings which have been treated to introduce the necessary fermentation bacteria, and hard cider or dilute alcohol is sprayed through the shavings from the top while oxygen is admitted from the bottom. In this way the alcohol and oxygen are brought into intimate contact, and the oxidation of the alcohol to acetic acid occurs rapidly as the liquid trickles down through the shavings. Vinegar should contain at least 4 per cent of acetic acid.

The gentle oxidation of an aldehyde produces an organic acid. You have seen how formic acid is produced from formaldehyde and how acetic acid is produced from acetaldehyde. Similarly, other organic acids may be produced by the gentle oxidation of other aldehydes. Many of the organic acids are important to us.

Several organic acids are related to fats. Butyric acid (C_3H_7COOH), palmitic acid ($C_{15}H_{31}COOH$), and stearic acid ($C_{17}H_{35}COOH$) are a few of the more complex acids in the methane series. Their acid radicals are found combined in fats, so the acids of this series are often referred to as the *fatty acids.* Butyric acid is a foul-smelling, oily liquid, present in rancid butter. Stearic acid, a white solid melting at about 70° C., is used in making soap, candles, and face creams. Another acid related to fats and oils is oleic acid ($C_{17}H_{33}COOH$) whose formula, when compared with that of stearic acid, shows two "unfilled" positions for hydrogen atoms. Because of these vacancies, oleic acid is an *unsaturated acid.*

• *Organic acids are found in fruits.* Many more organic acids occur uncombined or combined in fruits and vegetables. A few are listed for reference in the following table which shows their formulas and most common sources.

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FORMULAS AND SOURCES OF SOME ORGANIC ACIDS

Organic acid	*Where found*	*Formula showing replaceable hydrogen*	*Rational formula*
Citric	citrus fruits	$H_3C_6H_5O_7$	$CH_2COOH \cdot COHCOOH \cdot CH_2COOH$
Tartaric	grapes	$H_2C_4H_4O_6$	$COOH \cdot CHOH \cdot CHOH \cdot COOH$
Lactic	sour milk, sauerkraut	$HC_3H_5O_3$	$CH_3 \cdot CHOH \cdot COOH$
Oxalic	rhubarb, sorrel	$H_2C_2O_4$	$COOH \cdot COOH$
Benzoic	cranberries	$HC_7H_5O_2$	C_6H_5COOH
Malic	gooseberries, unripe apples	$H_2C_4H_4O_5$	$CH_2COOH \cdot CHOH \cdot COOH$
Salicylic	oil of wintergreen	$HC_7H_5O_3$	$C_6H_4 \cdot OH \cdot COOH$

• ***Amino acids are the "building stones" of protein foods.*** Another class of hydrocarbon derivatives is worthy of mention here because they are related to protein foods. When a hydrogen atom in ammonia is replaced by a hydrocarbon radical, a compound known as an *amine* is formed.[1] Thus CH_3NH_2 is methyl amine. The simplest amine of a ring hydrocarbon is anilin ($C_6H_5NH_2$) which is used in the manufacture of dyes. Since the amines may be regarded as being derived by replacing one hydrogen atom in the ammonia molecule (NH_3) with a hydrocarbon radical, they, as you might expect, show many of the properties of ammonia. Several of the amines possess the disagreeable odor of decaying protein

[1] When studying about the ionization of water, you learned of the formation of H^+ ions and OH^- ions. In an ammonia system of compounds, where liquid ammonia is the solvent instead of water, the liquid ammonia may be thought of as splitting up into H^+ ions and NH_2^- ions.

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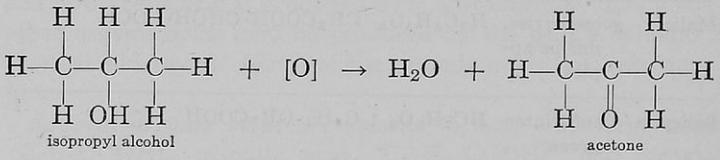
material. Putrescine $[C_4H_8(NH_2)_2]$ belongs to a class of compounds known as *ptomaines.* Many ptomaines are very poisonous.

Amino acids are organic acids which contain one or more amino groups. The simplest uncombined amino acid is glycine, amino acetic acid (CH_2NH_2–COOH). More than twenty amino acids are known. They are important in food chemistry because they are the "building stones" out of which proteins are made. (See page 540.)

• **Gentle oxidation of a secondary alcohol yields a ketone.** Note that both of the previously studied alcohols, which have been oxidized to form aldehydes, have been primary alcohols (page 488). A secondary alcohol yields a different kind of product as shown by the oxidation of isopropyl alcohol to form acetone:



Acetone, $(CH_3)_2CO$, is the simplest *ketone,* characterized by the CO group. The general formula for ketones is *R–CO–R.* Acetone is one of the most important solvents. It is used in the manufacture of varnishes, varnish removers, and smokeless gunpowders. Its use as a solvent for acetylene was mentioned on page 471.

Formerly, acetone was obtained by the destructive distillation of wood. The acetic acid in "wood vinegar" was neutralized with lime and the dried calcium acetate was heated:

$$Ca(C_2H_3O_2)_2 \rightarrow \underset{\text{acetone}}{(CH_3)_2CO} + CaCO_3$$

This decomposition is more easily understood if calcium acetate is written graphically as a derivative of acetic acid CH_3COOH. Note the following diagram.

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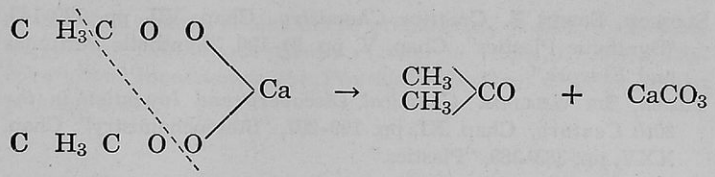
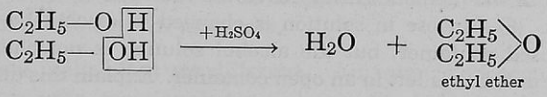


Today, a great deal of acetone is obtained by certain fermentation reactions of corn products. The distillation of these fermentation products yields about 30 per cent acetone, 60 per cent butyl alcohol, and 10 per cent ethyl alcohol.

• **Dehydration of alcohols produces ethers.** When ethyl alcohol is treated with a limited amount of sulfuric acid at a moderately low temperature, ethyl ether is formed:



You will note that this product is formed when *two* molecules of ethyl alcohol lose *one* molecule of water and that the sulfuric acid is the dehydrating agent. Any alcohol so treated will produce an ether, which may be considered as an "organic oxide." The general formula is *R–O–R*.

Ethyl ether is the most common ether. It is a light, colorless liquid with a pleasant odor. It is very volatile, boils at 35° C., and is highly flammable. While we generally think of ether as an anesthetic, it is also widely used as a solvent for waxes and gums and for fats and oils in food analysis.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XXIV, pp. 304-309, "Carbon Chains."

DARROW, F. L. *The Story of Chemistry.* Chap. XI, pp. 384-386, "Bakelite."

HOWE, H. E. *Chemistry in Industry.* Vol. I. Chap. XIX, pp. 329-339, "Synthetic Resins."

JAFFE, BERNARD. *Crucibles.* Chap. X, pp. 175-198, "Woehler."

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SLOSSON, EDWIN E. *Creative Chemistry.* Chap. VII, pp. 129-143, "Synthetic Plastics"; Chap. V, pp. 91-106, "Synthetic Perfumes and Flavors."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XI, pp. 199-207, "Stereochemistry"; Chap. XXV, pp. 383-389, "Plastics."

Putting Chemistry to Work

A

(1) What is the most common purpose of the concentrated sulfuric acid used in so many organic reactions? (2) Is the aldehyde C_4H_9CHO related to butane or to pentane? Explain your answer. (3) Suggest a method of preparing synthetic vinegar. (4) Starting with butane, give the names, the molecular formulas, and the structural formulas for all the products in the oxidation steps to butyric acid. (5) Palmitic and stearic acids are related to hydrocarbons in the methane series. Give the formulas for these hydrocarbons. (6) Glucose in solution is changed to alcohol by zymase in a closed container, but the alcohol solution is not changed to vinegar unless it is left in an open container. Explain this difference in behavior.

B

(7) Account for the derivation of the names, formaldehyde and acetaldehyde. (8) To what type of carbon compound does each of the following belong: C_2H_5Cl, $C_2H_4(OH)_2$, CH_3CHO, C_6H_5COOH, C_5H_{12}, CHI_3, $C_3H_5(OH)_3$, C_3H_7COOH, CH_3COONa? (9) Name each of the compounds listed above. (10) How is the amino radical related to ammonia? (11) The following amines were mentioned in this problem: CH_3NH_2, $C_6H_5NH_2$, and $C_4H_8(NH_2)_2$. Draw their structural formulas and name the hydrocarbon to which each is related.

Research and Activities That You Will Enjoy

A report: After outside reading and study, tell the class what you have learned about the importance of fermentation reactions. Do not fail to show the importance of enzymes.

A historical summary: Prepare and present to the class a very condensed summary of the history of organic chemistry. (See Chap. VII in French, *The Drama of Chemistry,* or other similar "condensed interpretations" of chemistry.)

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Another report: After outside preparation, present to the class all you can learn about plastics. (Refer to Tilden, *Chemical Discovery and Invention in the Twentieth Century,* or other similar popular books.)

Problem 53

WHAT ARE ESTERS: HOW DO THEY SERVE US?

The organic chemist today is not only improving many natural products but also he is "creating" new products which have not been found in nature. Early in his attempts to "beat nature at her own game," he learned to imitate the natural products found in fruits and flowers which appeal to man's senses of taste and smell. A large number of these organic substances are known as *esters.*

Esters are "salts" that are different. An ester is an organic salt formed by the reaction between an alcohol ("organic base") and an organic acid. You will notice that such a change resembles a neutralization reaction in which a base and an inorganic acid interact to form water and a salt. The chief difference between these two kinds of reactions is due to the fact that neutralization is an ionic reaction:

$$(Na^+ + OH^-) + (H^+ + Cl^-) \rightarrow HOH + (Na^+ + Cl^-)$$

On the other hand the formation of an ester (esterification) is not ionic because alcohols do not ionize appreciably and organic acids ionize only feebly. The main point in common in the two reactions is the formation of water as shown by the reaction between ethyl alcohol and acetic acid:

$$\underset{\substack{\textit{ethyl}\\ \text{alcohol}}}{C_2H_5\boxed{OH}} + \underset{\substack{\text{hydrogen}\\ \textit{acetate}}}{CH_3COO\boxed{H}} \rightarrow HOH + \underset{\text{ethyl acetate}}{CH_3COO{\cdot}C_2H_5}$$

The ester formed in this reaction is *ethyl acetate.* The ethyl group is supplied by the ethyl alcohol and the acetate by the

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hydrogen acetate (acetic acid). Ethyl acetate is a volatile, colorless liquid. Like esters in general, it has a fragrant, fruity odor. Alcohols may also react with some inorganic acids, as nitric acid, to form compounds called esters. The explosive nitroglycerin is an example. (See page 503.)

Another difference between a neutralization reaction and esterification is the degree in which they go toward completion. With strong acids and bases a neutralization reaction goes to completion. In the esterification reaction, on the other hand, as soon as water and the ester are formed, they begin to interact by hydrolysis to reverse the reaction. The reaction is forced toward the formation of the ester by the addition of concentrated sulfuric acid as a dehydrating agent. This acid absorbs the water and removes it from the field of action. The general equation for the formation of esters is:

$$\underset{\text{alcohol}}{R\text{–}OH} + \underset{\text{acid}}{\acute{R}\text{–}COOH} \rightarrow HOH + \underset{\text{ester}}{\acute{R}\text{–}COO\text{–}R}$$

Esters are found in flavoring extracts. Many of the sweet-smelling components in flowers and fruits, as well as in other parts of plants, are esters. Hence, perfumes often contain esters. Many esters are now produced synthetically as substitutes for natural flower and fruit essences. Following are listed a few esters and their characteristic odors. (It should be noted that many natural flavors are complex mixtures of hydrocarbons, alcohols, esters, aldehydes, and ketones. This is especially true of the aromatic flavors, such as oil of peppermint, spearmint, and cinnamon.)

SOME FAMILIAR ESTERS

Name of Ester	*Formula*	*Characteristic Odor*
Ethyl butyrate	$C_3H_7COO \cdot C_2H_5$	pineapple
Amyl acetate	$CH_3COO \cdot C_5H_{11}$	banana, pear
Methyl salicylate	$C_6H_4(OH)COO \cdot CH_3$	wintergreen
Amyl valerate	$C_4H_9COO \cdot C_5H_{11}$	apple
Octyl acetate	$CH_3COO \cdot C_8H_{17}$	orange
Methyl anthranilate	$C_6H_4(NH_2)COO \cdot CH_3$	grape

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Some esters are used as solvents. The characteristic odor of certain fingernail polishes and of "dope" for airplane wings is due to an ester which is used as a solvent in the material. Likewise, automobile lacquers contain esters as solvents because these volatile liquids evaporate easily. Three synthetic esters used in this way are ethyl acetate, butyl acetate, and amyl acetate.

Nitroglycerin is an ester of glycerin and nitric acid. "Nitroglycerin" is prepared by the action of nitric acid on glycerin in the presence of concentrated sulfuric acid as a dehydrating agent:

$$\underset{\text{glycerol}}{C_3H_5(OH)_3} + 3\ HNO_3 \rightarrow \underset{\substack{\text{glyceryl nitrate}\\(\text{"nitroglycerin"})}}{C_3H_5(NO_3)_3} + 3\ HOH$$

Since glyceryl nitrate ("nitroglycerin") is very unstable, it must be prepared and handled with extreme care. Even a slight shock is sometimes sufficient to cause it to decompose explosively. Because of the dangers involved in handling liquid "nitroglycerin," it is often soaked up in porous material, such as infusorial earth or wood pulp, wrapped up in stick form, and used under the name of dynamite. Both of these porous materials are highly effective as absorbents. Modern high-powered dynamite is made by impregnating nitrated wood pulp with "nitroglycerin." When such a mixture is detonated, the entire mass takes part in the reaction giving an explosion of great power.

Fats are esters of glycerol. A great variety of esters found in the seeds of plants and in the bodies of animals are fats. As a class of substances, they contain the glyceryl radical (C_3H_5) which is found in the familiar compound glycerin or glycerol [$C_3H_5(OH)_3$]. Since glycerol is a trihydroxy alcohol, the glyceryl radical has a valence of three. This means that an ester formed from glycerol and a monobasic acid, such as stearic acid, will contain *three* stearate radicals. Thus the formation of the typical fat glyceryl stearate (*stearin*) will be represented by the following equation.

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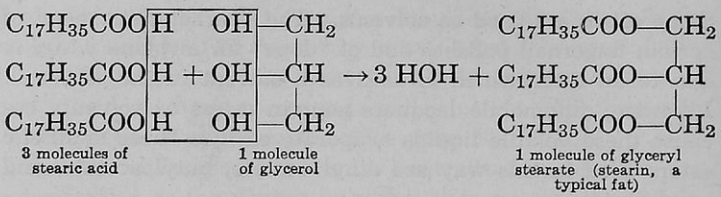

The formula of stearin is written somewhat more simply as $(C_{17}H_{35}COO)_3C_3H_5$. Several typical fats are listed in the following table for reference.

Fat	*Chemical Name*	*Formula*	*Melting point*	*Occurs in*
Butyrin	Glyceryl butyrate	$(C_3H_7COO)_3C_3H_5$	+75° C.	Butter
Palmitin	Glyceryl palmitate	$(C_{15}H_{31}COO)_3C_3H_5$	65° C.	Lard
Olein	Glyceryl oleate	$(C_{17}H_{33}COO)_3C_3H_5$	−4° C.	Cottonseed, olive, corn oils
Stearin	Glyceryl stearate	$(C_{17}H_{35}COO)_3C_3H_5$	71° C.	Beef tallow

The common fats used in foods, such as butter, lard, and beef tallow, are not limited to any one kind of acid radical as the preceding table might suggest, but they contain a wide variety of the fatty esters. Fats are very complex mixtures as shown by the following analysis of butterfat.

Kind and Quantity of Acid Radicals in Butterfat

(4)[1] Butyric	3.4 per cent	(14) Myristic	22.6 per cent
(6) Caproic	1.4 per cent	(16) Palmitic	19.3 per cent
(8) Caprylic	1.0 per cent	(18) Stearic	11.4 per cent
(10) Capric	1.6 per cent	(18) Oleic (unsaturated)	27.4 per cent
(12) Lauric	1.9 per cent		

Fats are glyceryl esters of mixed fatty acids, so the properties of different fats vary considerably, depending upon the

[1] The numbers preceding the names of the acids indicate the number of carbon atoms.

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components of the mixture. In general, animal fats, (stearin in beef tallow) are saturated, and the higher members have relatively high melting points; that is, they are solid at ordinary temperatures. On the other hand, several vegetable oils (olein in cottonseed oil) are unsaturated, have lower melting points, and are liquids. Be careful not to confuse vegetable oils (esters) with mineral oils (hydrocarbons).

Some liquid fats are changed to solid fats and used for cooking purposes. Largely due to custom, American housewives prefer solid fats for cooking. As the demand for solid fats caused the price to rise, an interesting thing occurred. Research showed that cotton seeds were rich in olein, an unsaturated liquid vegetable oil. It was found possible to introduce hydrogen atoms into the "vacant places" in the unsaturated olein molecules by heating the oil with hydrogen in the presence of finely powdered nickel as a catalyst. By this process of *hydrogenation,* the liquid fat is changed into a semisolid condition:

$$\underset{\text{olein, a liquid fat}}{(C_{17}H_{33}COO)_3C_3H_5} + 3\,H_2 \rightarrow \underset{\text{stearin, a solid fat}}{(C_{17}H_{35}COO)_3C_3H_5}$$

This discovery did two things: It gave a market to the southern planters for their excess of cottonseed oil, and it increased the supply of solid fats for a "solid-fat consuming" public. "Crisco," "Snowdrift," and "Spry" are examples of hydrogenated products. Likewise, oleomargarine, made from nut oils, may contain small amounts of hydrogenated fats.

Linseed oil is a fat that is used in paints. Why? Linseed oil contains esters of two acids, linoleic ($C_{17}H_{31}COOH$) and linolenic ($C_{17}H_{29}COOH$), which are even more unsaturated than oleic acid. On exposure to air, these oils combine with oxygen and liberate considerable heat. This property causes them to be known as "drying oils." If the heat from their oxidation accumulates, spontaneous combustion may occur. But this same property of combining with oxygen makes these "drying oils" useful in paints, for by oxidation they form a tough membrane which protects the painted material. Paints containing linseed oil or tung oil are said to become "dry" but

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the "drying" is due to the oxidation of the unsaturated fats. To hasten the process, various oxides or metallic soaps ("dryers") are mixed with the paint.

How fats are changed by hydrolysis. Everyone has experienced the disagreeable odor of rancid butter. This odor is due in part to the formation of foul-smelling butyric acid by bacterial action on the butyrin (fat) in the butter. A similar change, known as hydrolysis, occurs when any fat is treated with superheated steam. Three molecules of water react with each molecule of the fat to form three molecules of the fatty acid and one molecule of glycerin:

$$\underset{\text{glyceryl stearate (stearin)}}{(C_{17}H_{35}COO)_3C_3H_5} + 3\ HOH \rightarrow 3\ \underset{\text{stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{glycerin}}{C_3H_5(OH)_3}$$

A similar action occurs when fats are digested.

Soaps are metallic salts of fatty acids. When a fatty acid is treated with a strong base, a metallic salt of the acid is formed. This compound is known as a *soap*. The formation of sodium stearate, a typical soap, is represented by the following equation:

$$\underset{\text{stearic acid}}{C_{17}H_{35}COOH} + NaOH \rightarrow HOH + \underset{\text{sodium stearate (a typical soap)}}{C_{17}H_{35}COONa}$$

More often the melted fat, instead of the fatty acid, is heated with sodium hydroxide, which decomposes the fat and forms the soap and glycerin.

$$\underset{\text{stearin (a fat)}}{(C_{17}H_{35}COO)_3C_3H_5} + 3\ NaOH \rightarrow 3\ \underset{\text{a typical soap}}{C_{17}H_{35}COONa} + \underset{\text{glycerin}}{C_3H_5(OH)_3}$$

This reaction is known as *saponification,* or in a limited sense, soapmaking. Soaps formed in this manner are not single compounds, but mixtures of metallic salts of stearic, palmitic, and oleic acids. When sodium hydroxide saponifies a fat containing an excess of stearin and palmitin, a "hard" soap is produced. "Soft" or liquid soaps are the products of potassium hydroxide and olein. The home making of soap was formerly common, especially in rural regions. All forms of grease were

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saved during the year; this grease was boiled with lye or the "liquor" obtained by leaching hardwood ashes.

How soap is made commercially. Although a form of soap has been known and used since ancient times, modern soap-making is of relatively recent date. Today soap is manufactured on a vast scale. By far the largest amounts of commercial fats are used for this purpose.

1. *Saponification.* The raw vegetable oils and melted animal fats are run into very large kettles along with a dilute solution of caustic soda (NaOH) to produce an emulsion. These "soap kettles" are often large enough to hold a million pounds of materials. The fat is stirred and kept in a melted condition by passing steam through it. A more concentrated solution (12 per cent) of caustic soda is added and the mixture is heated by steam to the point where reaction begins. The heat of the reaction helps to keep the material boiling. The caustic soda saponifies the fat to form soap and glycerin.

2. *"Salting out" the soap.* The soap forms a colloidal dispersion in the water. The addition of salt causes the soap to coagulate and slowly rise to the top of the solution which contains sodium chloride and glycerin.

3. *Further treatment.* The collected soap may be washed to remove the soluble impurities and then it is sent to mixing vessels where materials such as coloring agents, perfumes, or fillers, are added to produce soaps for different purposes. From the mixer the soap goes to frames with removable sides where it is pressed into long slabs. The slabs are cut by wires into cakes which are dried, and pressed into final form.

4. *Recovering the other product, glycerin.* The solution ("spent lye") in the kettle contains salt, impurities, any excess of lye, and glycerin. The latter product is valuable and is usually recovered by distillation.

Readings for Pleasure and Profit

Haynes, Wm. *This Chemical Age.* Chap. VI, pp. 95-112, "Sweet Smells and Savory Odors."

Holmes, Harry N. *Out of the Test Tube.* Chap. XXI, pp. 241-252, "Fats to the Front."

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. V, pp. 75-84, "Cottonseed Oil"; Vol. I, Chap XVI, pp. 253-293, "Perfumes and Flavors."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. II, Chap. XXIX, pp. 924-961, "Oils and Fats"; Vol. II, Chap. XXXI, pp. 975-986, "Hydrogenation of Oils"; Vol. II, Chap. XXXIII, pp. 1003-1019, "Soap and Soap Products."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. V, pp. 91-106, "Synthetic Perfumes and Flavors"; Chap. XI, pp. 200-220, "Solidified Sunshine."

Applying in Life What You Have Learned in Chemistry

When the members of a class were asked to bring in some "oil" to be used in a soap-making experiment, one pupil brought in a can of auto lubricating oil.

Several members of the class "snickered" and then looked questioningly.

Whom was the "laugh on"? Explain.

Putting Chemistry to Work

A

(**1**) Why are reactions between organic compounds generally slower than those between inorganic substances? (**2**) How is the speed of organic reactions often increased? (**3**) Collodion is sometimes sold under the trade name, *New Skin.* What is it? (**4**) How do you account for the vast number of carbon compounds? (**5**) In former times housewives frequently made their own soap by boiling waste fats with a solution obtained by pouring water through wood ashes and slaked lime. Tell why soap can be made in this way. (**6**) Why is it difficult to form a lather with soap in ocean water? What kind of soap would you suggest for this purpose? (**7**) Why can organic chemistry no longer be accurately called "the chemistry of living things"? (**8**) What is meant by saying that a fat is saturated or unsaturated?

B

(**9**) What are some of the advantages of using structural formulas? (**10**) Will the soap made from one pound of fat likely weigh more or less than one pound? Prove your answer by chemical arithmetic. (**11**) Write equations: (a) complete burning of ethane; (b) complete combustion of ethyl alcohol; (c) ethyl alcohol and

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butyric acid interact; (d) a mixture of sodium acetate and sulfuric acid is heated gently; (e) alcoholic fermentation of sugar ($C_6H_{12}O_6$); (f) sodium hydroxide saponifies glyceryl butyrate. (12) Starting with ethane, show by means of equations how ethyl acetate *could* be made.

How Good Are You at Solving Problems?

(1) Calculate the weight of a liter of benzene vapor (S.T.P.).

(2) Compare the weights at standard conditions of gaseous benzene and benzine. (Assume C_6H_{14} for benzine.)

(3) The composition of a compound is C, 64.9%; H, 13.5%; O, 21.6%. What is the simple formula of the compound?

(4) The composition of a gaseous compound is C, 85.7%; H, 14.3%. 400 ml of the gas (S.T.P.) weigh 0.502 g. What is the correct formula of the gas?

(5) How many kilograms of calcium carbide are required to produce 1000 liters of acetylene (S.T.P.)?

(6) How many liters of carbon dioxide and of water vapor are formed by burning completely 1000 liters of acetylene? (All gases are measured under the same conditions.)

(7) Assuming no loss, how many grams of amyl acetate could be prepared from 4.4 g of amyl alcohol?

(8) What weight of propane will occupy the same volume as that of 5 grams of carbon dioxide (same conditions)?

(9) How many liters of *air* will be required to burn completely 30 liters of water gas which contains 50% CO and 50% H_2 by volume? (All gases are measured under the same conditions.)

(10) The percentage of alcohol in an alcohol-water mixture is frequently found by determining the specific weight of the mixture very accurately and from a table finding the corresponding percentage of alcohol. A small empty bottle weighs 15.85 g. Filled with water, it weighs 40.85 g. Filled with an alcohol-water mixture, it weighs 38.10 g. Determine the specific weight of the mixture and its percentage of alcohol by volume from the following table: 60% = 0.914; 65% = 0.902; 70% = 0.890; 75% = 0.877.

Research and Activities That You Will Enjoy

A forum: By means of a small group of prepared students, bring before the class a summary of the achievements of organic chemistry as they affect your daily lives.

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A display: Organize a display of synthetic organic products. Ask for contributions from the entire class. Indicate, in so far as possible, particular uses for these products.

A chart: Make a large wall chart showing the oxidation products of methane and ethane, with equations employing structural formulas.

Problem 54

WHAT IMPORTANT THINGS SHOULD YOU KNOW ABOUT CARBOHYDRATES?

What are carbohydrates? Sugars, starch, and cellulose all contain the three elements, carbon, hydrogen, and oxygen. Since the hydrogen and oxygen are usually present in the same ratio in which they are found in water (2:1), these compounds are known as *carbohydrates.* This relation makes the formulas of carbohydrates fairly easy to remember. Do not get the idea, however, that carbohydrates are composed of carbon and a certain amount of water.

The simplest carbohydrates are more or less sweet and as a class of compounds they are also known as *saccharids* (meaning "sugar" or "sweet").

TYPES OF CARBOHYDRATES

General Class Name	*Examples*	*Formulas*	*Common Names*
Monosaccharids (simple sugars)	Dextrose	$C_6H_{12}O_6$	Glucose, or grape sugar
	Levulose	$C_6H_{12}O_6$	Fructose, or fruit sugar
Disaccharids ("double" sugars)	Sucrose	$C_{12}H_{22}O_{11}$	Cane, beet, or maple sugar
	Lactose	$C_{12}H_{22}O_{11}$	Milk sugar
	Maltose	$C_{12}H_{22}O_{11}$	Grain sugar
Polysaccharids (complex carbohydrates)	Dextrin	$C_6H_{10}O_5$	
	Starch	$(C_6H_{10}O_5)_n$	
	Glycogen	$(C_6H_{10}O_5)_y$	"Animal starch"
	Cellulose	$(C_6H_{10}O_5)_x$	

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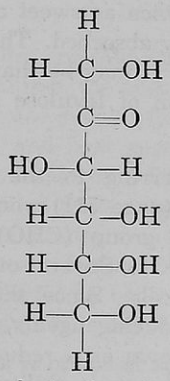
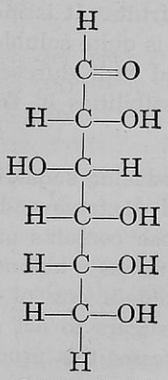
What are the different classes of carbohydrates? The most important carbohydrates may be grouped into three classes, depending upon their composition. In the table on page 510 note especially the similarity in the formulas of the different saccharids.

SIMPLE SUGARS

Even the simple sugars have large molecules. You will notice in the table that the monosaccharids are called simple sugars, that is, they are "six-carbon" sugars. Analysis shows that they have the same molecular (empirical) formula, but the difference in their properties shows that they have different structural formulas. You will recall that such compounds are called isomers (page 488). The structural formulas of dextrose and of levulose show a variation in the arrangement of the hydrogen and oxygen atoms around a central axis of carbon atoms.



levulose (fructose)



dextrose (glucose)

Glucose is a simple sugar found in ripe fruits. Glucose (or dextrose) is found in ripe fruits, especially grapes. For this reason it is also known as *grape sugar*. It is a white solid, not so sweet or crystalline as ordinary sugar (sucrose). It is very

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soluble in water and is easily absorbed through the intestines, when eaten in foods. Being a simple sugar, it does not need to be digested (broken into simple sugars). Glucose is always present in the blood of the human body, normally to the extent of about 0.1 per cent.

Glucose (corn sirup) is manufactured by treating cornstarch with steam under pressure in the presence of hydrochloric acid as a catalyst.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + n\,H_2O \rightarrow \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

This equation indicates that each complex molecule of starch is hydrolyzed yielding a large number of molecules of glucose, each of which is simple when compared with the parent starch molecule. Furthermore, since the conversion is not complete, corn sirup contains other carbohydrates in addition to the glucose.

Levulose is a simple sugar that is more than twice as sweet as glucose. Levulose (or fructose) is usually associated with glucose in fruits. It is more than twice as sweet as glucose, and like it, is quite soluble and easily absorbed. This sugar is found mixed with glucose in honey. It may be that the commercial possibilities in the utilization of levulose have been neglected.

What are reducing sugars? By referring to the structural formulas of dextrose and levulose (page 511) you will note that dextrose contains an aldehyde group (CHO) and that levulose contains a ketone group (CO). Several other sugars likewise contain one of these radicals. Since these groups cause the sugars to act as mild reducing agents, any sugar which possesses this property is known as a *reducing sugar*. Reducing sugars may be identified by their ability to reduce cupric hydroxide [$Cu(OH)_2$], in Fehling's solution or in Benedict's solution, to cuprous oxide (Cu_2O) which is recognized by its brick-red color. Physicians use such a test to learn if the urine contains glucose, a condition existing in the disease known as *diabetes*.

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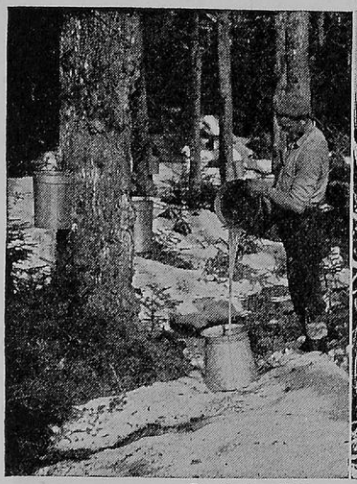

By Ewing Galloway

172. MAKING SUGAR IN VERMONT. Collecting maple sap.



By Ewing Galloway

173. GROWING SUGAR CANE IN CUBA. This cane is ready to cut.

DOUBLE SUGARS

Sucrose is the common sugar that you get from your grocer. This is, of course, the sugar with which you are most familiar. It is called cane sugar when it is refined from the juice of the sugar cane, and beet sugar when it is crystallized from the juice of the sugar beet. Sucrose also occurs in maple sugar.

In the United States about one and one-half million tons of beet sugar and more than three times as much cane sugar are used each year. Despite the widespread impression that cane sugar is superior to beet sugar, chemically the sucrose from these two sources is identical.

How sucrose is obtained and refined. The methods of extracting and purifying the sugar from sugar cane and beets are essentially the same. The cane is passed through crushers, shredders, and rollers to press out the juice containing the sugar. The washed beets are cut into slices and the sugar is extracted with warm water. The juice is filtered to remove fine fibers and treated with lime to precipitate the impurities.

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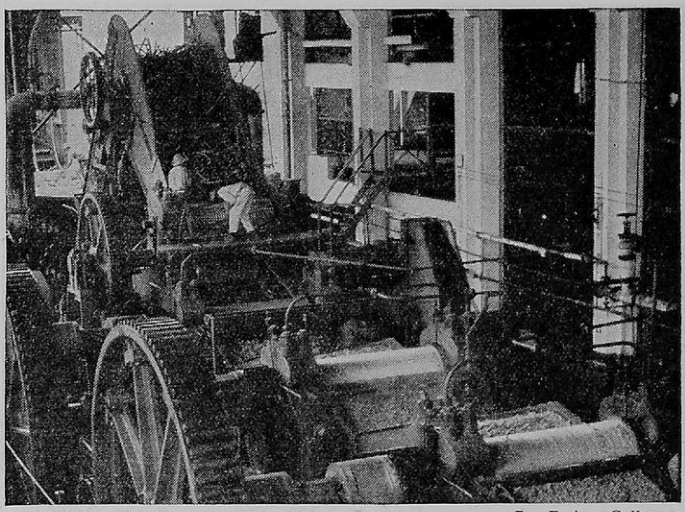

By Ewing Galloway

174. GRINDING SUGAR CANE AT SANTA JUANA, PORTO RICO

Carbon dioxide is then passed through it to remove the excess lime. The purified juice is evaporated in large vacuum pans which enable the solution to boil at about 65° C. without scorching or decomposing much of the sugar. A thick sirup is thus produced. As it cools, sugar crystallizes out and the crystals are separated from the sirup by whirling in a centrifugal machine. The brown sugar crystals are redissolved and the solution is decolorized by filtering through bone black. The clarified solution is again concentrated in vacuum pans and treated as before until crystals of the desired purity and color are obtained.

Caramel is sucrose that has been partially decomposed by heating. When sucrose is heated slowly, it melts forming a dark brown solution known as *caramel* which is used as a flavoring and coloring agent in various foods. At higher temperatures sucrose is completely decomposed, leaving a porous mass of very pure carbon.

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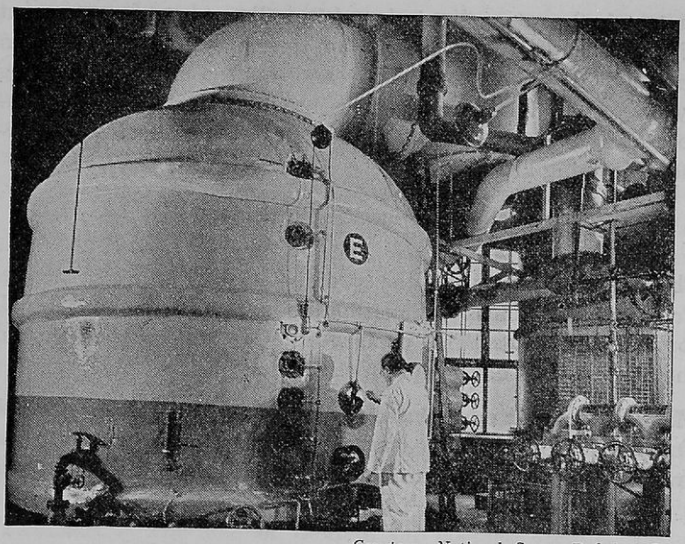

Courtesy, National Sugar Refining Co.

175. A LARGE VACUUM EVAPORATOR IN A SUGAR MILL

Sucrose can be converted into simple sugars. Sucrose gives a negative test with Fehling's solution, so it is not a reducing sugar. But after a solution of sucrose has been boiled with a little acid as a catalyst, a positive test is obtained. This shows that sucrose molecules have changed into molecules of a reducing sugar. Further tests have indicated that the two simple sugars, dextrose and levulose, are formed. The reaction is written:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}$$

This change is known as *inversion* (or hydrolysis) and the mixture of dextrose and levulose is referred to as *invert sugar*. In making homemade taffy and other similar candy from "granulated" sugar, a little vinegar or lemon juice is added to bring about inversion. The dextrose and levulose do not crystallize as readily as sucrose, so the candy is not so likely to "go to sugar" or become "grainy" due to sucrose crystals.

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Lactose is the sugar that is found in milk. About four per cent of the weight of milk is due to this sugar. It is less than one-fifth as sweet as sucrose and not so soluble. During hydrolysis, lactose is converted into two simple sugars, glucose and galactose. Lactic acid bacteria cause lactose to ferment, forming lactic acid:

$$C_{12}H_{22}O_{11} + H_2O \ (+ \text{ lactic acid bacteria}) \rightarrow \underset{\text{lactic acid}}{4\ C_3H_6O_3}$$

The lactic acid causes the protein in the milk to curdle. *Pasteurization* consists of heating the fresh milk to about 63° C. for thirty minutes. This destroys the lactic acid bacteria and the majority of disease-producing bacteria.

Maltose occurs in sprouting grains. The formation of maltose is due to the action of the enzyme, *diastase,* on the starch in the grains. In this way starch is changed to maltose. Further hydrolysis results in the maltose changing to glucose.

COMPLEX CARBOHYDRATES

No chemist has yet succeeded in making starch or cellulose. You have seen how sugars are broken down into simple sugars and even converted into alcohol, acetic acid, and lactic acid. Although the building-up process is much more difficult, many sugars have been synthesized in the laboratory on a noncommercial scale. But nature still holds the key to the synthesis of the complex carbohydrates, such as starch and cellulose. Soluble sugar is transferred to suitable places in the plant, changed to starch, and stored in this form. As further growth takes place, much of the starch is changed into cellulose.

Starch and cellulose are carbohydrates of huge molecular weights. While their simple formula ($C_6H_{10}O_5$) expresses their percentage composition, the actual numbers of atoms in these complex molecules are unknown and undoubtedly very large. Thus we are obliged to represent their formulas as $(C_6H_{10}O_5)_n$.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Starch is stored in the seeds, roots, and tubers of many plants. At the time the seed germinates, the starch is converted to maltose and glucose which serve as food for the beginning plant. Man has appropriated the starch of many plants for his own uses. In the United States the chief source of commercial starch is corn. Other common sources are wheat and potatoes. The use of starch as food is discussed in Problem 56.

Starch is insoluble in water, but, when boiled in water, the starch granules burst to form a cloudy, colloidal dispersion known as starch paste. Perhaps you have seen starch paste in the household laundry. With iodine, starch becomes colored a bluish black which serves as an *identification test for starch,* as well as for iodine.

Starch may be changed to dextrin by chemical action. Although dextrin is a complex carbohydrate, it is simpler than starch. Consequently, it is more easily digested. Dextrin has a slightly sweetish taste, as shown by toasted bread, especially "zweiback." The use of dextrin on postage stamps, bread labels, and envelopes illustrates its value as an adhesive.

Starch may be converted to sugars. Starch may be converted to sugars by boiling it with water and an acid catalyst. You will recall that this change occurs in making commercial glucose (corn sirup, page 512). Dextrin and maltose are intermediate products.

$$\text{Starch} \rightarrow \text{dextrin} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

Similar changes take place during the digestion of starch.

Cellulose [$(C_6H_{10}O_5)_n$] is found in the woody parts of plants and forms much of their framework. The cotton fiber is nearly pure cellulose. The cellulose in wood is combined with other substances (such as lignin), so only about fifty per cent of wood is cellulose. Cellulose is so important from a commercial standpoint that the *cellulose industries* (clothing, paper, and other cellulose products) receive special attention in later problems. The steady increase in the number of useable cellulose products makes it imperative that conservation of our forests and reforestation become even more a national policy.

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Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XXV, pp. 310-318, "More Carbon Chains."

HAYNES, WM. *This Chemical Age.* Chap. XIV, pp. 245-261, "Manna Becomes a Chemical."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XX, pp. 233-240, "Sugar and Sweetness."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. II, Chap. XLII, pp. 1173-1207, "Sugar"; Vol. II, Chap. XLIII, pp. 1209-1228, "Starch, Glucose, and Dextrin."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. IX, pp. 165-181, "The Rival Sugars"; Chap. X, "What Comes from Corn."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXVIII, pp. 423-437, "Sugar."

Putting Chemistry to Work

A

(1) What compound gives fresh milk its sweet taste? "sour" milk its sour taste? How do you account for the change? (2) What compounds are produced by the action of the enzymes in yeast in bread-making? What happens to these compounds when the bread is baked? (3) Why is saccharin sometimes used in foods in which glucose is substituted for sucrose? (4) Give an obvious reason why glucose can pass through membrane walls into the blood while starch cannot. (5) An unripe apple is sour while a ripe one possesses a fruity odor and a certain degree of sweetness. What relationship among organic compounds does this suggest?

(6) What is formed when sucrose burns? when it is heated? when it is boiled with hydrochloric acid? (7) How do you associate each of the following terms with starch: iodine, dextrin, photosynthesis, colloidal dispersion, hydrochloric acid, glucose, cellulose, corn, $(C_6H_{10}O_5)_n$? (8) In the refining of sucrose what is the function of each of the following: lime, carbon dioxide, vacuum pans, and bone black? (9) If 100 molecules of sucrose are hydrolyzed, how many and what kind of molecules are obtained?

Research and Activities That You Will Enjoy

An interpretation: Expand the topic, "A box of candy from a peck of corn."

A resumé: After reading chapter 9, "The Rival Sugars," in *Creative Chemistry,* present to the class a brief summary of it.

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Problem 55

HOW IS CELLULOSE USED TO MAKE PAPER AND OTHER IMPORTANT PRODUCTS SUCH AS CELLOPHANE?

Cellulose is the cell wall substance of all plants. When plants are young and tender, their cellulose is soft and pliable. At later stages of growth, the cellulose is penetrated by a stiffening substance called lignin, making the durable lignocellulose of the stems of plants and the wood of trees.

The annual production of cellulose, especially in warmer climates, is enormous. Most of the cellulose that is produced each season decays and enriches the soil for other plants.

Enormous quantities of goods are transported to all parts of the country. Many of these goods require containers: barrels, boxes, and bags which are composed largely of cellulose. Even the cord which binds many packages is a cellulose product, so also is a wide variety of products such as motion-picture films, phonograph records, varnishes, airplane "dopes," and high explosives.

When cellulose is made into paper, it is a means of recording human knowledge. From the days of the Egyptians, cellulose has transmitted the hard-earned wisdom of the race from one generation to another.

Paper may be made from straw, cornstalks, cotton, linen, or wood fibers. Most of our paper is now manufactured from wood pulp which has been a cheap source of cellulose. The supply of wood is diminishing, however, much more rapidly than the trees are producing it. We must soon depend on grasses, straw, and cornstalks as a source of paper, judging from present conditions. In fact, straw is used quite extensively to make paper for goods boxes. A similar paper can be made from cornstalks. More and more paper must come from these sources if the rapid decrease of our wood supply continues. The Sunday issue of one of our leading newspapers requires the wood pulp from fifteen acres of forest.

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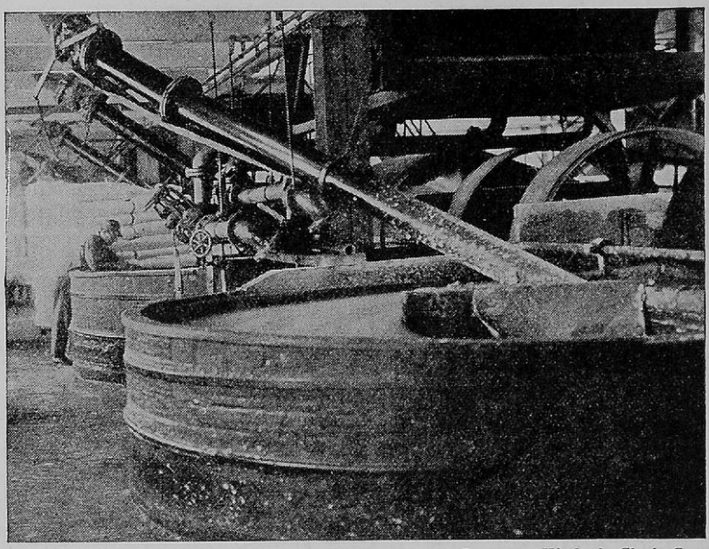

Courtesy, Kimberly-Clark Corp.

176. BEATERS IN A PAPER MILL. In this beater the cellulose fibers in wood pulp or rags are disintegrated and suspended in the water. The beating operation breaks up the fibers and hydrates the cellulose.

How paper is made. Wood is placed in piles and allowed to dry or season for from one to three years before it is used for papermaking. The bark, dirt, and knots are then removed, and the wood is mechanically chopped up into chips. In a large lead-lined digester the chips are "cooked" with calcium bisulfite; that is, if the *sulfite process* is used. This process is one of the most important papermaking processes.

Calcium bisulfite is made by burning sulfur and passing the sulfur dioxide through milk of lime (calcium hydroxide):

$$Ca(OH)_2 + 2\ SO_2 \rightarrow Ca(HSO_3)_2$$

When the cooking has reduced the wood to a pulp which is free from lumps, a large valve is opened, and the pulp is blown out into tanks where the cellulose fibers are thoroughly washed before they are brought to a paper-manufacturing

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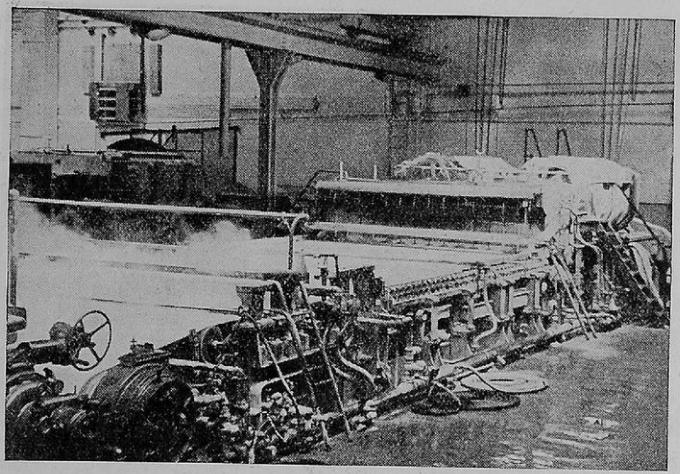

Courtesy, Kimberly-Clark Corp.

177a. THE "WET END" OF A PAPER MACHINE. Paper pulp suspended in water flows onto a fine-meshed, bronze screen. The water flows through the screen leaving the cellulose fibers on the screen where they form a web of paper. From here the paper passes over heated cylinders which remove the moisture.

machine. How the washed cellulose fibers are made into paper is explained under the pictures on pages 521 and 522.

The waste liquor used to wash the cellulose fibers cannot be used again. It needs to be purified before it is discharged into streams, however, because it is poisonous, gives off an offensive odor, and kills fish. In a small way this sulfite waste has been used in the tanning of leather, the surfacing of roads, and the binding of coal dust into briquets.

The sulfite process for the manufacture of paper is a typical paper process. There are several other manufacturing processes, however. The choice of the method to be used depends largely upon the purpose for which the product is made.

How paper is finished. Paper made from pure pulp is soft and very absorbent. Consequently ink spreads on it quickly. Your filter paper is paper of this kind. In order to prepare

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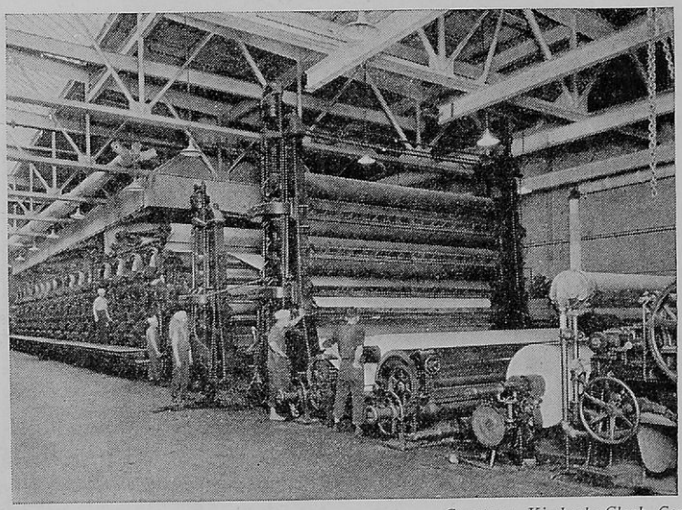

Courtesy, Kimberly-Clark Corp.

177b. THE "DRY END" OF A PAPER MILL. The web of wet cellulose fiber, formed at the "wet end," passes up and down over the heated rollers shown in the background. This treatment removes most of the moisture. When the paper is sufficiently dry, it is collected in huge rolls.

paper so it can be used with ink, various finishing materials must be added to it. Talc and China clay are used to fill up the spaces between the fibers and to make the sheet opaque. Since the fibers have a high absorbing power, a nonabsorbent coating is used so ink will not "run" when used on the paper. The materials most commonly used for this sizing are rosin soaps, casein, and glue.

How paper is modified for special needs. *Parchment paper.* Blotting paper, which you use almost daily, must be left in an absorbent condition so it will take up ink rapidly. A paper for wrapping foods such as butter must be the direct opposite in this respect. It may either be paraffined or parchmentized to make it nonabsorbent.

As you know, cellulose is a carbohydrate (page 516). If paper is put into concentrated sulfuric acid, it soon turns black

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because the acid takes up the elements that form water and leaves black carbon. If this acid is diluted and applied to paper for the right length of time, then washed off thoroughly, the fibers appear to melt into each other making tough semi-transparent parchment paper known as cellulose hydrate. You have seen it used for important documents, decorative lamp shades, and as a wrapper for certain food products. By a similar treatment or by the use of oils, a portion of an envelope is made transparent like a window, so there is no need of addressing the envelope. In many places glass milk bottles are being displaced by stiff paper containers that need not be washed or returned.

Currency, checks, and drafts are made of special paper. There was a time when people demanded "hard" money. Now they refuse to weigh themselves down with metal and demand "paper dollars." The chemist has been given a hand in the making of paper for use in currency, checks, and drafts. Tampering with the figures or attempting to erase letters from "safety paper" defaces the paper and makes apparent any attempted fraud.

From celluloid to cellophane—how "dissolved cellulose" is used to make many useful compounds. Cellulose fibers not only furnish you paper, but they also furnish a great variety of cellulose compounds that are formed when cellulose is mixed with certain chemical reagents, such as nitric acid. When cellulose and nitric acid react, a number of products can be formed, one of which is called pyroxylin.

Rayon is made of "dissolved cellulose." When pyroxylin is dissolved in a suitable solvent and a thin stream of the solution is squirted through a small hole, a fine glossy thread can be produced. This fine glossy thread is used to make a kind of rayon which is no longer used extensively. The rayon you use today, however, is also "dissolved cellulose," as you will find on page 569.

Celluloid is made of "dissolved cellulose." Pyroxylin mixed with camphor and a solvent produces *celluloid.*

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This material is made into combs, buttons, toys, fountain pens, handles for toilet articles and umbrellas. Celluloid is poured into thin sheets and used for making films for your camera and for motion pictures. Such films burn readily, so safety films are now extensively used. These safety films, however, are also "dissolved cellulose" (page 570).

Artificial leather is made of "dissolved cellulose." When pyroxylin is spread over a strong cloth, it may be given a grain which resembles leather. This "artificial leather" (fabrikoid) is widely used in making upholstery for furniture, purses, handbags, suitcases, sandals, and slippers. Cloth "soaked" with pyroxylin is used on the bindings of many of your school books.

Pyroxylin dissolved in a mixture of ethyl alcohol and ether is known as "collodion." If a thin layer of this solution is exposed to air, the solvent evaporates leaving a tough, colorless film which is useful as a protection for minor wounds or abrasions. Hence the names "liquid court plaster" or "new skin" are sometimes used. Collodion is used as "dope" for airplane fabrics and as films for cameras. It is also used in the manufacture of lacquers, patent leathers, artificial pearls, and cements that your younger brother uses to glue together his airplane models.

Cellophane is made of "dissolved cellulose." Cellulose may be soaked in sodium hydroxide, then dissolved and allowed to flow as a thin sheet into a precipitating bath. In this way there is produced a parchmentlike, transparent sheet called cellophane. It may be waterproofed or colored in a wide range of colors. The use of cellophane permits all sorts of articles of commerce to be displayed in individual showcases, largely protected from dust, bacteria, drying, and excess moisture. Cellophane raincoats and raincapes are both convenient and inexpensive.

How pyroxylin is made. Cellulose reacts with concentrated nitric acid to form cellulose nitrate, which is soluble in many solvents. This reaction is somewhat the same as the reaction

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of nitric acid with a base. The products are cellulose nitrate and water:

$$C_6H_{10}O_5 + HNO_3 \rightarrow C_6H_9O_4 \cdot NO_3 + H_2O$$

If the products remain mixed with the nitric acid and the cellulose, the water dilutes the nitric acid and the process stops. But if sulfuric acid is mixed with the nitric acid, the water is removed as fast as it is formed and the reaction, which is called "nitration," may be made to continue until several NO_3 radicals have been introduced into each of the cellulose molecules. If the nitration is stopped when three radicals are introduced into each molecule, the product has the formula $C_6H_7O_2 \cdot (NO_3)_3$. This product is pyroxylin, the chemical name of which is cellulose trinitrate. This compound has wide applications in modern chemistry, as you have seen. Pyroxylin is soluble in many solvents such as amyl acetate, methyl alcohol, glacial acetic acid, or acetone.

Why do manufacturers of pyroxylin also manufacture gunpowder? If the process of nitration by which pyroxylin is produced is allowed to continue, "higher nitrates" are formed such as the hexanitrate, commonly known as *guncotton* (see page 394). The molecules in guncotton are unstable and upon concussion they decompose with explosive violence. The products formed when guncotton explodes are largely colorless gases; there is little solid residue and almost no smoke. Guncotton is used, therefore, as the basis of *smokeless powder*. Safety in handling smokeless powder is obtained by stabilizing the guncotton by mixing it with another compound. For example, *cordite*, an explosive much used in England, is made by mixing guncotton with 30–58% "nitroglycerin" and a little vaseline. *Blasting gelatin* is prepared by mixing one part of guncotton with nine parts of nitroglycerin. It is a high explosive of great power.

Cellulose in everyday life. For further information concerning the use of cellulose to make rayon and other interesting products, turn to pages 568–570.

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Readings for Pleasure and Profit

HAYNES, WM. *This Chemical Age.* Chap. XV. pp. 262-280, "The Skeleton in the Vegetable Closet."

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. VI, pp. 133-158, "From Papyrus to Television."

Putting Chemistry to Work

A

(1) Name four necessary conditions for the natural production of cellulose. (2) Why was paper-making dependent for so many centuries on cotton and linen rags as a source of fiber? (3) Give two advantages of the "window envelope." (4) Why were slates formerly used in school? Why not now?

B

(5) From the wide variety of uses for cellulose, select one example and show how it is related to daily life in your community. (6) Why may cellophane be called "educated cellulose"? (7) To what extent does chemical knowledge contribute to material progress? (8) How does chemical skill fit into plans for the conservation of natural resources? (9) Why is the solubility of cellulose a requirement in preparing a pyroxylin paint, but the insolubility of it a requirement when washing your motorcar?

Research and Activities That You Will Enjoy

A report: (a) Find out what "Duprene" is. How is it used? (b) How is cellophane made waterproof? (c) How is the "watermark" put on paper?

An exhibit: Prepare an exhibit to show the steps in the manufacture of paper.

Looking Back into Unit 12

Be sure you know the purpose of this unit. Read again the material on page 460, "Looking Ahead into Unit 12." Then study the following Summary Test.

Summary Test

1. *What useful hydrocarbon products do petroleum and similar materials give you?*

(a) What is petroleum?

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(b) How are gasoline and other mixtures of hydrocarbons obtained from petroleum?
(1) How is the gasoline yield from petroleum increased?
(c) What is natural gas? How is it used?
(d) How are industrial gases produced and used?

2. *How can you picture hydrocarbon molecules?*
(a) How are the simplest saturated hydrocarbons constructed?
(1) What is a homologous series of hydrocarbons?
(b) How are typical unsaturated hydrocarbons constructed?
(c) How do hydrocarbons react?
(1) How are substitution products formed?
(2) How are addition products formed?
(3) How are hydrocarbon radicals formed?
(d) What are some useful halogen derivatives of hydrocarbons?

3. *How are alcohols related to hydrocarbons?*
(a) How is methyl alcohol related to methane?
(1) What are the property-uses of methanol?
(b) How is ethyl alcohol related to ethane?
(1) What are the property-uses of ethanol?
(2) What is denatured alcohol?
(3) How is it made and used?
(c) What other alcohols are useful? How are they useful?

4. *What other valuable products are obtained from alcohols?*
(a) How is formaldehyde related to methyl alcohol?
(1) What is formaldehyde?
(2) What is formalin? How is it used?
(3) How is formaldehyde related to formic acid?
(b) How is acetic acid related to ethyl alcohol through acetaldehyde?
(1) How is vinegar made?
(c) How are organic acids related—
(1) To fats?
(2) To fruits?

5. *How are esters useful?*
(a) How are esters produced? Give an illustration.
(b) How are esters used?
(c) What are fats?
(1) How can liquid fats be changed to solid fats?
(2) What vegetable oils are used in paints? Why are they used?

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(d) How are fats changed by hydrolysis?
(e) What are soaps?

6. *What important things should you know about carbohydrates?*
(a) What are carbohydrates?
(1) What are the different types of carbohydrates?
(2) How are they alike? How are they different?
(b) What are simple sugars? Give examples.
(c) What are reducing sugars? How are they detected?
(d) What are double sugars? Illustrate.
(1) How is sucrose obtained and refined?
(2) How is sucrose converted into simple sugars?
(e) What are complex carbohydrates? Give examples.

7. *How is paper made from cellulose?*
(a) What various materials supply the cellulose to make paper?
(b) How is paper made by the sulfite process?
(c) How is paper finished and modified for various purposes?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

This unit in chemistry gives a fine idea of *chemical architecture.* Although the structure of both *plants* and *animals* and their *life processes* are closely related to *organic chemistry,* you learn that organic chemistry is really the chemistry of *carbon compounds.*

You started in with the simplest *hydrocarbon, methane,* CH_4. By an *orderly system* of *addition* and *substitution* of other atoms, you first learned how other *simple molecules* are constructed; then you learned how more *complex molecules* are constructed. Thus you see *hydrocarbons* grow into *alcohols, alcohols* into *aldehydes, aldehydes* into *organic acids,* and then by putting alcohols and acids together you get *esters,* the organic salts. You should remember that the mechanics of graphic formulas and the exactness of chemical nomenclature, complex as they may appear on first inspection, form the basis for research in modern chemistry.

You find many familiar friends among the *hydrocarbons,* particularly *gasoline, natural gas,* and *acetylene.* You learn that your gasoline supply today is coming from many sources—from the *fractional distillation* of crude *petroleum,* from the *"cracking"* of the larger molecules of *kerosene* and *oil,* from the *polymerization* (building up) of some of the simpler hydrocarbon molecules, and

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Courtesy, Union Oil Co.

Refining Plant for Lubricating Oil.

even from the *liquefying* of some of the larger molecules in certain natural gases. Although chemistry is doing much to make fuels more effective and more efficient, natural resources are being used at a rate that should give us some concern and make us, as a nation, think of *conservation.*

You find that the *carbohydrates* are useful products: *sugars* and *starches* for foods; and *cellulose* for paper, clothing, and many other necessary articles. The chemist has been able to turn the cellulose of forests into *"artificial" products* that are now looked upon as necessities—rayon, cellophane, fabrikoid (artificial leather), picture film, and explosives.

It seems that the organic chemist can start with one organic product and from it can evolve a great many useful products. But progress does not end here. More and more complex become the products of research chemistry. Your next unit of study gives you a glimpse into this field.

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Looking Ahead into

Unit Thirteen

Your first concern in life should be the development and keeping of a strong, healthy body. Only by being healthy can you efficiently carry on your work and fully enjoy living. Good food is important along with sunshine, exercise and fresh air, pure water, rest and sleep.

In earlier units you have learned how the chemist safeguards your health through water purification and air conditioning. His efforts continue in your behalf when he tests foods for adulterants, standardizes foods to maintain the highest quality, and determines their nutritive values by means of physiological studies. A great variety of healthful foods is available.

It is the duty of every citizen to learn how the choice of a balanced diet helps to maintain health.

When disease threatens, it is the privilege of every citizen to use medicines many of which are not supplied by nature but by the chemist. When the natural supply is cut off, we can sometimes furnish a substitute as for example the use of atabrin in place of quinine to combat malaria. When the supply from nature is inadequate, then efforts are made to produce a similar synthetic drug, as illustrated by many common examples. Some recently discovered synthetic drugs have completely revolutionized certain phases of medical practice.

Problem 56. *What Should You Know about the Energy-giving Foods?*

Problem 57. *What Should You Know about Proteins, the Foods That Keep Your Body in Repair?*

Problem 58. *How Is the Body Chemistry Regulated by Minerals and Vitamins?*

Problem 59. *How Does Chemistry Help to Prevent and Cure Sickness?*

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Your Health: Nutrition, Medicine, Clothing, and How Your Clothing May Be Cleaned Properly and Dyed Colorfully

Problem 56

WHAT SHOULD YOU KNOW ABOUT THE ENERGY-GIVING FOODS?

More than 70 per cent by weight of our food materials belong to the class of compounds known as carbohydrates. They are the main products of living plants and are storehouses of the sun's energy. The sun furnishes the energy which is stored up in carbohydrates when plants take up carbon dioxide from the air and transform it into plant tissue. Carbohydrates and fats are our energy-giving foods.

Sugars and starches are important energy foods. Sugar is the first definitely known carbohydrate synthesized by plants. Other carbohydrates are made within the plant from sugar. Since sugar is soluble, it can be transferred by the sap to places where new growth is forming. Here it is changed into insoluble cellulose, the structure material of the plant. The plant also changes sugar into starch which collects in roots and seeds. Starch in seeds serves as a store of food to nourish the new plants when they sprout from the seeds. Every seed contains the enzyme diastase which, like a key, unlocks the insoluble starch. The enzyme changes the starch back into soluble sugar under the influence of heat and moisture. The sugar is then available for new growth.

Cereal grains such as wheat and rye furnish the flour used in the making of bread and other starchy foods. Potatoes and bananas contain the most carbohydrates among the vegetables and fruits.

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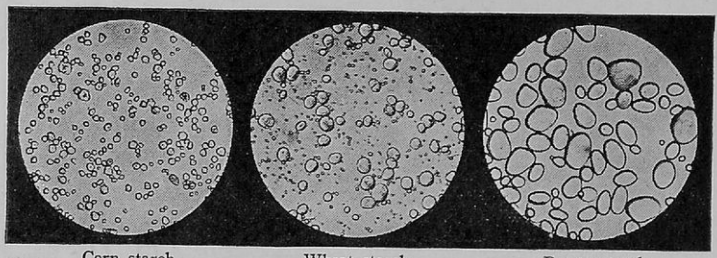

Corn starch Wheat starch Potato starch

Courtesy, Microanalytical Division, Food and Drug Administration

178. STARCH GRAINS UNDER THE MICROSCOPE. Starch grains consist of minute grains made up of the true starch material inclosed in a thin envelope of cellulose.

How starch is digested. Starch molecules are so large that they cannot be assimilated by your body. Digestion of starches consists of a combination with water, accompanied by a breaking down of the starch molecules thus making them smaller. This process proceeds by stages until the final product is the simple, diffusible sugar which is called glucose. Dextrin and maltose are intermediate products.

$$\text{Starch} \rightarrow \text{Dextrin} \rightarrow \text{Maltose} \rightarrow \text{Glucose}$$

Since the starch molecule is an indefinite multiple of $(C_6H_{10}O_5)$, the whole process may be summarized in the equation:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + n\ H_2O \rightarrow n\ \underset{\text{glucose}}{C_6H_{12}O_6}$$

The proper cooking of starchy foods enables them to be digested more easily. The enzyme ptyalin or amylopsin acts slowly on *raw* starch; but when the membranes of the starch granules are ruptured by cooking, the enzyme then acts more rapidly (Fig. 179).

How sugar is digested. Sugars are our most easily digested foods. The simple sugars such as dextrose and levulose require no chemical change. They are already in such a condition that they can pass through the walls of the intestinal tract and be assimilated. The more complex sugars such as sucrose

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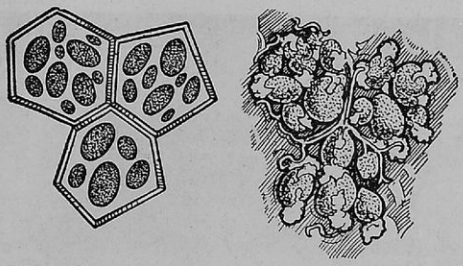

179. STARCH GRAINS BEFORE AND AFTER BOILING. The diagram at the left shows starch grains in plant cells. The diagram at the right shows the cell walls broken and the cell contents escaping into the solution to form a colloidal sol.

and maltose must be converted into simple sugars by the action of enzymes before they can be absorbed from the alimentary canal and used as food.

Do not eat too much sugar. Sugars are a very concentrated food. If you eat sugar in too large quantities, you may fail to eat other types of foods in sufficient quantities. Sugars are soluble and quickly assimilated into the blood system, so they are an *emergency* food. A solution of glucose is injected into the blood stream following a major surgical operation if the patient shows signs of collapse. Immediate energy is then available for recovery. If a person eats a large quantity of sugar at one time, an excess may be present that cannot be used. This is stored in the liver, as glycogen. If the storage capacity of the liver is exceeded, the excess passes into the blood and is converted into fat or eliminated as waste. The normal content of 0.1 per cent in the blood must be maintained for health. When the excess (that is not converted into fat) reaches about 0.18 per cent, the kidneys begin to remove the excess.

Eating too much starchy food frequently means overweight. Since starches require some time to digest, no sudden excess of sugar in the blood is possible when starchy foods are eaten, even in considerable amounts. Since the liver can store no more than approximately a pound of sugar as glycogen,

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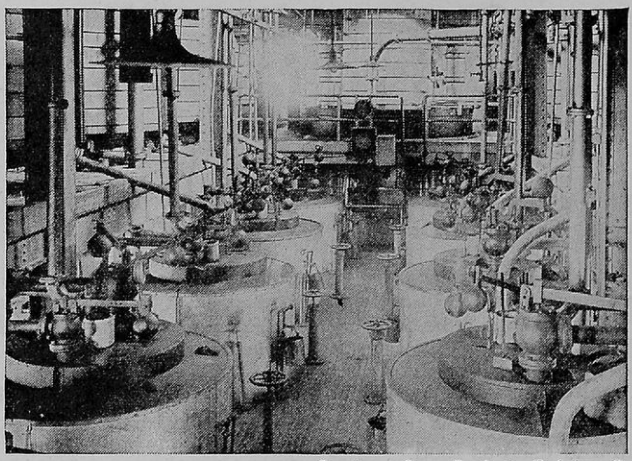

Courtesy, Corn Products Refining Co.

180. MAKING SUGAR FROM STARCH. This battery of bronze converters changes starch to dextrose under pressure using hydrochloric acid as a catalyst. Supply tanks are located at the right and left above the converters. At the far end are the neutralizing tanks where the acid is changed to salt by reaction with sodium carbonate.

any excess is converted to fat for storage or eliminated by the kidneys. Just as glycogen is the working reserve of energy, so fat is the storage reserve. This stored food may raise the problem of overweight. When you eat enough carbohydrate foods to supply all the energy you need, no fat of your body will be used. To reduce one's weight safely, however, the carbohydrate foods must *not* be eliminated entirely from the diet; neither must they be limited too greatly. A good rule is: if you want to "go on a diet," see your doctor.

Fats are reserve energy foods. Fat particles are present in the living cell. The full purpose of fat is not known, but it is known that it may be used by the body to supply energy. One gram of fat furnishes 9.4 large calories of heat as compared with 4.2 calories from a gram of carbohydrate. For this reason, fats are frequently classified with carbohydrates as fuel foods. The body does not use fats for fuel purposes when

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Courtesy, U. S. Department of Agriculture, Farmers' Bulletin No. 1637

181. TOPPING SUGAR BEETS. After sugar beets have been pulled and thrown into piles, they are topped. These beets contain about 16% sugar.

carbohydrates are supplied in abundance. Fats, therefore, are a *reserve* fuel food.

How fats are digested. Fat molecules are "split" by reacting with water under the influence of an enzyme, lipase or steapsin, somewhat similarly to the way starches are digested. Glycerin and a free fatty acid are formed. These products pass through the walls of the lower half of the small intestines and are remade into finely emulsified fat particles as they appear in the nearby lymph vessels. During the digestion of fats, these lymph vessels appear white like milk because of the emulsified fat. For this reason, this part of the lymph system is called the lacteals. The new fat is not the same as the original, but its composition depends on the place in which it is deposited in the body. Hydrocarbon oils are not fats so they cannot be digested.

Some fats are carriers of vitamin A. Some fats of animal origin act as carriers of an important growth-producing material known as vitamin A. You will learn more about vitamins later in this unit.

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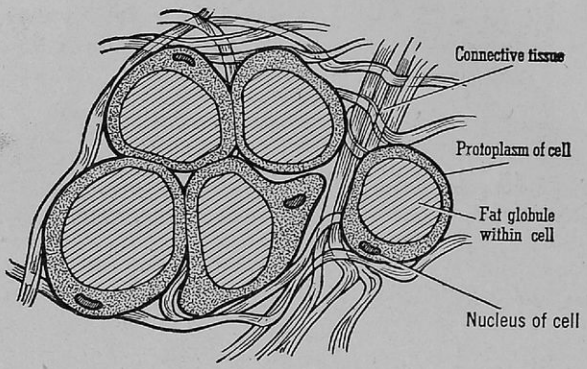

182. CELLS AND TISSUES OF THE BODY SHOWING HOW FAT IS STORED IN THE BODY. The fat is stored in the cells and is not a necessary part of them.

Cellulose is not a food, but it is useful in foods. The grass-eating animals are able to digest cellulose and obtain nutriment from it because of special adaptations of their stomachs for the purpose. In the human alimentary system, cellulose is indigestible. However, indigestible cellulose furnishes the necessary bulk to food to give the needed activity to the alimentary tract. During digestion, sugars and starches are extracted from their natural sources leaving the cellulose behind. Meats, eggs, fats, milk, white bread, sweet and starchy desserts leave very little residue after digestion, so the lower bowel needs bulky food to give it the normal functionings. For this reason, natural fruits and vegetables should have a prominent place in the diet.

Readings for Pleasure and Profit

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XXII, pp. 253-266, "Now What Shall We Have to Eat?"

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. IV, pp. 68-98, "Feeding Millions."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. IX, pp. 165-181, "The Rival Sugars"; Chap. X, pp. 182-199, "What Comes from Corn?"

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Applying in Life What You Have Learned in Chemistry

Join the argument? A small group of students were discussing the topic, "Eat What You Like *versus* Like What You Eat." What contributions would you make?

"John! John! Don't eat so fast! There's no fire to go to."

What harmful effects may result from hurried eating? What can we do to get people—young and old, but especially young persons—to eat more slowly?

You are likely to overeat only of carbohydrates and proteins. Why?

Putting Chemistry to Work

A

(1) Explain in definite ways just how closely chemistry is related to living things. (2) Explain why an abundance of food may be insufficient for proper nutrition. (3) Which type of food do we eat in the greatest quantity? (4) What element in our food is obtained from air by plants? (5) What type of food should be limited in the diet for reducing the weight of a person? (6) State three or more uses of starch in the order of their importance. (7) Starch and some sugars require digestion before they can be used in the body. Glucose requires no digestion. Explain the reason for this difference. (8) Suggest in order of importance several ways of obtaining sufficient bulk in the diet.

B

(9) Why do many plants grow better in the sunshine than in the shade? (10) How is it possible for a person to fail to be healthy even if he has a complete knowledge of nutrition? (11) State the advantages of twice-baked bread ("zwieback") and grapenuts in comparison with regular bread. (12) Explain the name, glyceryl ester, as the class name for fats. (13) A few drops of starch sol made blue with iodine will lose its color in a few minutes if saliva is mixed with it. Explain. (14) Why do vegetables lose little, if any, of the nutritive part of the food when they are dried or dehydrated? (15) In what ways is body fat desirable and in what ways undesirable?

(16) Which of the following may be able to use considerable sugar: a hard-working person doing manual labor, a child sick in bed, a telephone girl, a long-distance runner, a salesclerk, a schoolboy of eight?

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Research and Activities That You Will Enjoy

A "square-table" discussion: Two students compare the advantages with the disadvantages of modern civilized living. Two others compare the advantages with the disadvantages of living among the American Indians or on South Sea Islands.

An argument: One hears a great deal of objection to eating "oleo" as a butter substitute. Do you think these objections are well founded? Is it just to have a heavy government tax on margarine butter substitutes? Discuss either side of the question.

An outside speaker: Ask your family physician to visit your class and tell about the use of insulin in the treatment of diabetes, or talk on the problems of overweight and underweight. Or, interview him at his office and report to the class all the interesting things you learn.

Problem 57

WHAT SHOULD YOU KNOW ABOUT PROTEINS, THE FOODS THAT KEEP YOUR BODY IN REPAIR?

You are a collection of a vast multitude of living cells. These cells are made up in great part of protoplasm which is a mixture of proteins. Your body, therefore, is largely a "collection of proteins." Even the cells of your bones are protein in which has been deposited mineral material (largely calcium phosphate) which keeps the bones rigid.

Protein molecules are the giants of the molecular world—how proteins differ from other foods. Proteins differ from other foods in that they are far more complex. Protein molecules are giants as compared to other molecules. The molecule of albumin, a typical protein, is estimated to be $C_{696}H_{1125}O_{200}N_{190}S_{18}$. Note that in addition to carbon, hydrogen, and oxygen (which are the *only* elements in *carbohydrate* foods) the molecule of albumin contains *nitrogen.* Nitrogen is the characteristic element of *all* proteins; sulfur is present in practically all of them. Nitrogen makes up about 16 per cent of the weight of proteins. Phosphorus and iron may also be present in other proteins.

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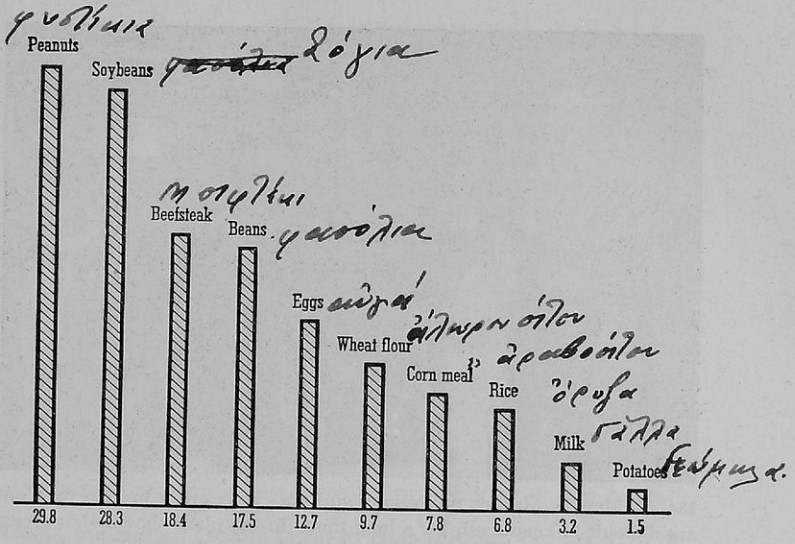

183. PERCENTAGE OF PROTEINS IN SOME COMMON FOODS. This graph shows the relative quantity of proteins in common foods. The figures indicate percentage of protein.

Proteins are formed in the cells of plants. You have found that plants manufacture carbohydrates. Plants also synthesize amino acids and from them manufacture proteins. Animals have a limited capacity to synthesize these acids.

A few typical proteins are: *albumin* from the whites of eggs; *myosin* from lean meat; *fibrinogen* in blood; *gluten* from wheat; *zein*, the protein found in corn; *elastin* from ligaments; *keratin* from hoofs, horns, and hair. These last are not foods but when hydrated they form gelatin which is used as food.

Pure proteins are odorless and tasteless; most of them are colorless. Practically all proteins except the hemoglobins are colorless and all are odorless and tasteless. When proteins decompose, the elements nitrogen, sulfur, and phosphorus are responsible for forming many decomposition products having bad odors.

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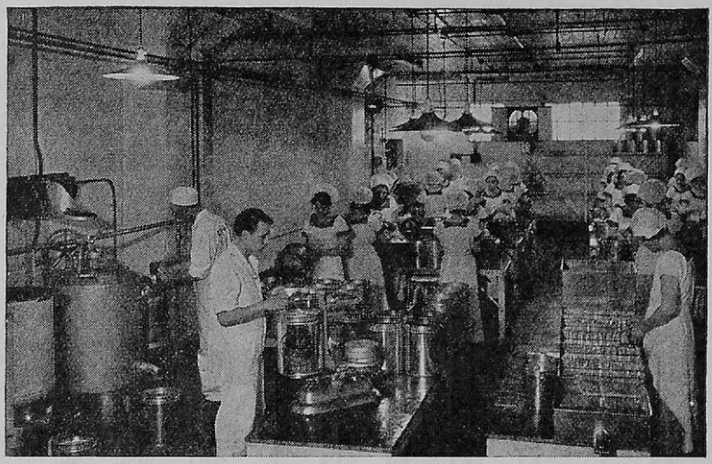

184. A MODERN METHOD OF PRESERVING EGGS. Eggs are a protein food and are difficult to keep fresh for a long time. In the plant shown above, eggs are broken, packed in cans, and frozen.

Most proteins are colloidal suspensions—other properties of proteins. A number of proteins can be crystallized from solution, but so-called solutions of the majority of them are really colloidal in form, being gels with a little water or sols with much water. (See page 419.)

Proteins are made of amino acids. You learned that the starch and cellulose molecules are large multiples of the unit $C_6H_{10}O_5$. Somewhat similarly the protein molecule is a combination of various amino acids. There are 22 known amino acids, so a large variety of proteins is possible in the various combinations of the amino acids. Some simple proteins are combinations of only 4 different amino acids, while others may contain 15. The structural formula of glycine, the simplest amino acid, is shown below. It is amino acetic acid.

$$\begin{array}{l} H_2C\text{—}NH_2 \\ | \\ COOH \end{array}$$

glycine, the simplest amino acid

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

You will recall that the NH_2 group is known as the amino group. Likewise the COOH group is the typical carboxyl radical already noted as a constituent part of all organic acids. The value of a protein is determined by amino acids derived from it.

How you can test for proteins in general. *Xanthoproteic test on solid protein.* When any protein is heated with concentrated nitric acid, a yellow color develops. "*Xanthos*" means a yellow color, hence the name. Application of ammonia deepens the color to orange.

Biuret test on "solution" protein. If protein "in solution" is heated with an equal volume of 10 per cent sodium hydroxide and about two drops of a very dilute copper sulfate solution, a lavender color shows undigested protein. A reddish color shows partially digested protein such as peptones, and no color indicates completely digested proteins or amino acids.

Protein molecules are too large to pass through the walls of the intestines—how proteins are digested. The large size of the protein molecules makes it necessary to divide them until the pieces are small enough to diffuse through the walls of the intestines and into the blood vessels. The manner of digestion of starch and protein is similar. Influenced by enzymes, the molecules unite with water and then separate into two portions. One of these parts is an amino acid. The amino acid part is small enough to diffuse, but the other part requires a continuation of this process of hydrolysis and splitting until diffusion size is reached.

COMPARISON OF THE DIGESTION OF STARCH AND PROTEIN

STARCH + water + enzyme	PROTEIN + water + enzyme
↓	↓
Dextrin (Red) ——→ Maltose	Proteose → Amino acid
↓	↓
Dextrin (Colorless) → Maltose	Peptone → Amino acid
↓	↓
Maltose ——————→ Glucose	Peptid → Amino acid
↓	↓
Glucose	Amino acid

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

The amino acid molecules (page 540) are broken from the protein masses and transported to the tissues where they are built into protein again. This is very similar to the way that stones of convenient size are broken from ledges of rock in a quarry and transported to the place where they are joined again in the walls of a building.

Proteins are a common cause of allergy. An increasing number of persons are sensitive to contact with proteins in various forms. This sensitivity is known as an allergy. Pollen, bacteria, hair, and feathers are sometimes responsible for hay fever and asthmatic conditions. Certain food may cause hives. Injections of serums containing proteins into the blood frequently cause a skin rash. It is well known that proteins and their incompletely digested products often have a detrimental effect upon the system.

Certain protein molecules are thought to cause some of our worst diseases. Many of our worst diseases are known as virus diseases since they are initiated not by bacteria or other forms of germs but by a submicroscopic something known as virus. Recent researches make it appear that strains of virus are neither tiny plants nor tiny animals, but *large protein molecules* that have the power of starting disease. Infantile paralysis and measles are thought to be virus diseases.

What happens to the food you eat? The long tube known as the alimentary canal is a chemical factory for processing foods for use in the body. Whatever nutriments are obtained must pass through the walls of this tube and the walls of blood vessels in order to be distributed by the blood stream to all parts of the body. The nutriment particles, then, must be very small.

The food is first ground by the teeth and softened by saliva, which not only aids in swallowing but also starts the chemical action. At body temperature chemical action is slow, so the changes must be hastened by enzymes or food catalysts. One of the early enzymes discovered was found in yeast which ferments sugars. The word *enzyme* means "in yeast." This

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name is now used for all organic catalysts associated with living organisms. Just as a key is made to operate a particular lock, so each enzyme accelerates the digestion of a particular kind of food. The first enzyme encountered in digestion is present in saliva. Its function is to help transform insoluble starch into soluble sugar. Other enzymes are produced by various glands which pour their secretions into the alimentary tube to mingle with the food. The following table of enzymes is given for reference.

ENZYMES WHICH AID IN DIGESTION

Enzyme	*Source*	*Food Acted on*	*Digested Product*
Ptyalin	mouth	starch	dextrin
Pepsin	stomach	protein	proteoses and peptones
Rennin	stomach	casein	paracasein
Lipase	stomach	fat	fatty acids and glycerol
Trypsin	pancreas	protein	peptones, peptids, amino acids
Steapsin	pancreas	fat	fatty acids and glycerol
Amylopsin	pancreas	starch	maltose, glucose
Erepsin	small intestine	proteoses, peptones	amino acids
Sucrase	small intestine	sucrose	glucose, fructose
Maltase	small intestine	maltose	glucose
Lactase	small intestine	lactose	glucose, galactose

When these enzymes have performed their work, the nutriment particles are small enough to diffuse through tissues to the cells where they are built into new tissue or are oxidized to release energy. Indigestible residues and waste products are passed on through the tube.

Readings for Pleasure and Profit

BORTH, CHRISTY. *Pioneers of Plenty.* Chaps. XIII-XV, pp. 241-276, "Too Much Food and Milk."

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. III, pp. 34-67, "Keeping Well."

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Applying in Life What You Have Learned in Chemistry

"I'll declare! That Miss So-and-So is the most 'finicky' person I ever saw. Why, just last night she dropped in to see us and when our fine large cat came into the room, she just choked up and almost coughed her head off. She just had to get out of there. Now you know our sweet Rex, he never hurt a soul."

Can you show that Mrs. Thinklittle was not very well informed?

See what you can learn about different types of allergy—hay fever, hives, and the like. Is air conditioning a relief for allergic persons?

How can you make cocoa without coagulating the albumen in the milk?

Putting Chemistry to Work

A

(1) Of the three classes of foods, carbohydrates, fats, and proteins, which occurs in the greatest variety? (2) What is the main reason why proteins need to be digested? (3) How is the chemistry of the digestion of starch similar to that of proteins? How is it different? (4) A digestive enzyme is used to remove the useless protein, elastin, from hides before they are tanned in making leather. Would not this enzyme also digest other useful proteins from the hide? (5) In what way are nuts a substitute for meats? Why do nuts furnish more energy per pound? (6) Explain the coagulation of milk when it "sours." (7) Give a reason for the thorough chewing of starch and also protein.

B

(8) Why is cottage cheese a good food for a reducing diet? (9) When eggs are poached, why is it preferable to drop them into hot water rather than cold? (10) A freshly emptied milk bottle can be washed clean with cold water, but not after it becomes dry. Explain. (11) The grain that can be grown on a plot of ground will feed 60 men for one day. If the grain is fed to cattle and converted into beef, it will feed considerably fewer men for one day. How does this affect the prices of these foods? In what way is there a gain in value? (12) Liquid protein is coagulated by heat and acids. Explain the formation of a "skin" on the surface of heated milk. (13) Bouillon cubes are said to be meat extract. If they dissolve completely in hot water, can they contain protein?

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Research and Activities That You Will Enjoy

A report: See what you can learn about vacuum distillation and the production of powdered milk by this means. Report what you learn to the class.

Problem 58

HOW IS THE BODY CHEMISTRY REGULATED BY MINERALS AND VITAMINS?

If you stay healthy, you must have certain minerals in your food—what are they? The big four elements in foods are *carbon, hydrogen, oxygen,* and *nitrogen* which on the average compose 96 per cent of an ordinary assimilated food. Nine other absolutely necessary elements are *calcium, phosphorus, potassium, sulfur, sodium, chlorine, magnesium, iron,* and *iodine* in the order of the quantities used in the body. They make up only about 4 per cent of the human body. Note that four of these are nonmetals but all nine are classed as *minerals* because they remain as an inorganic nonvolatile ash after the food is burned.

Minerals make your body fluids alkaline or acidic—why is this important? A most important function of minerals is to render the body fluids either alkaline or acid for the proper control of chemical action taking place in a body organ. Metals form bases and nonmetals form acids. By a simple experiment you can see that in the presence of hydrochloric acid the enzyme, pepsin, digests readily the cooked white of an egg. However, in a neutral solution there is little evidence of digestion. On the other hand, the enzyme ptyalin is prevented from digesting starch by the presence of acid, but rapidly converts it to sugar in mildly alkaline condition. The normal condition of the general body fluids (blood and lymph) is slightly alkaline. Likewise the digestive enzymes work best in mildly alkaline solutions with the one exception of those in the stomach.

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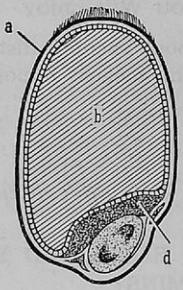

The mineral content of a wheat grain is largely in the outer layers (a) which go into the bran. White flour is made largely from the starchy endosperm (b). The germ (d) contains the fat found in wheat. This is left out of white flour because the fat lowers the keeping properties of the flour.

185. SECTION OF A GRAIN OF WHEAT

Why don't you select foods that give you enough minerals? By the various processes of elimination there is a constant loss of mineral matter by the body. This loss must be replaced if you maintain your health. Whole wheat contains about 2 per cent mineral matter. The white flour in general use contains about 0.5 per cent. A diet containing only products made from white flour will be deficient in these valuable mineral substances.

Whole-wheat flour, and oatmeal made by steaming, rolling, and partially cooking oats contain practically all of the mineral matter of the grain. Polished rice and barley, which have had the outer coat of the grain removed, are quite deficient in mineral matter.

When you eat an apple, why not eat the peeling too? In fruits and potatoes the minerals are concentrated just beneath the skin. When the peeling is removed and discarded, much of the valuable mineral is lost. The potato has a high mineral content as well as a high starch content. If it is peeled, then cooked by boiling in water, only starch remains; practically all the mineral is lost. If washed and baked in the skin, no mineral need be lost.

When you eat fruits, keep in mind that poison sprays are quite generally used to kill plant diseases and parasites. Even a very small residue of poison, such as arsenic, may be dangerous. *Wash* fruit before eating it.

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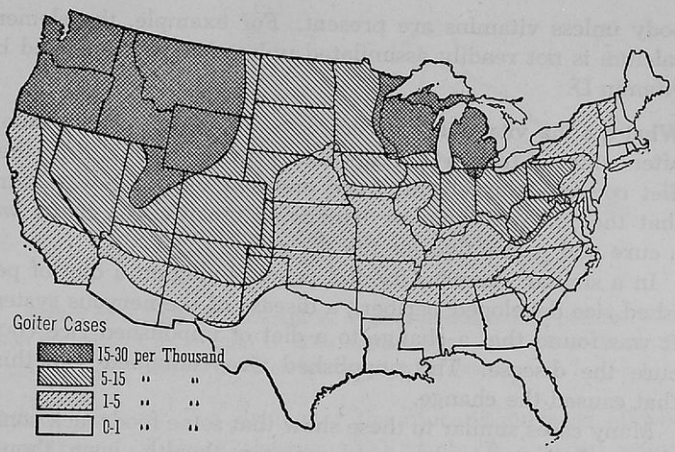

186. PREVALENCE OF GOITER IN THE UNITED STATES. Goiter is caused mainly by a lack of iodine. It is more prevalent where the iodine has been washed from the soil by the ground water, as in certain highlands or in places remote from the ocean.

Don't lose the minerals when you cook food. Many vegetables are cooked in boiling water. If the cooking water is discarded, the minerals that dissolve are lost as food. The amount lost may range from 20 to 50 per cent of the total mineral.

Are you getting all the minerals you need—why not make a checkup? If you will take care to prepare and eat the food chiefly as *nature made it,* there will be little mineral loss. Do you select whole grain cereals? Do you eat apples, peaches, pears, and plums with the skins (after first properly washing them)? Do you cook fresh vegetables by "steaming" in very little water rather than boiling them in great quantities of water?

Such foods as bacon, lard, suet, butter, salad oils, sugars, and starches which enter largely in modern diet contain comparatively little mineral matter.

Minerals are closely associated with vitamins in their occurrence in foods. Sometimes minerals are not used by the

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body unless vitamins are present. For example, the element calcium is not readily assimilated unless it is accompanied by vitamin D.

What are the vitamins? In the days of sailing vessels sailors often suffered from a disease called scurvy. At that time their diet consisted largely of bread and salt meat. It was found that the juice of limes or lemons or other citrus fruits was a cure and preventive for the disease.

In a similar manner Oriental people living on a diet of polished rice developed beriberi, a disease of the nervous system. It was found that a change to a diet of unpolished rice could cure the disease. The unpolished rice contained something that caused the change.

Many cases similar to these show that some foods lack something which is necessary to maintain health, even though there may be a perfect balance between carbohydrates, proteins, and fats. Research has shown that these substances, called vitamins, are present in some foods in small amounts. Their presence is necessary to the proper functioning of the body. Since they are present in minute quantity, they probably act as *catalysts* in controlling certain bodily functions.

A deficiency of vitamin B produces a general lowering of body efficiency. Even a slight deficiency of vitamin B may produce a general lowering of body efficiency. A greater deficiency causes beriberi, a disease in which partial paralysis of parts of the body occurs.

This first-discovered vitamin has now been prepared in crystalline form and contains nitrogen and sulfur ($C_{12}H_{16}N_4OS$). It appears to be more like the proteins. It is found most abundantly in yeast and the whole cereal grains. Proper use of vitamin B helps to insure a good appetite and a general good tone of the digestive tract.

Vitamin A promotes the proper growth of children and helps maintain health in adults. Vitamin A acts as a regulator of the condition of the mucous membranes. Consequently it helps to protect the body from some of the infectious germs which

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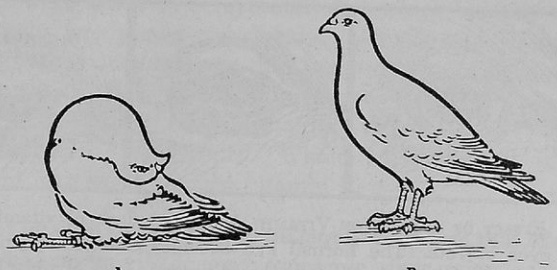

A B

187. EFFECT OF A LACK OF VITAMIN B. Pigeon A was fed on polished rice which is deficient in vitamin B. The same pigeon is shown at B, much improved after being fed with yeast.

produce disease. The drying of the mucous surfaces allows the entrance of these organisms. Vitamin A also promotes the proper growth of children.

When vitamin A is lacking in the diet, an infection of the eyes is one of the first symptoms. Blindness may be the final result of this trouble known as ophthalmia.

Cream and butter fat have a yellow color which is due in part to the presence of carotene ($C_{40}H_{56}$), the coloring matter in carrots. Usually wherever this color appears in natural foods the presence of carotene is indicated. Carotene combines with two molecules of water and forms two molecules of *vitamin A:*

$$C_{40}H_{56} + 2\ H_2O \rightarrow 2\ C_{20}H_{30}O$$

The leaves of lettuce, spinach, water cress, kale, broccoli, and the tops of turnips, beets, and radishes, are also good sources of this vitamin.

The lack of vitamin C causes scurvy. Vitamin C is a sugar-acid having the formula, $C_6H_8O_6$.

The cereal grains, meats, and fats contain very little, if any, of this needed food factor. Persons subsisting for a length of time on stored foods develop symptoms of scurvy—soreness and stiffness of joints, bleeding gums, and loose teeth. This is the chief criticism of the bread-butter-meat sandwich type of

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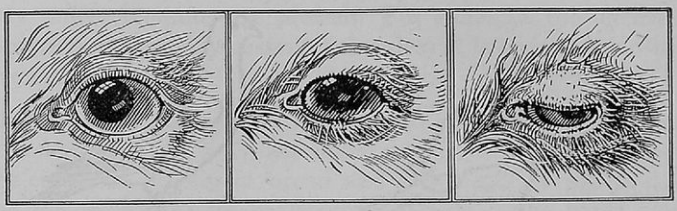

188. EFFECT OF A LACK OF VITAMIN A. How a lack of vitamin A affects the eyes of rats. The normal eye becomes swollen by infection and becomes worse with the destruction of tissues. Loss of sight by ophthalmia may be prevented if the vitamin A is supplied in stage II.

meal. The enormous increase in the use of fresh vegetables and fruits during the past two decades has made this disease much less common.

Vitamin C also aids in the building of good teeth, helps one to maintain a buoyant health, and has some relation to the ability of a person to resist infection.

The best sources of vitamin C are citrus fruits, tomatoes, green and red peppers, and other fresh vegetables and fruits.

Vitamin D controls bone formation; its lack causes the disease called rickets. In the past large numbers of children in industrial districts suffered to some extent with rickets, a disease causing imperfect growth of bones. This disease is a nutritional ailment due to a lack of vitamin D. Even today many children in the United States have this trouble in some degree since vitamin D is lacking in many common foods. Without vitamin D, calcium and phosphorus, which are the chief bone-forming elements, are not properly used.

Today there is little excuse for any child's having a deficiency of vitamin D since it is richly present in cod-liver oil. Good grades of cod-liver oil can be purchased reasonably. Some cod-liver oils have been given a "super" amount of this vitamin. Even an exposure to sunlight aids in the assimilation of calcium and phosphorus so that normal bone growth is possible.

Why is vitamin E needed? Evidence of another missing factor in the diet was obtained by the experimental feeding method.

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White rats were fed with a restricted diet which contained all four vitamins mentioned previously. Growth and physical well-being were normal except that the young were born dead a week or so early. When other rats were fed the same diet but with the addition of foods containing vitamin E, the young were quite normal when born. Whole wheat, wheat germ, lettuce, and lean meat contain vitamin E.

The lack of vitamin G (B_2) causes pellagra, a disease that affects one's mental activity. War and economic depression restrict the diets of many people. A disease called pellagra was widespread in the southern states in the springtime of 1917-1918, involving about 200,000 persons. Their diets were usually limited to the grocery store type of white flour, corn meal, polished rice, sugar, molasses, and salt pork.

The symptoms of pellagra are a sore tongue and mouth and thickened skin where exposed. The digestion and mental activity are affected. If persons with pellagra are supplied with milk, lean meats, eggs and fresh vegetables, vegetable oils, or yeast, marked improvement is noted.

What foods furnish you with vitamins? In the appendix on page 776 is given a chart which shows the common sources of different vitamins. Refer to it now.

What foods are rich in vitamin A? What foods are good sources of vitamin B? of vitamin C? of vitamin D? of vitamin E?

Readings for Pleasure and Profit

DARROW, F. L. *The Story of Chemistry.* Chap. VII, pp. 278-281, "Vitamins."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XXIV, pp. 414-419, "Vitamins and Mineral Matter."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XXII, pp. 253-266, "Now What Shall We Have to Eat?"

HOLMES, HARRY N. *Have You Had Your Vitamins?*

STOKLEY, JAMES. *Science Remakes Our World.* Chap. IX, pp. 92-110, "Vitamins."

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Applying in Life What You Have Learned in Chemistry

Blanche R., poor girl, was a faddist. If it was not one fad, it was sure to be another. She had read about "acidosis," and at once became intrigued with the word.

She reasoned that since lemons, oranges, and other citrus fruits were often sour, they would give her "acidosis." They might even cause those little pimples on her face. It didn't occur to her that she might be eating too much candy.

What would you tell Blanche?

Putting Chemistry to Work

A

(1) List the types of foods that are good sources of vitamin A, of vitamin B, of vitamin C, of vitamin D, of vitamin G. (2) Name two foods that are abundant sources of all four of the following vitamins: A, B, C, D. (3) What three fruits are the most important from the standpoint of their vitamin content? (4) List the four important vegetables on the basis of their vitamin content.

(5) Show how the vitamins may be obtained without using out-of-season and expensive foods. (6) A large family of restricted means lived on a small farm and could obtain only milk, coarse bread made from home-ground wheat and corn, potatoes, and vegetables. Comment on the effectiveness of this diet. (7) What is responsible for the higher energy values of quite a number of fruits and vegetables (bananas, carrots, etc.)? (8) A meal consisted of noodle soup, baked beans, bread and butter, coffee, and ice cream. Point out any particular faults of this meal.

B

(9) What three garden foods contain an abundance of at least three vitamins and can be stored through the nongrowing season? Are they cheap or expensive? Why should all children be trained to eat and relish them? (10) Cereals are deficient in what essentials of diet? How are they often made still more deficient in their preparation for the table?

(11) On whom does the obligation of providing a suitable diet for the family rest? State the responsibility for each one concerned. (12) In what way is the following meal unbalanced? Cream of mushroom soup, roast beef with gravy, rice croquettes, potato salad, apple pie with cheese, iced tea. (13) Why do so many children have rickets to some degree? (14) The water in which a portion of car-

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

rots was boiled was evaporated in a dish weighing 41.123 g. After being heated to redness the dish weighed 41.215 g. The total ash in this portion of carrots was 0.46 g. What percentage of mineral was extracted in the cooking?

Research and Activities That You Will Enjoy

A report: Food adulteration and its detection. (See Schlink, "Eat, Drink, and Be Wary," *Consumers' Test Manual,* Consumers' Research Inc., Washington, N. J., or other books on food analysis.)

A project: Prepare a menu of meals for a day according to the standards of nutrition. Give an estimate of the cost of the foods of each meal.

Problem 59

HOW DOES CHEMISTRY HELP TO PREVENT AND CURE SICKNESS?

In medieval times medicine and alchemy, the forerunner of modern chemistry, were closely associated. Many of the alchemists were searching for the "Elixir of Life," a magical potion which would cure all of man's ills, restore lost youth, and prevent the approach of old age. During this search, the physiological properties of many substances were discovered. Many powerful drugs and potent poisons were found, some of which were used for medicines. In general, however, the medicines used to combat disease were curious mixtures of substances chosen because of their scarcity, or because of superstitious ideas of their curative effect. Powdered mummy dust, lizard skins, the entrails of toads, and other things of this sort entered into medicines which were supposed to cure the sick.

Modern chemistry examined the old remedies. With the development of modern chemistry and the development of experimental methods, chemists began to examine critically the old remedies. It was soon shown that some of them had no curative value, and these were discarded. Those which had some value were carefully studied, and their physiological

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effects were noted. In this way many products which tradition had kept in the list of medicinal substances were no longer used by reputable physicians. A study of the effects of those products that had value lead to a more rational treatment of many diseases. It is interesting to note, however, that some worthless remedies still persist as "household remedies."

The chemist extracts the pure curative agent from the crude drug. Many of the substances retained as medicines were of vegetable origin. Plants collected at different seasons of the year or under different conditions often showed great differences in their physiological effects. In investigating the causes for these differences, chemists found that the effects were produced by substances of definite composition, present in small amounts in the crude drug. Chemists began to extract these pure substances from the mass of fiber and other tissues of the plant. This was an important step for it made it possible to administer definite doses, the effect of which could be foretold. In this way quinine was extracted from Peruvian bark, and cocaine from the leaves of the coca plant.

The chemist synthesizes the pure curative agent in the laboratory. After having isolated and purified the pure curative agent from the crude drug, the next step was to determine its formula and then to reproduce it in the laboratory. It was in such an attempt to synthesize quinine that Perkin, a young English chemist, stumbled upon the first anilin dye in 1856.

The ability to synthesize pure drugs makes it possible to secure an ample supply of the drugs when the natural supply may be limited or difficult to obtain.

The chemist improves on nature. Some of the pure curative agents found in plants have some undesirable properties. In the study of the structural formulas of such compounds the chemist frequently has been able to improve on nature by retaining the desirable properties and getting rid of the undesirable properties. The case of cocaine is a striking example of this. Cocaine is a white crystalline substance which, when injected in dilute solution, produces local insensibility

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to pain. Used this way it is possible to perform minor operations without the trouble of using ethylene gas, ether, or chloroform. But cocaine has undesirable properties. It is quite poisonous and it is a habit-forming drug. The structural formula of cocaine was determined and a careful study made of it. It was found that only part of the molecule was responsible for the production of local anesthesia, while another part was closely related to the poisonous principle in hemlock, and a third part seemed to be responsible for the habit-producing effects.

After these facts had been determined, it was possible to construct a molecule containing the group of atoms which produce the desirable anesthetic results, and to omit the groups of atoms which caused the poisonous and habit-forming reactions. The products such as procaine, butyn, and metacaine have largely displaced cocaine as a local anesthetic.

The chemist creates new compounds to combat disease. A study of structural formulas and the determination of the physiological effects of certain atomic groupings opened a new field to the synthetic chemist. Some diseases had no known remedies. To meet the situation, could the chemist prepare a compound that had no counterpart in nature? The work of Ehrlich, a German chemist, shows how chemistry solved such a problem.

When the Germans went into German East Africa, they found the natives suffering from sleeping sickness, a disease caused by a form of elongated flattened parasite which inhabits chiefly the liquid portion of the blood. Ehrlich tried to find a compound which would kill the bacteria and not the man. After making some two hundred compounds he found one that did the work. He then attempted to find a specific cure for the dread disease, syphilis, which is caused by the presence of a spiral organism. After 605 compounds were made and rejected he produced the 606th, known as arsphenamine or salvarsan. This compound is a "specific" for the disease syphilis, except in its most advanced stages. Nature produces no compound resembling arsphenamine so the

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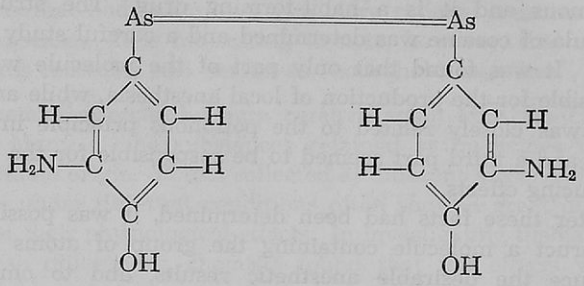
chemist and his laboratory is responsible for curbing the ravages of one of the world's most dangerous diseases. The formula for arsphenamine is as follows:



What are the "Wonder Drugs"? A recent example of the method of developing new medicine is offered by the valuable drugs known collectively as sulfa- drugs. The parent substance of this group is sulfanilamide, $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$. It is a specific remedy for such dread diseases as erysipelas, "blood poisoning," and meningitis. It saved many lives in recent military surgery. Other sulfa- drugs are prepared by replacing one of the hydrogen atoms of the final NH_2 with various groups of atoms. The resulting products produce different effects as shown in the following table. Notice how the formulas are similar.

Sulfanilamide: $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$

Sulfapyridine: $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C_5H_4N$, used for several types of pneumonia

Sulfathiazole: $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C_3H_2NS$, used for boils and gonorrhea

Sulfadiazine: $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C_4H_3N_2$, effective against many infections and has the advantage of being less irritating than other sulfa- drugs

Sulfaguanidine: $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CN_2H_3$, useful in treating intestinal diseases such as dysentery and cholera.

Sulfamerazine: $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C_5H_5N_2$, recommended for infections; a recent discovery.

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Penicillin. Recently a new and useful drug, penicillin, has been used. It is highly effective, even against some infections which are not controlled by the sulfa- drugs. It is successful in controlling pus-forming germs and seems to produce no injurious effect upon healthy living cells. It may be applied locally or injected into the blood stream since its action is mild.

Penicillin was first produced from a common mold, a method which yields relatively small quantities. Efforts to produce this useful drug in greater quantities are meeting with success, and other similar drugs made from other molds have been produced.

The chemist synthesizes vitamins. In the preceding problem you learned that you must have small amounts of vitamins in your food to regulate some of your bodily activities. Some of these vitamins have been isolated, their formulas have been determined, and they have been synthesized. It is reasonable to believe that in a short time laboratories may be able to synthesize all the known vitamins.

The chemist synthesizes hormones, secretions of animal glands. Until comparatively recently, many glands in the human body were considered useless. We now know that the secretions of many glands, which formerly were considered of no value, have a decided influence on health. These secretions have been examined and from them have been isolated compounds which act catalytically in regulating the action of many of our organs. One of these compounds, insulin, has come into general use to regulate the oxidation of sugar in the blood. Adrenalin and thyroxin are other examples of these "hormones." Several of these are now being synthesized in the laboratory, so people whose glands are unable to secrete a sufficient quantity for their needs can live normal lives through the aid of the chemist.

The chemist has provided anesthetics. One of the greatest boons that chemistry has given medicine was the discovery of anesthesia. Before 1842 all operations were performed

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with the patient conscious and often struggling. Strong men held the patient while the surgeon operated. Under such conditions, delicate operations inside the body were impossible, and the shock to the nervous system of the patient was so great that only a person with a strong constitution was able to survive a major operation.

In 1842 Dr. Crawford W. Long of Georgia was the first physician to use ether as an anesthetic. He successfully performed a number of operations and convinced himself that ether relieved the patient of pain. For some reason Dr. Long's experiments were not publicized. In 1844 Dr. Horace Wells, a dentist of Connecticut, used nitrous oxide on himself while a tooth was extracted. He felt no pain. In 1846 Dr. Wm. Morton of Boston gave the first public demonstration of the use of ether as an anesthetic in a celebrated operation at the Massachusetts General Hospital. Numerous physicians were convinced of the value of ether. Their support brought it into general use. The anesthetic properties of chloroform were discovered shortly afterward in England.

Within the last few years ethylene gas has come into quite general use as an anesthetic. When inhaled with oxygen, it produces fewer disturbances than when anesthesia is produced by some of the older anesthetics. Recovery to the conscious state is very quick, and it is accompanied with fewer unpleasant aftereffects.

The work of the chemist Pasteur led to an important discovery concerning the cause of disease. One of the greatest discoveries in medical history was made by Pasteur. He was a French chemist whose work in the field of medicine began about 1854. He was called to a brewery to see if he could find out why its beer turned sour. After some study, he found that all samples of beer which turned sour contained myriads of microscopic organisms. He soon showed that the cause of the souring was due to the activity of these organisms (acetic acid bacteria). A study of the organisms led to the discovery of others, and he finally was able to prove that similar organisms were the cause of many diseases. It was also shown that

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gangrene and pus formation in wounds were caused by the presence of bacteria.

The discovery of anesthetics had made surgery possible, but too often the patient had died from infection after the operation. A famous French surgeon had said, "In a hospital a pinprick is a door open to death." In 1868, sixty per cent of the patients in a Paris hospital who suffered amputations died of infected wounds. With the discovery of Pasteur that infection was caused by bacteria, the way was open for reform. Lister in England adopted some simple methods using carbolic acid (phenol) solutions to sterilize instruments, dressings, and wounds. By the use of such methods, the death rate from amputations in Lister's hospital dropped to about 10 per cent the first year. The discovery of antiseptics in surgery is the chemists' second great gift to surgery.

At the present time we have many antiseptics to use. Phenol is still used and the strength of other antiseptics is still measured by their "phenol coefficient." Among the common antiseptics in use are iodine solutions, hydrogen peroxide, boric acid, hexylresorcinol, neutral hypochlorite solutions, and others. Each one has its definite use.

The danger and fear of infected wounds has, in a great measure, been done away with. The careful practice of antiseptic methods in hospitals has reduced the dangers of the operating room, so that today a person approaches the operation for the removal of an appendix with less fear than formerly accompanied the removal of an ulcerated tooth.

Reports from the Solomon Islands showed that the mortality rate for American wounded there was less than one per cent, the lowest rate in history. Prompt injections of blood plasma and use of sulfa- drugs were responsible.

The chemist aids the doctor in the prevention of disease. The work of the chemist in preventing disease is of greatest importance to public health. The chlorination of the water used in cities has had an enormous effect in suppressing diseases such as typhoid fever which is usually caused by contaminated water supplies. In Chicago the typhoid death rate dropped

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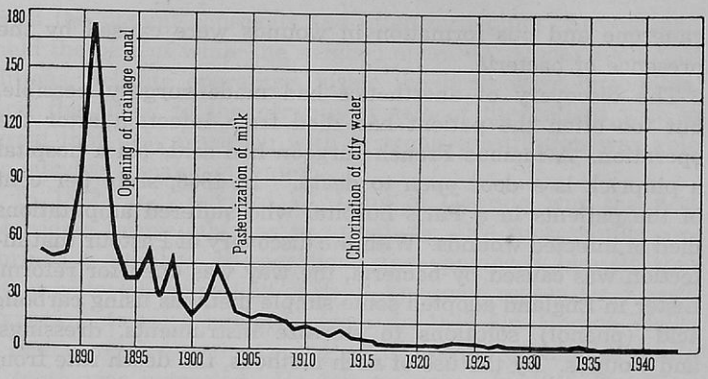

Courtesy, Chicago Board of Health

189. DRAMATIC DROP IN THE DEATH RATE FROM TYPHOID FEVER IN CHICAGO. In 1893 the Drainage Canal was opened. This diverted the sewage of the city from Lake Michigan which was used as the city's water supply. In 1903 milk sold in Chicago was required to be pasteurized. In 1913 chlorine was first added to the city water. This chart shows strikingly how the scientist may influence public health.

from 8 per 100,000 to less than 1 per 100,000 after the chlorination of the water supply.

In a similar manner the inspection of our food supplies, and the improved methods of storing and preserving foods, all of which are carried out under chemical control, have greatly reduced the danger of infections arising from spoiled or contaminated food. The pasteurizing of milk and other dairy products and the sanitary methods enforced in dairies which supply milk to the great cities insures a pure supply of these healthful foods at all times.

The sanitary disposal of sewage and garbage in cities is another great aid to health. Until modern times, garbage was dumped in the street and allowed to decay and rot. As late as 1898 this was still the practice in the poorer parts of the city of Havana. During the American occupation of Cuba in 1898 General Wood issued orders to clean up the city. In some places rotting refuse was found covering the pavement two feet deep. With proper disposal of garbage and sewage there

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was an immediate improvement in the general community health. The use of scientifically controlled sewage disposal plants has greatly lessened the danger of contamination of many natural water supplies.

Chemistry has done much to aid the science of medicine, but much still remains to be done. Tuberculosis, pneumonia, and cancer still need to be conquered. The pure principles contained in serums and vaccines need to be studied and isolated. The serums now used contain only small amounts of the pure active substances mixed with large quantities of inert material, some of which may be harmful. The isolation and synthesis of these active principles offers a wide field for the trained chemist of the future.

Readings for Pleasure and Profit

HAYNES, WM. *This Chemical Age.* Chap. VII, pp. 113-128. "In Vitro, In Vivo"; Chap. VIII, pp. 129-148, "The Sulfanilimide Family."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XVII, pp. 198-209, "Man against Pigmies"; Chap. XXIII, pp. 267-278, "Shall We Have Medicines and Anesthetics to Order?"; Chap. XXIV, "Let the Yeasts, Molds, and Bacteria Do Their Work."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXII, pp. 333-345, "Drugs and Hormones."

STIEGLITZ, JULIUS (EDITOR). *The Future Independence and Progress of American Medicine in the Age of Chemistry.* "Chemistry in Medicine."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. VIII, pp. 85-91, "Chemical Cures."

Putting Chemistry to Work

A

(**1**) Why should highly poisonous substances not be kept in medicine cabinets? (**2**) What is meant by the term "habit-forming drugs"? What has the chemist done to decrease this menace? (**3**) What is your opinion regarding the value of chlorine in protecting human life? (**4**) "An ounce of prevention is worth a pound of cure." Discuss this saying and cite illustrations regarding its truth. (**5**) What are hormones? What is insulin? What is its function? (**6**) Why is self-medication usually questionable? (**7**) What is pasteurization? What is accomplished by pasteurization?

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B

(8) Why are there so few young people who have "bowlegs" like older persons? (9) Criticize the method of remedying vitamin deficiency in the diet by vitamin tablets obtained at drugstores. (10) Comment on the statement: "A Board of Health should keep out of politics." (11) What does the term "patent medicine" mean? Ask your physician about their medicinal value in general. (12) See what you can learn about the advantages and any disadvantages of different anesthetics; of sulfa- drugs; of penicillin.

Research and Activities That You Will Enjoy

John J. Abel of Johns Hopkins University obtained the hormone called *adrenalin* from the suprarenal capsules located on the kidneys of sheep. He also prepared pure insulin for the first time. Investigate his achievements and give a report.

A worthy plan: Outline a definite plan of conduct that will prevent any need for drugstore cathartics or laxatives.

A chart: Refer to a good physiology text and then prepare a chart on the various ductless glands, their location in the body, their hormones, and the function of these hormones. Explain your chart to the class.

Looking Back into Unit 13

Be sure you know the purpose of this unit. Read again the material on page 530, "Looking Ahead into Unit 13." Then study the following Summary Test.

Summary Test

1. *What should you know about the energy-giving foods?*
   (a) What foods produce energy?
   (b) How is starch digested?
   (c) How is sugar digested?
      (1) Why should you not eat too much sugar?
      (2) What effects may result from overeating starchy foods?
   (d) How do fats serve as a reserve energy food?
      (1) How are fats digested?
   (e) How is cellulose useful in the diet?
2. *What should you know about the foods that keep your body in repair?*
   (a) What type of food repairs your body?
      (1) How are protein molecules different from those of carbohydrates and fats?

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(2) What are some general properties of proteins?
(3) How can you detect proteins?
(b) How are proteins digested?
(1) How are proteins constructed?
(c) How are certain proteins related to allergy?
(d) How are enzymes useful in the digestion of foods?

3. *How is the body chemistry regulated by minerals and vitamins?*
(a) Why are minerals necessary in your food?
(b) How can you obtain sufficient mineral matter in your food?
(c) What are vitamins? Why are they important in your diet?
(d) How are the various vitamins related to proper growth and to the maintenance of health?

4. *How does chemistry help prevent and cure sickness?*
(a) What contributions did alchemy make—
(1) To medicine?
(2) To modern chemistry?
(b) What attitude did modern chemistry take toward old remedies?
(c) What are the three stages of chemical progress in getting new medicines with which to combat diseases?
(d) What did a study of animal glands reveal?
(e) How has the chemist alleviated pain?
(f) What great benefits have you derived from the work of Pasteur?

Closing the Unit

Normal people desire to live well, and to be well. In this unit you were shown some of the different ways to accomplish these desires. It was a surprise to you, perhaps, to find how much *chemistry* is involved in the manufacture of your *food* and in its digestion. And it seems that *medicine* is based fundamentally on chemistry. Today chemistry is making synthetically in the laboratory substances such as vitamins, hormones, sulfa- drugs, and the products of molds that are used for medicinal purposes.

It has been said that "all roads lead to chemistry." Does not the material in this unit lead *you* closer to chemistry?

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Looking Ahead into

Unit Fourteen

Cotton and linen made from plants, and silk and wool from animals are the most commonly used natural fibers. But chemists are now contributing synthetic fibers, including rayon and nylon. Although rayon is called a synthetic fiber, the raw material from which it is made is natural cellulose from plants such as wood or cotton. Nylon is more truly a synthetic fiber in that it is made from the raw materials, air, water, and coal.

Some of our synthetic textile fibers are classed as plastics which are woven into useful and decorative clothing. The chief importance of plastics, however, lies in the extent to which they may be used as substitutes for many metal objects.

The embarrassing shortage of commercial metals, which developed in many nations because of war, led manufacturers to use plastics in countless ways. This situation produced a rapid development in the plastic industries.

The manufacture of plastics already has become a new major industry. Some people have even referred to this age as the "age of plastics."

In a similar manner the sudden elimination of the sources of natural rubber stimulated the manufacture of rubber-like compounds. How are some of these new materials made?

Problem 60. *What Should You Know About Clothing?*

Problem 61. *What Makes It Possible for You to Have Colorful Fabrics?*

Problem 62. *How Can Clothing Be Cleaned Satisfactorily?*

Problem 63. *How Are Plastics Made and Used?*

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Your Clothing: Nature's Fibers, Manufactured Fibers, Colorful Dyes, Proper Cleaning, Plastics, Rubber

Problem 60

WHAT SHOULD YOU KNOW ABOUT CLOTHING?

What kinds of textile fibers are used for clothing and for other purposes? The clothing you are now wearing is made of cloth manufactured from threads. Thread is made by twisting together fine filaments of fibers some of which are produced by animals, some by plants, and some by the chemist.

Typical *animal fibers* are wool, hair, and silk. All these fibers, being of animal origin, are forms of protein.

Typical *vegetable fibers* are obtained from cotton, kapok, flax, hemp, and jute. The seed pods and seed hairs of the kapok plant are similar to those of the milkweed. Both cotton and kapok fibers are almost pure cellulose and require no treatment before spinning and weaving.

Flax, hemp, and jute are the inner bark or bast fibers obtained from the stems of plants. Their natural fibers are held together by gums and lignin which must be removed so the fibers can be spun into thread. Flax threads are then made into linen cloth. Hemp is used for ropes. Jute fibers are made into burlap and sackcloth.

Artificial fibers are of many kinds. Rayon is prepared from cellulose, which may be obtained from the wood of trees or from other plants. Nylon is prepared from the raw materials: air, water, coal. Rock and glass can be spun into fine fibers. Mineral wool is a fibrous material prepared from molten rock or from black-furnace slag. Asbestos is the only natural mineral fiber although metals may be plated on fibers, or metal threads may be interwoven for decorative cloth and screens.

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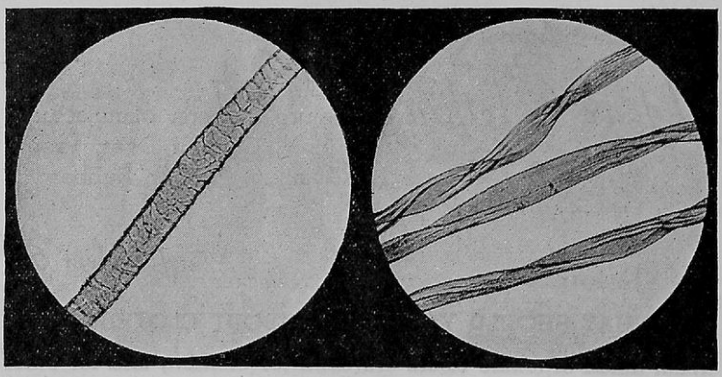

Wool Cotton

190. HOW FIBERS LOOK UNDER THE MICROSCOPE.

Sheep furnish wool for woolen goods which transmit heat very slowly. Woolen clothing transmits heat very slowly, so it is effective for winter wear. Its fibers are very elastic, and the surface scales interlock when moist heat and pressure are applied. For this reason, wool clothing keeps its shape well. The length of raw wool fibers varies from about one to ten inches. The quality differs, but worsted yarns made from virgin, long-fiber, combed wool give the best service.

Worn woolen cloth may be shredded and the resulting shorter and less elastic fibers, called "shoddy," may be woven into cloth. Although a garment may be 100 per cent wool it may not hold its shape if the wool is "shoddy." Under the microscope the fibers of shoddy appear broken, with frayed ends and with the characteristic scales largely lost. In 1939 the Federal government passed a law requiring that all woolen products must have a label showing plainly the percentage of virgin wool, or new wool; of reprocessed wool, recovered from cloth which has never been worn; of reused wool, from garments that have been worn; and of all other fibers which may constitute more than 5 per cent of the product.

What is in a cold cream? Before wool is manufactured into fabrics, the natural oil must be removed. This natural

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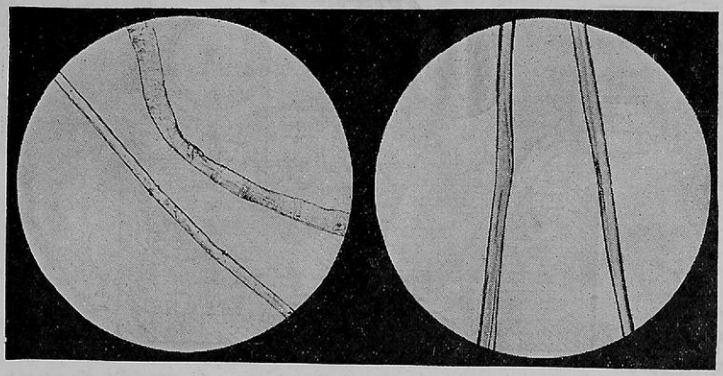

Linen Raw Silk

191. HOW FIBERS LOOK UNDER THE MICROSCOPE.

oil is called lanolin. It is sometimes used in salves, cold creams, and mentholated ointments.

The inner bark of the flax stalk furnishes linen fibers. This inner bark is composed of cellulose cemented together by resinous materials which are decomposed by fermentation when the stalks of the flax plants are moistened. In Ireland, where famous linen is made, the flax plants are cut and allowed to remain on the ground to soak up the Irish rains. After fermentation, the stalks are pounded and the fibers are combed to free them from the woody tissue.

Flax fibers are composed of cells which taper to a point at the ends. They are porous, and they absorb oil and dyes more readily than cotton. Good linen cloth is quite difficult to tear. The torn edge does not curl.

Both linen and cotton are not good heat insulators and are less suitable than wool for protection against cold.

The cotton plant furnishes the least expensive cloth. Cotton fibers are single-celled tubes filled with liquid during growth. At maturity the liquid ceases to form, so the tubes flatten and develop twists. This characteristic is the easiest means of identifying cotton fibers under the microscope. The twist is useful; when the fibers are spun into thread, they interlock

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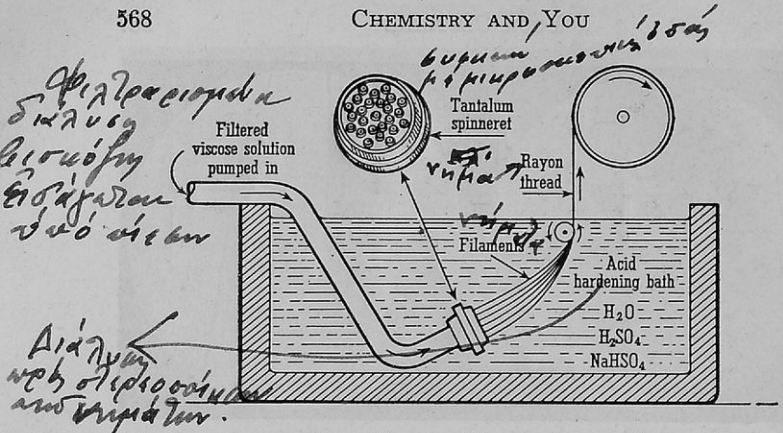

192. FORMATION OF RAYON FIBERS. The solution containing the dissolved cellulose is forced through tiny openings in a tantalum spinneret into a precipitating bath where it solidifies and forms fibers.

and hold together somewhat as the scales of wool fibers do.

How can you make cotton look "like silk?" In 1850 John Mercer noted that when cotton cloth (cellulose) is soaked in a 30-per-cent solution of sodium hydroxide, a cellulose hydrate is formed. When cotton cloth treated in this manner is washed and dried under tension, the fibers are untwisted and the cloth acquires a bright lustre like that of silk. This process is called mercerization.

Caterpillars furnish the silk used in silk fabrics. Silk is derived from the cocoons of the silkworm, the caterpillar of the silk moth. The silk worms are killed by heating them after they have wound around themselves fine silk fibers which are often over half a mile in length.

Raw silk is covered with a gum, sericin, which forms about 25 per cent of its weight. Ecru silk still contains much of its sericin. Other kinds may have much of it removed.

Trees furnish cellulose for rayon fabrics. Rayon can be made from any kind of cellulose, which is the material that makes up the walls of plant cells. Trees such as spruce are a good source of cellulose. Rayon fibers are made by forcing "dissolved cellulose" through small holes. In this way the stream

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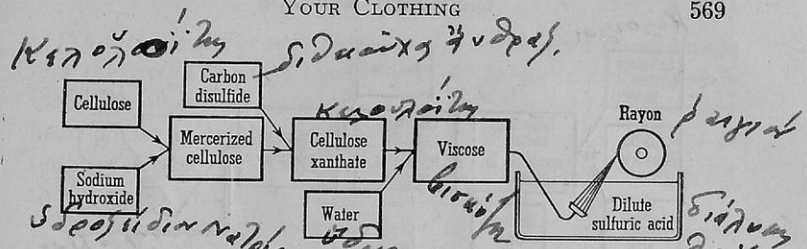

194. RAYON BY THE VISCOSE PROCESS. Cotton or wood pulp is treated with sodium hydroxide and carbon disulfide forming a thick, sirupy, colloidal sol. After the sol is aged, it is precipitated as a fiber in a bath of sulfuric acid.

of cellulose solution is changed into a continuous fiber or filament. There are different methods of preparing rayon filaments; consequently, there are different kinds of rayon.

The pyroxylin process for producing rayon is the oldest process. In this process cellulose is treated with a mixture of nitric acid and sulfuric acid to form a cellulose nitrate called pyroxylin. The pyroxylin is dissolved in an alcohol-ether mixture and forced through small openings. When the filaments dry out, they are pyroxylin filaments or one kind of rayon. Pyroxylin rayon burns too readily for use in clothing and consequently this process has been displaced by other similar processes, but pyroxylin is still widely used to produce a variety of fine products. (See page 523.)

The viscose process for producing rayon is the most common process. In this process cellulose is soaked in a solution of sodium hydroxide to form a cellulose hydrate which is then dissolved in carbon disulfide (CS_2), making a molasses-like or viscous solution, hence the name *viscose*. This solution is forced through a spinneret into a precipitating acid bath to make fine fibers of regenerated cellulose. In sheet form this material made by the viscose process is *cellophane* which makes an individual showcase for foods and clothing when they are displayed for sale.

The acetate process for producing rayon is somewhat more expensive than other processes. This process produces cellulose acetate by using acetic acid instead of either nitric

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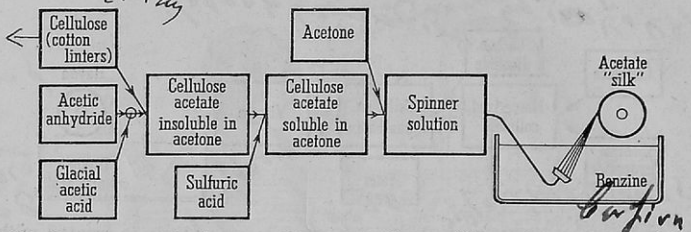

195. RAYON BY THE ACETATE PROCESS. Cotton fibers are treated with a mixture of acetic acid and acetic anhydride. This forms a product insoluble in acetone. Treatment with sulfuric acid converts it to a form of cellulose acetate soluble in acetone. After it is dissolved in acetone, it is passed through a spinneret into a precipitating solution to form the fiber.

acid or sodium hydroxide. Rayon made by the acetate process is used to make special fabrics such as "celanese silks." Since this product will not burn rapidly, it is used to make such things as safety motion-picture film and coverings for airplane wings.

Some fabrics are now made from milk. A textile fabric resembling natural wool has been developed in Italy from the casein of milk. It is called "aralac," "lanital" or "milk wool." It is made by forcing a solution of casein through a spinneret into an acid precipitating bath, in much the same manner as the solution of cellulose is used to produce rayon. Casein is also used in the production of photographic film, linoleum, costume jewelry, buttons, handles, adhesives, felt hats, leather.

Coal, air, and water furnish materials for nylon. The raw materials used in preparing nylon are phenol (from coal), nitrogen and oxygen (from the air), and hydrogen (from water). Hence nylon is manufactured from coal, air, and water.

Nylon is made by "persuading" smaller molecules to combine so that larger molecules are built up; such a process is called polymerization. If this building of larger molecules is stopped at the right point, a solid product is obtained which can be melted and forced through small holes to make fine filaments and thread. This thread may be woven into "nylon hosiery" or into useful fabrics.

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What is the difference between the nylon used in stockings and the nylon used in toothbrushes? If the molten nylon is forced through large holes, it forms thick filaments which may be used to make the bristles of toothbrushes, the strings of tennis rackets, the leaders for fishing tackle, the sutures for the surgeon, and many other useful things.

The name "nylon" does not refer to a single chemical compound but to a class of compounds of similar structure. Hence one sample of nylon may differ slightly from another if they are not made from the same "dibasic acid" or the same "diamine" as explained in the following paragraph.

How nylon is made. In the process of building the large molecules that make up nylon, two materials are necessary. One is an "organic acid" that has *two* COOH groups such as the following. In each of the following three formulas note that there are two COOH groups, one on each end.

$$\mathrm{HOOC \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH}$$
$$\mathrm{HOOC{-\!\!-\!\!-}CH_2{-\!\!-\!\!-}COOH}$$
$$\mathrm{HOOC{-\!\!-}(CH_2)_x{-\!\!-}COOH}$$

The bottom formula represents *any* of the acids which are suitable for producing nylon; in the formula x represents a variable number of CH_2 groups.

The other essential material in the manufacture of nylon is a "diamine" which means that the material has two NH_2 groups which are related, as you can see, to ammonia NH_3. The formula for a simple diamine is $H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$. Note that there is an NH_2 group at each end.

The first reaction between the organic acid and the diamine consists in the elimination of a molecule of water:

$$\mathrm{HOOC \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO\ \boxed{OH+H}\ HN \cdot CH_2 \cdot CH_2 \cdot NH_2 \rightarrow}$$
$$\mathrm{HOOC \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot HN \cdot CH_2 \cdot CH_2 \cdot NH_2 + H_2O}$$

You can see by looking at the preceding equation that the two different molecules "hitch together" at the COOH part of one molecule and the HHN (or NH_2) part of the other molecule.

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The resulting complex molecule of the product also has COOH at one end, and it has an NH_2 group at the other end. Hence the enlarged molecules can again "hitch together" at these two ends, and the polymerization process may be repeated over and over. Molecules of enormous size may be built up; that is, molecules of enormous size as compared to other molecules. If the building up process is stopped at the right point, "nylon" can be made from the product.

How does the chemist obtain certain qualities in fabrics? These are common methods of treating fabrics.

1. *Giving a soft finish:* casein, soaps, waxes, fats, glycerin.
2. *Giving body stiffness:* starch, dextrin, gelatin, glue, gums.
3. *Preventing mildew and moth damage:* zinc chloride, cresols, boric acid, salicylic acid, or naphthenic oils.
4. *Filling and weighting of fabrics:* barium sulfate, magnesium silicate (talc), calcium sulfate, aluminum silicate (China clay), or calcium carbonate (whiting). Silk is weighted with the salts of the metals, tin, or iron. These salts also help to hold dyes and make fast colors.

How can you be sure that you get the kind of cloth you pay for? The finishing of textiles frequently covers up the fibers so they are not easily recognized. Inspection alone may not be sufficient to determine the quality. Chemistry enables us to uncover the true qualities that are so often concealed.

Various tests enable you to identify fibers. When a flame is applied to animal fibers, they give off the disagreeable odor of burning hair or feathers. They do not continue to burn when removed from the flame. They shrivel and a tarry residue collects in a knob at the ends of the threads. On the other hand, vegetable fibers when ignited continue to burn with an odor characterized as "burning rags."

If dry wool is heated in a test tube, water vapor is given off; ammonia and hydrogen sulfide are also driven off; both of these substances are characteristic of the decomposition of proteins by heat. When silk is heated, it liberates ammonia but no hydrogen sulfide since silk contains no sulfur.

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Table XII in the Appendix summarizes the action of various chemical reagents upon the five common textile fabrics.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. X, pp. 168-204, "Textiles."

HAYNES, WM. *This Chemical Age.* Chap. XVI, pp. 298-315, "New Fabrics, New Fibers."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XVI, pp. 186-197, "Silks and Cellulose."

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. VII, pp. 159-201, "All the Comforts of Home."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. VI, pp. 107-128.

STOKLEY, JAMES. *Science Remakes Our World.* Chap. V, pp. 48-58, "Chemical Clothes."

Putting Chemistry to Work

A

(1) How would you determine, without serious injury to it, whether your necktie is silk or some form of rayon? (2) If a mixed-fiber piece of cloth weighing 6 grams lost 2 grams when heated in hydrochloric acid, what percentage of silk did it contain? (3) "The savage discovers. The barbarian improves. The civilized man invents." Show that this is true with reference to clothing. (4) We already have much more than the savage. Why do we feel the necessity of further invention? (5) What do you consider the best advertisement for any merchant?

B

(6) How are vegetable fibers easily distinguished from animal fibers? (7) A mass of thread weighing 4.2 grams remained from a 21-gram piece of cloth, after being heated in a sodium hydroxide solution. Give the percentage of the two types of fibers in it. (8) Why is considerable skill required to distinguish cotton from linen? (9) Why are cotton and linen not reworked into textiles like woolen rags are? (10) Why is natural wool oily? What are some uses for lanolin? (11) Comment on this saying by Slosson: "At last man has risen to the level of the worm and can spin threads to suit himself." (12) Why is wool said to be "warm clothing"? (13) Explain how collodion serves us in several ways. (14) What can the consumer do to protect fair dealing? How can chemical knowledge help?

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Research and Activities That You Will Enjoy

A special report: Learn how *neocarmine W* is used in identifying the various textile fibers.

Interesting reports: (a) What is mineral wool? rock wool? How are they used in heat-insulating houses? Why is mineral wool used in packing nitric acid bottles for shipment? (b) See what you can learn about clothing made from spun glass.

Problem 61

WHAT MAKES IT POSSIBLE FOR YOU TO HAVE COLORFUL FABRICS?

For centuries dyes were obtained from natural products. Tyrian purple came from a sea snail; a scarlet dye came from the cochineal insect; a deep blue came from the indigo plant; turkey red, from the madder root; brown, from butternut hulls; and black, from logwood. Many of the natural dyes were dull or muddy in color. Those which were bright soon faded and lost their charm.

Chemists make better dyes than nature provides. In 1856 an English lad of seventeen was trying to prepare the drug, quinine, in the chemical laboratory. He unexpectedly obtained a beautiful violet dye which is known as mauve. William Perkin thus produced the first dye made by chemical means alone. Four years later the dye of the madder root, alizarin, was synthesized in the laboratory. These were the beginnings of a great industry.

For thirty-five centuries indigo held first place in the dyer's art because of its superior qualities. About four-fifths of the world's textiles have been dyed in dark colors. In India alone 1,500,000 acres were devoted to the culture of the indigo plant. In 1880 German chemists solved the problem of the preparation of indigo dye from naphthalene which we know as moth balls.

A comparison of natural and man-made dyes brings out the following facts.

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1. Man-made dyes (synthetic dyes) can be produced for about one-fifth the cost of the naturally grown article since by-products such as coal tar are used.

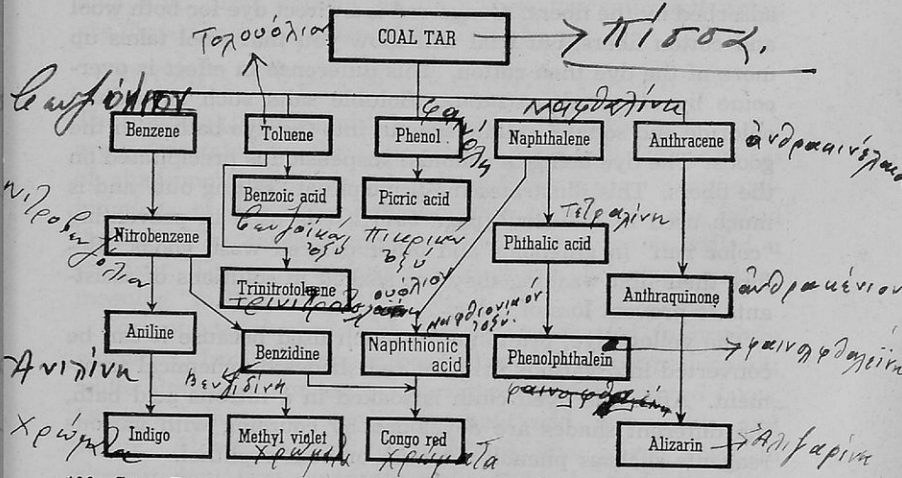
2. The average synthetic dye is much brighter in color than natural dyes.

3. Synthetic dyes are chemical compounds, so they are dependable and uniform in quality.

4. Nature has made less than 100 dyes; the chemical industry has produced over 5000, and the possible number is unlimited. Upwards of 1200 have been produced on a commercial scale. The greater part of these exist nowhere in nature.

5. By proper selection of synthetic dyes and modification of the dyeing operation, every color wished for can be made.

Chemists produce all colors of the rainbow from coal tar. When coal is destructively distilled to obtain coke, much volatile matter is driven off in gaseous form. From the gas a very odorous black liquid is condensed which is known as coal tar. It was



196. SOME PRODUCTS FROM COAL TAR. This chart shows some of the intermediate products in the course of producing dyes from coal tar. The products on the lower line are well-known dyes. Steps in their preparation can be traced by the arrows.

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once a troublesome waste product. Now it is a valuable source of dyes, drugs, perfumes, and explosives. The compounds given first (Fig. 196) are not present in coal tar but are formed during the distillation. The next products are known as intermediates from which the dyes are finally made.

The dyes which adhere to fabrics are called direct dyes. There are some coloring matters which dye cotton and other vegetable fibers in a neutral or alkaline solution without the aid of a fixing agent or mordant. They dye animal fibers in a similar manner and also in an acid bath. The direct dye stuffs are mainly used in cotton dyeing, and calico printing, and in dyeing artificial silk made by the viscose process. Certain direct dyes are used on wool which give fast colors. Prominent examples of direct dyes are Congo red, primuline yellow, diamine blue and diamine scarlet.

Some dyes need chemical assistants. Dyes are usually mixed with a liquid before they are applied. The dye particles are adsorbed by the fibers. Congo red is a direct dye for both wool and cotton fibers, but trial will show you that wool takes up more of the dye than cotton. This difference in effect is overcome by *chemical assistants*. Soluble salts such as sodium chloride and sodium sulfate are put into the dye bath with the goods. The dye being in colloidal suspension is precipitated on the fibers. This illustrates the principle of "salting out" and is much used in industry (page 507). It is used in preventing "color run" in ginghams and other colored wash goods. Before their first washing they are soaked in solutions of assistants to prevent loss of color.

The yellow dye, primuline, is much used because it can be converted into various brilliant red shades by chemical treatment. After the dyed cloth is soaked in a nitrous acid bath, the different shades are developed by coupling with various reagents such as phenol, resorcin, or beta-naphthol.

Some synthetic dyes have different colors under different conditions and serve as indicators. If a dye has one color in the presence of hydrogen ions (acid) and a different one in the

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presence of the hydroxyl ions (base), it may be used as an *indicator*. Litmus and red cabbage are vegetable indicators. Many dyes are so used. Congo red [$Na_2(C_{32}H_{22}N_6S_2O_6)$] is the sodium salt of a dibasic acid. It is a brilliant red in the presence of hydroxyl ions. Hydrogen ions change it to a dark blue. In cities where traces of acids are present in the air, goods dyed with congo red become dull by action of the acid changing the color. The color may be restored by dipping the goods in a dilute solution of washing powder or other mildly alkaline solution. If colored goods are stained by fruit juices, the result is similar and the remedy is the same. If alkaline solutions do not restore the color, the stain may be caused by the presence of the hydroxyl ion. If so, a trial test of dilute vinegar may remove the stain by restoring the color.

How chemists make color stay in vegetable fibers. Almost any dye is made fast in vegetable fibers by a cleverly devised process. First, the fiber is soaked in a soluble salt of chromium, aluminum, iron, copper, or tin. Then the saturated fibers are dipped into a solution of a soluble base:

$$Al_2(SO_4)_3 + 6\ NH_4OH \rightarrow 2\ Al(OH)_3 + 3(NH_4)_2SO_4$$

The colloidal particles of the dye carry a negative charge and are precipitated by the positively charged colloidal particles of aluminum hydroxide in the vegetable fibers. Such combinations of dyestuffs with insoluble hydroxides are called "lakes." The reagent combining with the dye is called a *mordant*. The word is derived from the French word *mordre* meaning "to bite."

Compounds of chromium are the most used to produce mordants. Iron and copper mordants are the most permanent; while aluminum and tin produce the brightest colored lakes. Other substances so used are tannic acid, fatty acids, and sulfur. Aluminum and tin mordants give a red color to alizarin dye; iron mordants make it black; and chromium turns it brown. Logwood takes different shades of blue with aluminum and chromium mordants and becomes black with iron salts.

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How "vat dyes" help solve the problem of fast colors for fabrics. The dye called indigo is insoluble when it shows its characteristic color. In this insoluble form it can be applied only to the outside of fibers as paint is put on wood. A knowledge of chemical properties again provides a solution of the problem. A soluble colorless form of indigo can be made by reducing it in an alkaline bath. This is done in large vats, hence the term "vat dyes." This *soluble* indigo penetrates the fibers. When exposed to air it combines with oxygen at once and becomes the insoluble blue dye. Many other dyes are likewise applied to fibers in a similar manner. They are fast to the highest degree in light and washing. Vat dyes are used for the best grades of cotton goods.

The dye factory may become a munitions plant over night. Since the first step in the manufacture of dyes consists in the preparation of nitro compounds, the operations are almost identical with those in the manufacture of explosives. In a few hours the equipment for making dyes can be converted to the preparation of high explosives for use in warfare.

Readings for Pleasure and Profit

FURNAS, C. C. *The Storehouse of Civilization.* Chap. IX, pp. 363-368, "Dyes."

HAYNES, WM. *This Chemical Age.* Chap. III, pp. 40-59, "Black Tar to Bright Dye."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XIX, pp. 223-232, "Born to the Purple."

HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. XXI, pp. 357-367, "Chemistry in the Textile Industry"; Vol. II, Chap. IV, pp. 58-81, "The Chemical Rainbow."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. II, Chap. XLV, pp. 1255-1284, "Dyestuffs and Their Application."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. IV, pp. 59-90, "Coal Tar Colors."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century.* Chap. XXI, pp. 310-333, "Production of Dyes."

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Putting Chemistry to Work

A

(1) Consider and state how your satisfaction of living would be affected if you should become completely color-blind. (2) Compare your opportunity for the use of color with that of a person of your age 100 years ago. To whom is credit due for your more colorful existence? (3) Is it fair to say that man is superior to nature in the making of colors? Explain.

B

(4) Many dyes are not "fast colors" for vegetable fibers. How has the chemist remedied this defect? (5) Explain the basis of distinguishing fibers such as linen and cotton by the use of dyes. (6) Why was "Wearing the Purple" a sign of great wealth in ancient Rome? Why is it not still a sign of wealth today?

Research and Activities That You Will Enjoy

A report: After outside reading in a physics book on the subject of color, tell the class how color is related to the different wave lengths of light. Be sure to distinguish between pigments and colors. Is the color of a red dress in the object or in your eye or brain? Explain.

William Henry Perkin: You may wish to read and report the story of young William Henry Perkin's discovery of the first coal tar dye. You may wish to follow the history of the dye industry as control passed from England to Germany and finally to America.

Problem 62

HOW CAN CLOTHING BE CLEANED SATISFACTORILY?

The problem of keeping clothing clean and presentable is becoming more and more complicated. Where a few years ago a garment contained only one kind of fiber, now it may be made of a variety of fibers. As an example, one of the latest fabrics for men's suits consists of three kinds of fibers: wool for shape-keeping qualities, cotton for coolness, and rayon for luster effects. In cleaning such fabrics, it is necessary to make a careful study of the cleaning operations so the fabric will not be injured.

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Different methods are used to clean clothing. Dust and other dry dirt may lodge in the meshes of cloth. Mechanical brushing, beating, and suction are sufficient to remove nearly all of it. If the soiling material is plastic like mud or moist food, much of it can be removed mechanically when dry. Some quantity of it will still cling to the fibers to make noticeable spots that can be removed only by the use of some cleaning medium, generally a liquid. The first important property of such a liquid is its ability to wet the dirt and the fibers to be cleaned. When water is used, better results are obtained by adding soap. Other cleaning liquids are benzol and carbon tetrachloride.

How soap assists water in cleaning. The skin secretes an oil. This oil keeps the skin soft and pliable. Wherever clothing touches the skin, the oil with accumulated dirt rubs off and clings to the clothing. You have seen the behavior of water when sprinkled on a greasy surface. It collects in drops because "oil and water do not mix." From the molecular standpoint, the cohesion between the water molecules is so much greater than the adhesion between the water and the grease, that the water is pulled together in drops. Water alone cannot wash grease from clothing, for it clings to the fibers more than it does to water. By decreasing this cohesion or surface tension of water, soap makes the water more willing to take hold of the grease. This is the first stage in washing with soap.

The soap has now altered the properties of the water for the task of cleaning, but the grease still clings to the fibers more than it does to the water. The second effect begins when the clothing is rubbed or moved vigorously in warm soapy water. The heat and the vigorous moving change the grease to colloidal particles in the water, forming what is called an emulsion. The slippery soap mixture with its surface greatly increased by admixture with air bubbles (suds) spreads rapidly over the oil particles by adsorption, reducing their cohesion. They now remain as a stable emulsion with water and are washed away with it.

The dirt that was held to the fibers by the oil is now released. But the dirt is strongly adsorbed by soap, giving it a

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slippery coating, so its hold on the fibers is released. In the same way, the dirt is added to the colloidal mixture in the water and is washed away.

A new kind of detergent is now in use. The problem of effective washing with water is now attacked from a new angle. The soap industry has found a new arrangement of elements that forms a soluble cleaner irrespective of the metal salt that may be in the water. It is sodium lauryl sulfate [$NaCH_3(CH_2)_{10}CH_2SO_4$] and is given the short name of "Dreft." This is an example of a class of compounds called hymolal salts—*high mole*cular *alc*ohol salts. It forms suds profusely in cold water no matter what hard water is used with it, so softening processes are unnecessary.

Different fibers require different methods of cleaning. Animal fibers are seriously injured by soap and water at boiling temperatures. If they are washed with water, it must be only warm. Blankets and knitted goods are about the only wool or silk fabrics that are cleaned with water. Careful handling is required so they will not be stretched or shrunk out of shape. Machine handling that forces the water through the fabric (without rubbing) and rinsing in a whirling dryer are improved methods in washing.

The shrinking of washed garments is a common undesirable effect of washing with water. Purchasers of garments have been accustomed to allow for this by selecting a larger size. Now many cotton garments have been preshrunk so that there is little shrinking in the wash. The added process increases the cost of the garment.

For all colored goods the first cleaning problem is: How will the cleaning process affect the dye? Laundries must know this by experience (or test), or garments may be ruined. The cleaning processes become more technical as the nature of our clothing becomes more complex. Use of the products of a technical age requires technical skill in their maintenance. Here we are confronted with a dilemma. We must either acquire this technical skill for ourselves or pay the one who supplies it in service.

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Dry cleaning without water. Except for superficial sponging, soap and water cannot be used successfully to clean tailored garments of silk or wool. Other detergents are now in use. As early as 1848 a light oil of turpentine was used. Benzine soon came into use because of its cheapness. Benzol, the hydrocarbon (C_6H_6), was added to the list. Carbon tetrachloride is increasing in use because it is not expensive and because its nonflammable nature makes it safe. These liquids are excellent solvents of grease. They affect few dyes, cause no shrinkage, and cause no shift in paddings. They evaporate readily and can be recovered from vapor form for further use by adsorption on activated carbon. When garments are much soiled, a special soap free from water is dissolved in benzine to reinforce its detergent properties. Ammonia may also be used.

Each class of "spot" has its own solvent. Before garments are put into the benzine bath, a specially trained person examines them for stains and "spots." To the dry cleaner there is a difference between spots and stains. A spot, such as may be caused by ink, blood, or fruit juices, is not a stain until heat has been applied. As a stain, it cannot be removed without injury to the fabric.

The spot is laid on absorbent material and the cleaning liquid most effective for the kind of spot is applied first around the spot and then upon it. Any sponging is done toward the spot. Excess of the liquid passes into the absorbent material.

Kind of stain or spot	*Cleaner*
Sugar, glue, blood	Sponge with water
Grease, all kinds	Carbon tetrachloride
Paint and varnish	Special varnish remover
Fruit juices	Hot water, hydrogen peroxide
Ink, rust	Hypochlorites
Grass, gum	Alcohol, ether
Acids	Ammonia
Bases	Vinegar

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Readings for Pleasure and Profit

HOWE, H. E. *Chemistry in Industry.* Vol. II, Chap. XXI, pp. 360-377, "Soap—Cleanliness through Chemistry."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. II, Chap. XXXV, pp. 1034-1047, "Laundering."

U. S. DEPT. OF AGRICULTURE. *Farmers' Bulletin 1474.* "Stain Removal from Fabrics: Home Methods."

Putting Chemistry to Work

A

(1) To what extent does our clothing serve for protection and how much for our own pleasure? (2) To what extent is clothing an index of the person within? (3) How is water made more "willing" to do cleaning? Explain. (4) How does soap make an emulsion of oil and water permanent? (5) What precautions must be taken when removing spots with gasoline? (6) A paste of vinegar and salt removes rust from textiles. Explain. (7) Why do the sodium ions (of a soluble sodium salt) in water not interfere with the cleaning action of soap?

B

(8) How much do we depend on dress to show our personality and how much do we use our own individual qualities for this purpose? (9) Laundries have advertised that they do not use harmful hypochlorites in bleaching, only sodium chloride and electricity. What may be formed by the electrolysis of sodium chloride? (10) Some laundries advertise: "Absolutely no chemicals used." Can such a claim be justified? Explain. (11) If hard water is used in the laundry, a dull gray deposit may appear on the garments. Explain how this is formed and how it may be prevented. (12) What precautions are necessary in laundering nylon stockings?

Research and Activities That You Will Enjoy

A helpful chart: Prepare a set of directions showing how to remove spots of different types from fabrics. (See *Farmers' Bulletin, No. 1474* on removal of spots from clothing.)

A caution: What dangerous results may come from rubbing silk too vigorously while dry cleaning it with naphtha? What other precautions *must* you follow if you insist on dry cleaning at home with flammable cleaning agents?

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Problem 63

HOW ARE PLASTICS MADE AND USED?

You perhaps have seen athletes rub their shoes over rosin, or violinists rub their bows over the same kind of substance.

For generations mankind has found many ways for using the different substances known as resins. These are hard, glass-like, noncrystalline solids which are insoluble in water but soluble in many organic solvents. They are either softened or melted by heat. The resins include such materials as rosin from the turpentine pine tree; amber, a fossil resin from cone-bearing trees; copal and kauri, resins which are useful in making varnishes; and lac, the secretion of an insect, from which shellac is made.

As uses for natural resins increased, the supply became inadequate, and chemists became interested in the production of *synthetic resins,* now commonly called *plastics.* These materials resemble natural resins in appearance and behavior. The name plastic is used because the materials can be molded or pressed into intricate forms under heat or pressure or both. They were discovered in the chemical laboratory largely by accident and at first were considered a nuisance. Within the past quarter century they have assumed rapidly increasing importance. In times of metal shortage they become vital. For a great variety of purposes they are now used in the place of metals.

Plastics are closely associated with some of our artificial fabrics and are produced by building up large molecules from smaller ones. In fact among the materials used to produce "artificial fabrics" are some which make excellent plastics; for example, cellulose trinitrate used for celluloid.

What was the first successful plastic? It was about 1908 when Dr. L. H. Baekeland, an American chemist, began to produce a plastic and to adapt it to various useful purposes. It is made by forming a compound from formaldehyde and phenol (carbolic acid). The product, called *bakelite,* is inexpensive. It is

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light in weight, difficult to melt, "nonburnable," insoluble in ordinary solvents, and a good insulator. It can be molded easily into intricate shapes. Metal parts for electrical connections may readily be imbedded in bakelite.

Bakelite has been a leading plastic for more than twenty years during which time it has contributed to the development of the electrical industries and to the efficiency of the modern telephone. Automobiles use bakelite gears which are made by impregnating strong fabric with bakelite. Such gears are better for the purpose than the metal formerly used. You perhaps have used combs, handles for innumerable toilet articles, buttons, desk sets—all made of bakelite or a similar product. Bakelite is heat resistant and is not injured by water or chemical solvents; it is an excellent insulation material. Like the natural resins, bakelite is also the basis of important varnishes and lacquers.

How is bakelite made? The manufacture of bakelite and other plastics depends on building up large molecules from materials that have smaller molecules. The raw materials used to produce bakelite are formaldehyde, HCHO, and phenol, C_6H_5OH. These relatively simple molecules, under suitable conditions, readily form long chains or an intricate network of chains with interlocking cross connections. In this way giant molecules are built up with the properties of a resin.

In the manufacture of bakelite a water solution of formaldehyde is boiled with phenol in the presence of a catalyst such as sodium hydroxide or ammonia. After a time a product is obtained which, when subjected to heat and pressure in a mold, forms a solid which is not changed by the application of further heat, at least within ordinary temperatures. Coloring matter may be added, but colors are usually limited to the darker shades. The cost is normally low, and may be still further reduced by adding up to 40% wood flour, while at the same time the tensile strength is materially increased.

When the manufacture of bakelite was begun, phenol was obtained as a "by-product" in the manufacture of coke; phenol

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was called a *coal tar* product. Formaldehyde was obtained by the gentle oxidation of methyl alcohol, which in turn came from the distillation of wood. Both these raw materials were originally available in large quantity and at low cost. But the demand for both phenol and formaldehyde has far exceeded the supply from natural sources, so now both raw materials are produced synthetically in order that you may have an adequate supply of bakelite and other plastics.

How are other plastics made by polymerization reactions? You noted that bakelite is manufactured by making large molecules out of smaller ones. In this process, called "condensation," water is eliminated. Another method of building up large molecules to form plastics consists of polymerization, without the elimination of a molecule such as a water molecule.

A good example of this type of polymerization is found in the behavior of styrene, $C_6H_5 \cdot CH : CH_2$. This compound is a colorless mobile liquid whose molecules when heated unite with one another. The process may be repeated forming a "poly" plastic known as *lustron*. It is clear and glassy, particularly resistant to shock, and a very excellent insulating material. Several similar plastics are made.

The plastic known as *lucite* or plexiglas is also very clear and is sometimes used to replace glass in lenses and prisms. A bent rod of lucite may be used to throw light "around a corner," a behavior that is useful to dentists and physicians.

When any of these plastics are heated, they soften and flow, so they may be repeatedly subjected to the molding process. This behavior differs sharply from that of bakelite.

How is artificial rubber related to the plastics? Another development of the plastic industry is the making of various forms of artificial rubber. Artificial rubber is made by building up large molecules by the methods of condensation and polymerization. At least twenty-seven types of artificial rubber have been proposed. Some of them start with very simple raw materials; it is common to say that the starting points are such materials as air, water, coal, and limestone.

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Courtesy, Bureau of Agriculture

CONTOUR FARMING. To decrease the loss of soil by erosion, good farmers plow their fields "on the level." The water then does not gather enough force to wash away the soil.

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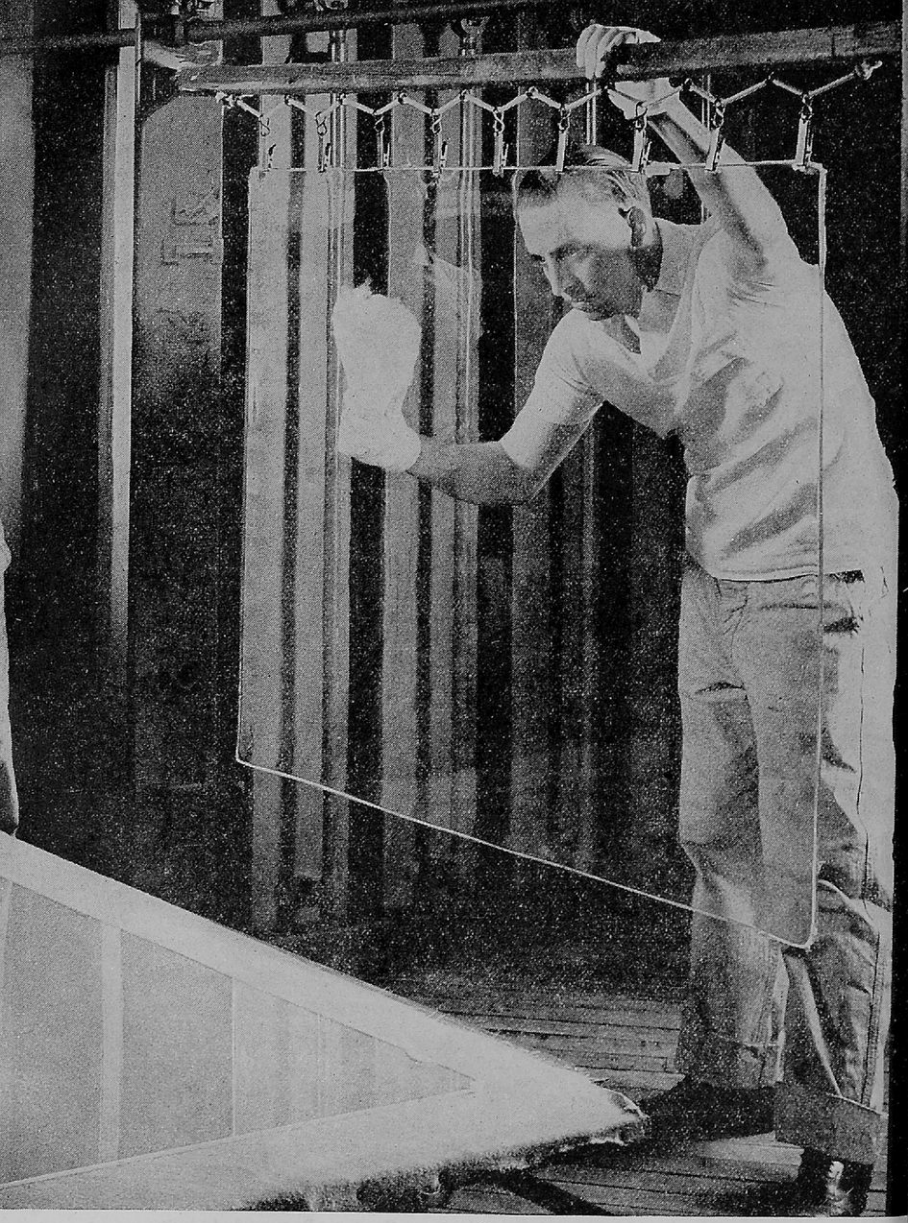

Courtesy, E. I. du Pont de Nemours and Co.

A Glass-like Plastic That Does Not Break Easily. Lucite sheets can be heated readily and shaped as required for cock-pit enclosures and noses for airplanes. Lucite also can conduct light around a curve and is used in making a combined tongue depressor and throat illuminator.

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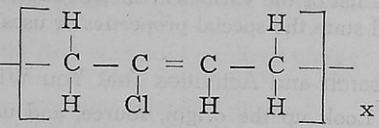
Neoprene or DuPrene is made by the polymerization of acetylene. At one stage in the process HCl is used, and this acid introduces chlorine which is retained in the finished product. The finished product is some multiple of the formula:



Neoprene resembles natural rubber in appearance and behavior and has the advantage of resisting deterioration due to age and disintegration caused by gasoline and oil. Facts concerning other artificial rubbers are summarized in Table XXIII in the Appendix.

Readings for Pleasure and Profit

HAYNES, WM. *This Chemical Age.* Chaps. IX-XII, pp. 168-225, "The Great Caoutchouc Mysteries"; "The Elastic Eldorado"; "Not Rubber, but Rubberlike"; Chaps. XVIII-XIX, pp. 316-352, "The Herald of the Plastic Age."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. VI, pp. 59-69, "Rubber from Tree and Test Tube"; Chap. IV, pp. 35-47, "The Realm of Plastics."

Synthetic Rubber, Chemical and Metallurgical Engineering, *49* [2] 113 (Feb. 1942) and [3] 78 (Mar. 1942); Industrial and Engineering Chem. News Edition *20* 536 (Apr. 25, 1942).

Putting Chemistry to Work

A

(1) Show the relationship between plastics and textiles.

(2) List various ways in which plastics may be used to relieve the shortage of metals.

(3) What different treatment would be necessary for making cellulose nitrate into fabrics and into plastics?

(4) List the articles in your room at home which are made of plastics.

(5) Explain and illustrate the following terms: polymerization, condensation, lacquer, polymer, copolymer.

B

(6) How are transparent umbrellas and raincoats made?

(7) What is bakelite varnish and for what purpose used?

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(8) Look up the methods of preparing acetylene, ethylene, methyl alcohol, formaldehyde, urea, and see if you can justify the statement that plastics and artificial rubber are made from air, water, coal, limestone, and other simple raw materials.

(9) Make a list of the various artificial rubbers which have been suggested and state the special properties or uses recommended for each.

Research and Activities That You Will Enjoy

A report. Look up the origin, source, and uses of the natural gums. Include their use in making varnish.

Interesting topics: (a) The characteristic facts about the American turpentine industry and the uses of rosin. (b) The synthetic production of phenol and formaldehyde. (c) The materials used for automobile lacquers. Give an example.

Looking Back into Unit 14

Be sure you know the purpose of this unit. Read again the material on page 564, "Looking Ahead into Unit 14." Then study the following Summary Test.

Summary Test

1. *What should you know about clothing?*
   (a) What kinds of textile fibers are used for clothing?
   (b) What are the kinds and sources—
      (1) Of animal fibers?
      (2) Of vegetable fibers?
   (c) How is rayon made?
   (d) How is nylon made and used? How is it different from rayon?
   (e) What finishing treatments are given to textiles?
   (f) How can you be sure that you are getting the kind of cloth you pay for?
2. *What makes it possible for you to have colorful fabrics?*
   (a) How has the chemist improved on natural dyes?
   (b) What chemical "assistants" has the chemist provided in dyeing? Explain.
   (c) How can some dyes be used as indicators?
   (d) Why can a dye factory become a munition plant almost overnight?
3. *How can clothing be cleaned satisfactorily?*
   (a) What different methods are used to clean clothing?
   (b) How do soaps assist water in cleaning?

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(c) Why do different kinds of fibers require different methods of cleaning?
(d) What is dry cleaning? How is it accomplished?

4. *How are plastics made and used?*
(a) What are the general properties of plastics? Name some natural resins.
(b) What was the first successful synthetic plastic?
(1) How is it made? How is it useful?
(c) How is polymerization related to plastics?
(d) What are the names of some types of synthetic rubber?
(1) For what purposes are some types of synthetic rubber better than natural rubber?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related*, the principles should be understood and *applied*.

Closing the Unit

In this unit you have encountered some of the most important developments in present-day existence: the new fabrics, the dyes with which they are colored, the successful cleaning of clothing, the plastics, and artificial rubber. These are among the most vital requirements in our national life. If you could find no other reason for studying chemistry, the material in this unit would be of sufficient importance to justify the effort.

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Looking Ahead into

Unit Fifteen

Air, water, and earth—you are vitally dependent upon all three. You know that air supplies oxygen for your breathing and for fires and that it supplies carbon dioxide for plants. You know that water is necessary for life. Do you know how you are also dependent upon the "good earth"?

The earth is your physical home. It is your source of mineral substances. You may push your head into the clouds and explore with your mind and imagination the realms beyond, but you must keep your feet on the ground—only the "good earth" can support you. It is mantled with soil in which the food plants grow.

Industry is dependent upon the earth as a source of indispensable raw materials. The earth supplies mineral fuels, various salts which were laid down from ancient oceans by evaporation, building stones, and ores from which come the metals demanded by an industrial age.

The earth has had a long time—perhaps millions of years—to build up a reserve supply of materials. These natural resources will undoubtedly last for a long time to come, but they are not limitless. Conservation of natural resources is a problem of which every thinking person should be aware.

Problem 64. *How Can the Good Earth Continue to Feed You Well?*

Problem 65. *How Does the Good Earth Supply the Building Industry with Its Materials?*

Problem 66. *How Does Industry Get Some of Its Most Needed Chemicals from the Good Earth?*

Problem 67. *Silicon Is the Good Earth's Second Most Common Element. What Should You Know about This Element and Its Compounds?*

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The Good Earth: How the Good Earth Feeds and Shelters You and Furnishes You with Useful Chemicals and Industrial Products

Problem 64

HOW CAN THE GOOD EARTH CONTINUE TO FEED YOU WELL?

All animals are dependent upon plants for food—either directly or indirectly. The home of plants is the soil; it is their source of mineral substances. You depend upon the Good Earth for the nourishment which sustains your life. Chemically, you are unalterably tied to the soil.

The farmer should grow crops that suit his soil. Soils are formed by the decay of organic matter and by the weathering of different kinds of rocks. There are, therefore, different kinds of soils. The farmer should raise crops that can grow satisfactorily in the soil on his farm. Common kinds of soil include:

Clay soils—Hard, finely divided, sticky; formed from the weathering of slates, shales, and rocks containing feldspar.

Sandy soils—Light, coarse, porous; formed from the weathering of sandstone or granite.

Humus—Formed by the decomposition of organic matter.

Loam—A mixture of clay and sand containing humus.

Since most soil has been transported from the place where it originated, the average soil is a mixture of these different soil types.

Loam soil has a characteristic dark color. When it contains a sufficient amount of humus it is generally considered the most desirable type of soil.

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Humus improves the texture of most soils by keeping them porous so they do not become too compact. However, humus improves sandy soil by increasing its ability to retain water. Humus also aids in bringing about the solution of essential minerals in the soil and in the development of the necessary soil microörganisms.

On what does a plant feed? Plants feed on carbon dioxide from the air, water taken in through the roots, and small amounts of mineral matter dissolved in the water. Less than twenty elements are considered necessary for plant life. Of these necessary elements, nitrogen, phosphorus, and potassium are three elements whose compounds are frequently lacking in soils.

Nitrogen is built into the protein of the plant. The healthy green color in growing plants is attributed to a sufficient supply of nitrogen. A lack of it produces yellow plants with stunted growth. Much of the nitrogen in a plant generally finds its way to the seed. Too much nitrogen may extend the growing season. This may cause too dense a growth of foliage and retard the maturing of the seed or fruit of the plant, consequently decreasing the yield.

Phosphorus also becomes a constituent part of the protein of the plant. It stimulates early growth and balances the nitrogen by hastening the maturity of the plant and increasing seed production. Phosphorus also becomes an important part of the seed.

Potassium is not a constituent part of starches and sugars, but it does play an important part in their formation. Such root crops as beets and potatoes do not produce satisfactory yields if this element is lacking. It is said that plants grown on potassium-deficient soils are more susceptible to disease.

Calcium enters into the formation of cell tissue and the woody fiber of the plant. It is especially required by leguminous crops, such as peas, beans, clover, and alfalfa.

In considerably less amounts, *sulfur, iron,* and *magnesium* are essential plant foods. Sulfur is a necessary constituent of some proteins. Iron and magnesium are essential to

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chlorophyll formation. Magnesium also appears to influence the effectiveness of phosphorus.

Why do soils go wrong? Analyses of soils may show a large supply of the essential plant food elements, but nature has wisely made this plant food available in small amounts each successive year. Continued cropping of a soil, with no consideration of the loss of mineral matter taken out by the plants, leads sooner or later to serious crop losses. Wheat contains almost two per cent of ash (mineral matter)—about three-fourths of which is potassium phosphate. When a farmer sells 100 pounds of wheat, he is selling 1½ pounds of potassium phosphate taken from his farm. This must be returned to the soil if he is to maintain its fertility.

Soils also may become useless for agricultural purposes because of waterlogging, lack of rainfall, dust storms, lack of humus, and soil acidity.

One of the most common causes of curtailed crop production is soil acidity. This may be due to the formation of acids in the soil through natural processes. Carbon dioxide dissolves readily in water to form carbonic acid which changes insoluble carbonates into soluble bicarbonates (page 438). Complex silicates may make soil acidic. Decaying organic matter and some commercial fertilizers, such as potassium chloride, tend to increase soil acidity. An acid (sour) soil is often characterized by the growth of redtop and various "sour" grasses.

Why should lime be applied to some soils? Lime is good for acid soils. Soils which have a limestone origin are excellent for many plants, especially clover and similar leguminous crops and root crops. If a soil is deficient in lime, some form of it should be applied. The most common corrective in use is finely ground limestone which is mainly calcium carbonate, but may contain some magnesium carbonate. If hydrated lime [$Ca(OH)_2$] is used, it should be applied in a finely ground form or left in piles in the field where it will air-slake by taking on carbon dioxide. Care must be used to avoid adding an excess of lime to soil since it may destroy the humus.

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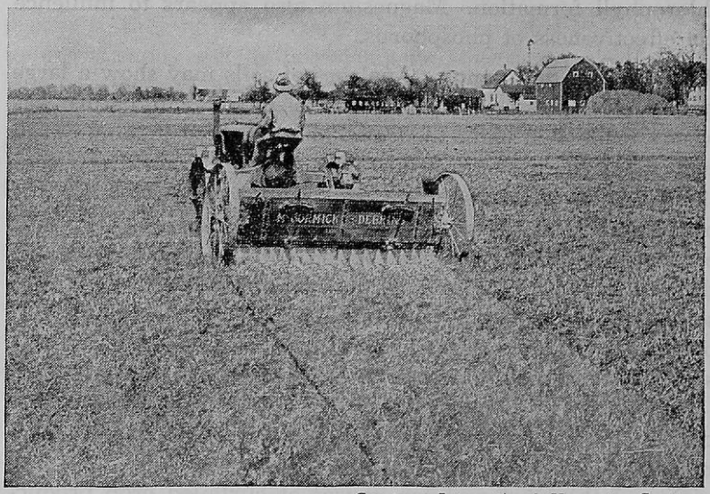

Courtesy, International Harvester Company

197. APPLYING LIMESTONE TO SOIL. Where soil is too acidic, its condition can be remedied by the application of lime or finely ground limestone to neutralize the acid.

How can the farmer keep his soil producing? Successful farmers use various methods of maintaining soil fertility. The oldest and still one of the best methods is utilizing all barnyard manures. Plowing under growing green crops, known as green manures, is an excellent supplement. Leguminous crops may be grown for green manures and also to build up the nitrogen content of the soil. In the last 50 years commercial or chemical fertilizers have become almost a necessity on many farms. An examination of successful farming shows that a combination of these practices is used, together with a wise rotation of the various crops. This insures a more balanced removal and replacement of the essential plant foods.

Barnyard and green manures contain the most necessary fertilizing elements, nitrogen, phosphorus, and potassium, although usually the phosphorus is not present in large enough quantities and should be supplemented with "superphosphate."

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Courtesy, International Harvester Company

198. A MANURE SPREADER. The commonest form of fertilizer in use is barnyard manure. Here it is being spread on the soil.

It is best to apply fresh manure to the soil before the soluble fertilizing compounds have been leached (washed) out. Aged manure may have a higher content of fertilizing elements per ton, but much loss has resulted when one considers that several tons of fresh manure are necessary to yield a ton of aged manure. Then, too, the fresh manure furnishes a great deal of humus to the soil.

Green manures are such crops as clover, rye, vetch, alfalfa, and soy beans. They are plowed under while still green. While they do add some fertilizing substances, they greatly improve the texture of the soil by the addition of humus. Most of these crops are *legumes*, which have the ability to withdraw nitrogen from the air (page 366). This nitrogen is not only built into the main plant structure but is deposited as soluble nitrogen compounds in nodules on the roots. Certain nitrogen-fixing organisms must be present to produce satisfactory growth of these plants and to bring about this fixation of the nitrogen.

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Courtesy, Swift & Co., photo, Kaufmann & Fabry Co.

199. How Deficient Soils Affect a Plant. Note the plant whose soil contains all the necessary elements.

Why does the farmer use commercial fertilizers? Soil may need some essential plant foods which the farm does not produce. Then the farmer should resort to commercial fertilizers. These may be organic substances such as vegetable wastes and the by-products of slaughter houses and fish-packing plants, or they may be mixtures of inorganic compounds containing nitrogen, phosphorus, and potassium.

Nitrogen fertilizers. Among the first nitrogen fertilizers used by American farmers were sodium nitrate and guano from South America. Guano is the combined refuse and carcasses of birds along the Pacific Coast of South America, which had been depositing for centuries; it has been practically exhausted. Chile saltpeter, or sodium nitrate, occurs in vast deposits in Chile and forms one of its greatest export industries. The crude rock deposit is called caliche. It is mined and crushed, and the sodium nitrate is dissolved out and allowed to crystallize. Prior to 1914, Chilean nitrate furnished more nitrogen fertilizer than all other sources combined.

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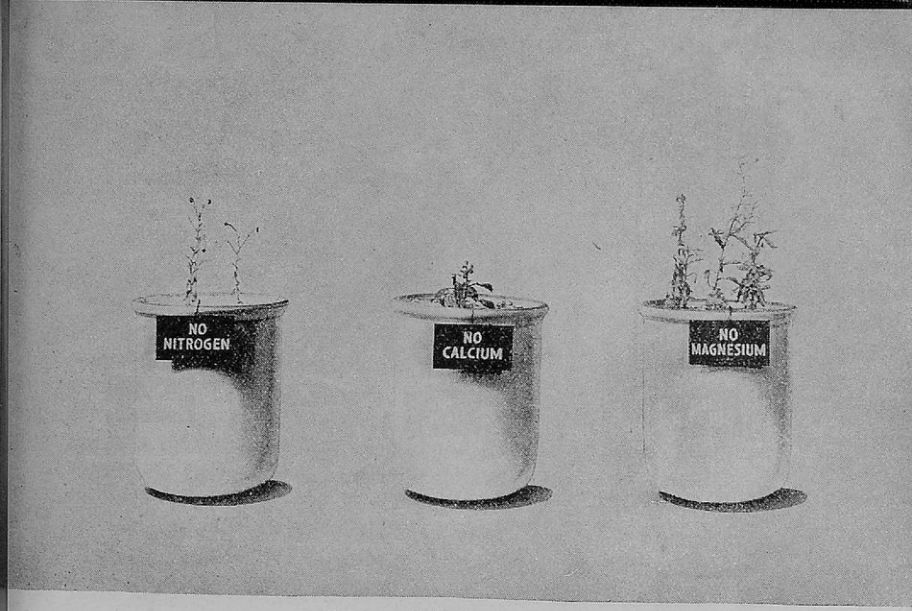

Courtesy, Swift & Co., photo, Kaufmann & Fabry Co.

200. How Deficient Soils Affect a Plant. Compare the different plants shown in figures 199, 200, and 201.

Today a great deal of sodium nitrate is manufactured in the United States by neutralizing sodium hydroxide with nitric acid, the latter being prepared from atmospheric nitrogen. You already have learned of the preparation of ammonium sulfate fertilizer in connection with the manufacture of coke (page 429). Ammonium sulfate led the field of nitrogen fertilizers in 1918, but now nitrogen fertilizers prepared from fixation processes are more important.

Nitrogen is commonly used by the plant in the nitrate form. Bacteria in the soil convert other nitrogen compounds, such as ammonia, to the nitrates. Since these bacteria require a warm soil, nitrate fertilizers are better for early spring use than other nitrogen fertilizers. Later in the season one is as good as the other. Calcium cyanamide ($CaCN_2$, page 371) is a valuable nitrogen fertilizer. However, its use is limited because in large amounts it has a toxic effect on the soil.

The trade names of important nitrogen fertilizers include: dried blood, tankage (animal refuse from which fat has been removed), bone meal (ground bones), cottonseed meal (ground

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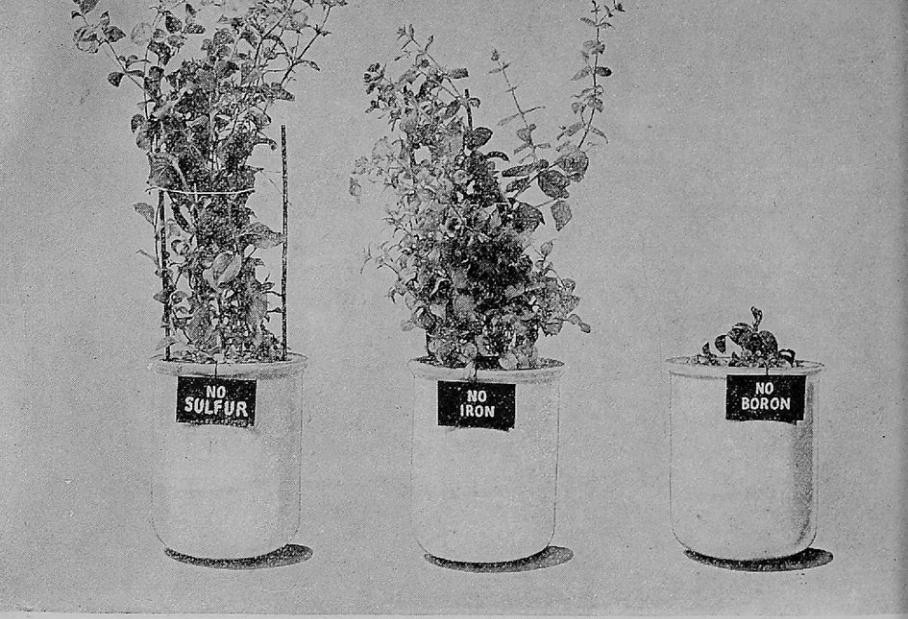

Courtesy, Swift & Co., photo, Kaufmann & Fabry Co.

201. How Deficient Soils Affect a Plant. Does iron or sulfur have as much effect on the growth of this particular plant as other elements have?

cottonseed), cyanamide (calcium cyanamide), nitrate of lime (calcium nitrate), sulfate of ammonia (ammonium sulfate), Chile saltpeter or nitrate of soda (sodium nitrate).

Phosphorus fertilizers. Phosphate rock, containing calcium phosphate, is widely scattered over the earth. The supply in this country is estimated to be around ten billion tons. To date most of the phosphate rock has come from eastern United States sources, but vast deposits are also found in several western states (Idaho, Montana, Wyoming, Utah, and in the Rocky Mountain region). In areas close to the rock phosphate mines, the finely ground, untreated rock may be effectively used, although in this insoluble form phosphorus is not available until the calcium phosphate is acted upon by soil acids. In all other regions it is more economical to buy the higher grade, treated material known as the "superphosphate" form.

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In manufacturing this, the finely ground phosphate rock is treated with sulfuric acid to form the *soluble* monocalcium phosphate. The calcium sulfate which does not change, may be left in the fertilizer, or it may be partially removed with the inert materials:

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \rightarrow \underbrace{Ca(H_2PO_4)_2 + 2\,CaSO_4}_{\text{superphosphate}}$$

The superphosphate hardens very quickly and later is finely ground and bagged for the market. A new process, employed by TVA for making superphosphate, eliminates the use of sulfuric acid and may make this type of fertilizer available to farmers at reduced cost. Another source of phosphorus, available for plants, is the basic slag from steel manufacture; it is more important in European countries than here. The trade names of important phosphate fertilizers include: rock phosphate [impure $Ca_3(PO_4)_2$], superphosphate [$Ca(H_2PO_4)_2$], superphosphate mixture [$Ca(H_2PO_4)_2$, $CaHPO_4$ and $CaSO_4$], bone meal [$Ca_3(PO_4)_2$ and N compounds], bone black [$Ca_3(PO_4)_2$ and C], basic slag [$Ca_4P_2O_9$ and $CaSiO_3$].

Potassium fertilizers. Clay and loam soils have large supplies of potassium tied up in insoluble minerals. The potassium slowly becomes available, but not fast enough for the demands of twentieth-century agriculture. Up until 1914, the deposits of potassium salts in Stassfurt, a region between Germany and France, were furnishing the world with practically all of its potassium fertilizers. When the World War cut off that supply, the United States found deposits at home. Development of these was started but later abandoned. At the present time, some potassium chloride is being taken from salts evaporated from Searles Lake in the arid region near Death Valley, southern California. Another vast deposit of potassium salts, with from 5 to 23 per cent potash, underlies western Texas and southeastern New Mexico at depths varying from 350 to 1800 feet below the surface. Much of it occurs as polyhalite, a mixed sulfate of potassium, calcium, and magnesium.

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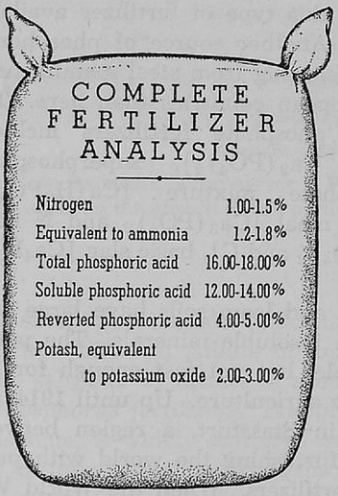
Many potassium fertilizers are mixed salts whose low cost tends to hold down the use of the more expensive but higher purity fertilizers. Hardwood ashes, containing potassium carbonate, have long been used for their potash content, but this source is now very limited. Tobacco waste and sugar factory wastes contain worth-while amounts of potash, and the tobacco contains some nitrogen and phosphorus. Some of the trade names of potassium fertilizers are: muriate of potash (KCl), trona potash (KCl), sulfate of potash (K_2SO_4), kainit (crude mixture), hardwood ashes (K_2CO_3).



The manufacturers of commercial fertilizers are required to put on the label the analysis which shows the active ingredients in the fertilizer. This enables farmers to choose the proper fertilizer. Can you see that this means that the farmer should have some chemical knowledge to use fertilizers successfully? Chemistry is entering more and more into the everyday life of everyone. Here our daily bread depends upon the intelligent use of chemical principles.

202. THE LABEL ON THE BAG TELLS THE STORY

The farmer should buy fertilizers "with his eyes open"; every bag of fertilizer contains a statement of what is in the bag. When commercial fertilizers became the "fashion," the farmer was exploited due to his lack of information and to unfair practices of manufacturers. At first most of these fertilizers were composed of animal wastes, but gradually chemicals were added. Since at first the farmer could not distinguish low-

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grade from high-grade fertilizers, certain government requirements were made. Now it is necessary for the manufacturers to put an analysis statement on every bag of fertilizer (Fig. 202).

The analysis of a fertilizer is made on the basis of available plant food. The nitrogen content is expressed as the percentage of either nitrogen or ammonia (NH_3), phosphorus as phosphorus pentoxide (P_2O_5), and potassium as potash (K_2O). Complete fertilizers are designated in such ratio as 1, 8, 2, which means that they contain 1 per cent of nitrogen, 8 per cent of available phosphorus (P_2O_5), and 2 per cent of water-soluble potassium (K_2O). In some states 1 per cent of ammonia is still used as the basis of nitrogen content.

How can the farmer raise better crops by controlling plant diseases and pests? The farmer should co-operate with government agencies to find methods of agriculture which help control plant diseases and pests. For the control of many diseases and pests, co-operative methods are more valuable than individual action. The farmer can, however, largely control many of the plant diseases and pests by his individual efforts to save his own crops from loss.

How chewing and lapping insects may be controlled. For chewing and lapping insects, stomach poisons must be applied in the dust or liquid form. Most common insecticides for insects of this type have been *arsenical poisons* such as lead arsenate. It can be mixed with other sprays and applied with water or as a dust. Calcium arsenate is used principally on cotton. Sodium fluosilicate is a new insecticide used to advantage against the Mexican bean beetle. Paris green [$Cu(C_2H_3O_2)_2 \cdot Cu_3(AsO_3)_2$] is an older stomach poison which was first used to combat the Colorado potato beetle in 1865. If arsenical poisons are too concentrated or too soluble, they may "burn" the foliage of the plant.

In the development of arsenical sprays, efforts have been made to improve the "sticking" properties of the sprays so that rain will not wash them off. However, arsenical poisons are poisonous to human beings. For this reason chemists

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Courtesy, International Harvester Company

203. SPRAYING AN ORCHARD. The fruitgrower must constantly fight insect pests in his orchards. Here a poisonous mixture is being sprayed on trees. This may leave poison on the fruit. Always wash your fruit before eating it.

have searched for an insecticide which would be a "specific" (poison) for insects but harmless to animals and man. *Hellebore,* made from the powdered root of the white hellebore plant, is poisonous to insects but not to man or animals. One of the more recent and valuable stomach poisons that is almost harmless to animals and humans is an organic compound called pheno-thiazine.

How sucking insects may be controlled. For sucking insects, there is no completely satisfactory method of control before the time of attack. They must be killed by *contact poisons* in spray or dust form. These poisons kill by entering the body as liquids or gases to produce a harmful chemical reaction on the body contents. Sometimes the spray or dust enters the breathing tubes and smothers the insects. Nicotine or nicotine sulfate under various trade names

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such as *Black Leaf 40* are used effectively. Very finely powdered sulfur or lime sulfur, a complex mixture of compounds resulting from heating lime and sulfur, are also effective either as dust or in water. Oil emulsions, such as kerosene, soap, and water, are used to advantage in some cases. Contact insecticides should have the property of sticking when applied and they must cover the insect to be effective.

One of the most promising organic contact sprays has a simple organic structure consisting of a chain of twelve carbon atoms with a terminal CNS group. Its trade name is *Loro*, and chemically it is lauryl rhodanate or lauryl thiocyanate. This simple "12-carbon" chain has some special virtue as a contact insecticide which other similar compounds do not seem to possess.

Because volatility is desirable, organic sprays for flies consist of shorter carbon chain compounds. Such a spray, upon striking the fly, paralyzes it and kills it.

Insects enclosed in greenhouses or bins may be killed by fumigation with hydrocyanic acid, carbon disulfide, nicotine, or sulfur dioxide. Each of these poisons has specific directions and adaptations which must be known and followed. Grasshoppers, cutworms, army worms, and flies may be destroyed by poison baits in which strong stomach poisons are mixed with materials known to be attractive to them.

How plant diseases may be controlled by chemical treatment. Chemicals used in the treatment of plant diseases are protective measures. Many sprays are not effective unless they are applied before the fungus has established itself on the host. Sulfur and lime-sulfur are excellent fungicides. A spray fungicide must be applied as a fine mist so that the plant is entirely covered with a thin film. If a fungicide is to be applied as a dust or powder, it should be very finely divided and should be dusted on the plant while it is covered with dew.

Of the effective copper fungicides, Bordeaux mixture is probably the best known. It is made by mixing copper sulfate, lime, and water, the proportions of each depending upon the type of plant and the use to which it is to be put. The

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copper sprays are more powerful than the sulfur sprays and therefore cannot be applied to all plants or at all times of the growing season. Each plant and its particular disease, whether a mold, mildew, rust, or smut must be studied and the grower must rely upon the findings of experimental stations and reputable authorities as to spray materials and the most effective time for spraying.

Seeds and such tubers as potatoes are often soaked in, or sprayed with, formaldehyde to insure disease-free conditions at planting time.

Readings for Pleasure and Profit

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XIII, pp. 195-197, "Soil Bacteria"; Chap. XVII, pp. 261-270, "Rocks, Clay, and Soil"; Chap. XXIII, pp. 382-399, "Plant Food; Diseases and Pests."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XVII, pp. 198-209, "Man against Pigmy"; Chap. XXVII, pp. 305-315, "The Farm as a Factory."

HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. VIII, pp. 103-118, "Chemistry in the Fertilizer Industry."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XXI, pp. 559-589, "Fertilizers."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. II, pp. 21-23, "Nitrogen Fixation"; Chap. III, pp. 34-58, "Feeding the Soil."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. VII, pp. 70-84, "Chemistry and the Farmer."

Applying in Life What You Have Learned in Chemistry

"That's queer," said Gerald. "We were told in the unit on health to eat fruits with their skins on. Now we learn that most fruits are sprayed with poisonous insecticides. I don't like it."

"That's easy," answered Nancy. "Why don't you . . . ?"

Can you finish Nancy's suggestion?

What do you think of a very dilute hydrochloric acid bath for all sprayed fruits?

Suppose your father brought home a sample of lawn fertilizer marked, "10-6-4." He does not know what it means. Tell him about it.

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You inherit a farm. You soon find that the land has been "overcropped" and robbed of its fertility. How would you go about building up the soil?

A farm hand who was making Bordeaux mixture dissolved the copper sulfate in an iron kettle. How would you explain his error to him?

Calcium arsenate has been dusted on cotton fields from airplanes to combat the boll weevil. Do you consider this an extravagantly wasteful method? Explain.

Putting Chemistry to Work

A

(1) Food is sometimes considered the third essential to man. What are the first two essentials? (2) Can plants grow on rocks? Give reasons. (3) Soils are made principally from rocks. Explain how briefly. (4) Why can plants use the minerals in soils more readily than those in rocks. (5) How did soils improve with the continual growth of plants before man began to use them? (6) How may a soil contain the necessary plant food elements yet produce a poor crop? (7) Why is a fertilizer called *complete* when it contains only *three* necessary plant food elements? (8) Which of the three elements, nitrogen, phosphorus, and potassium is likely to be exhausted first?

(9) Account for the increased demand for commercial fertilizers. (10) Commercial fertilizers put on sandy soil often wash away without doing much good. Explain. (11) Soy beans are being widely planted in our prairie states. What effect should they have on soil fertility? (12) What do you think of potassium ammonium hydrogen phosphate (KNH_4HPO_4) as a "concentrated" fertilizer?

B

(13) How does the fertilizer industry use sulfuric acid? (14) Explain how bacteria are related to the rotation-of-crops practice. (15) Why are legume crops especially valuable as green manure? (16) What single word can you use to replace the term "organic plant food"? (17) Potassium compounds on a nichrome wire in a flame give a violet color when viewed through a blue glass. How could you use this test to detect potassium compounds in plants? (18) Distinguish between *insecticides* and *fungicides*. List a few of each. (19) For what condition would you use Bordeaux mixture?

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(20) "In the battle for supremacy of man over insects, the chemist is on the front lines." Point out some of the chemist's problems in this fight. Why must he have our co-operation? (21) What are the seven plant food elements most generally considered essential to satisfactory plant growth? How do these elements affect plant growth in general?

Research and Activities That You Will Enjoy

"Where's-the-enemy" talk: Prepare and present a talk using the theme: "The United States each year is suffering from the attacks of invaders to whom it pays tribute to the tune of almost two billion dollars. The enemy I refer to is the ever-increasing insect horde which threatens our lives, homes, crops, and forests. As a nation, we are not yet aware of the danger, although many of us are beginning to suspect vaguely that a tremendous contest is taking place."[1]

A "vigilante" forum: Organize a small group of interested students to learn facts and prepare recommendations on the "insect pest situation." One student may visit a gardener to learn about insect pests and plant diseases, another may visit a seed store to learn about types of insecticides and fungicides, while another may make appropriate posters "Declaring War," and so on. Then combine and summarize the reports for the class. Invite additional class suggestions.

Reported interviews: (a) If possible, talk with a prosperous farmer or nurseryman to get his ideas on maintaining soil fertility. (b) Visit a farmer or seed store in your vicinity to learn what the most common fertilizers are. Try to learn also their trade names and compositions.

Special reports: (a) The simple geology of igneous, sedimentary, and metamorphic rocks. (b) Types of soil in your vicinity and their origin. To what types of crops are they best fitted? (c) See if you can locate some acid soil to demonstrate to the class how you test it. Suggest a remedy. (d) "Soil-less" gardening. (e) Procedures through the ages in the use of "fallow ground." (f) What kind of plants have you seen growing on rocks? Ask a biology instructor about lichens and algae. Tell how they grow.

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[1] "Insect Friends and Foes," by Dunn, in *Popular Science Talks*, Vol. X. (Philadelphia College of Pharmacy.)

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Problem 65

HOW DOES THE GOOD EARTH SUPPLY THE BUILDING INDUSTRY WITH ITS MATERIALS?

The good earth supplied the wood used in your home. Wood is still used to a great extent in the construction of homes and other buildings. Wood demands care. It is subject to weathering and decay and requires periodic painting. Wood is subject to the ravages of dry rot and insect pests (termites) which undermine from within. One of the greatest users of wood, the railroads, now seek to preserve their ties and poles by impregnating the wood with coal tar creosote. Zinc chloride, sodium fluoride, and a few other chemicals are also employed as wood preservatives.

Unless the United States seeks a better balance between use of its wood supply and reforestation, the future of the wooden American home seems doomed.

The good earth supplied the stone used in your school building. Many buildings in the United States are built of various kinds of stone such as sandstone, limestone, marble, or granite, depending on the tastes or whims of the architects and builders.

Sandstone is a sedimentary rock, formed by the settling and natural cementing of sand. The "wearing qualities" of sandstone depend a great deal on how tightly the binding material (mortar) holds the stones together. Besides its use in buildings, sandstone is also used for grindstones, millstones, flagstones, crushed stone for road construction, and ballast. Many of the early railroad and highway bridges were constructed of this substance. Sandstone is found in limited sections in Ohio, Pennsylvania, New York, and California.

Limestone for building purposes is quarried mainly in Indiana, Missouri, Minnesota, and Kentucky. It is impure calcium carbonate. Its colors and varying degrees of hardness indicate the impurities, which may be iron oxide, silica, clay, or carbonaceous matter. At the time of quarrying, both

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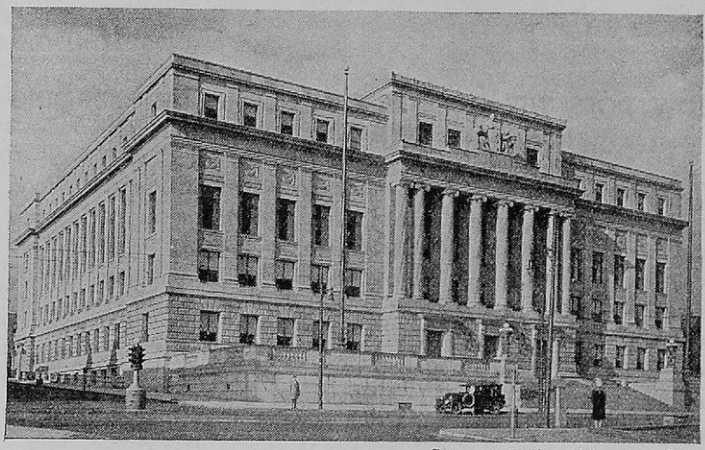

Courtesy, Indiana Limestone Corp.

204. LIMESTONE AS A BUILDING MATERIAL. Limestone is one of our commonest building materials. This beautiful building is made of Indiana limestone.

limestone and sandstone contain much water which makes them more easily workable. As they dry out, soluble cementing materials deposit and make the stones more durable and less workable. Some famous limestone structures are the Washington Cathedral, Radio City in New York City, City Hall in Chicago, and Terminal Station in Cleveland. Pennsylvania, Michigan, and Ohio produce much limestone for other purposes such as crushed stone for road construction, Portland cement, flux in the purification of metals, lime, and many others.

Marbles from a chemical standpoint are highly crystalline formations that have developed by the action of heat and pressure upon limestones and dolomite ($CaCO_3 \cdot MgCO_3$). From a commercial standpoint marble is any limestone, whether crystalline or not, that will take a high polish and will give pleasing color effects. The variety of colors and designs of polished marble make it very valuable for interior

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finish. One of the most noted marble interiors is that of the Staircase and Reading Room of the Congressional Library at Washington. Other notable marble structures are the Lincoln Memorial at Washington, the Amphitheater at Arlington Cemetery, and the New York Public Library. Vermont leads in marble production, but quarries are found in Georgia, Tennessee, New York, and Colorado.

Granite is an igneous rock consisting of a mixture of feldspar, quartz, and some mica. Maine, Vermont, Massachusetts, California, and North Carolina have the principal quarries. Granite offers several colors including white, gray, brown, and green. It has great strength and durability and takes a high polish, making it especially valuable for monuments, statues, and high-class building. Often the lower stories of high buildings are constructed of granite. Paving blocks of granite are used in some cities on streets that must withstand heavy trucking traffic.

Slate has played an important part in the building industry as a roofing material. It is a metamorphic rock derived from clays. It has the advantage of cleaving in quite definite lines. Its colors include red, blue, black, purple, and green. Pennsylvania is the chief producing state. Slate, known as "mill stock" is used for blackboards, flooring, vats, tubs, table tops, and the like.

Artificial building materials. Cement is an artificial building material that has quite revolutionized the building and construction industry. Cement is discussed later.

The good earth supplied the mortar used between the bricks and stones of your school. From the beginning of building with hand-laid stones or bricks, lime has entered into the mortar with which these stones or bricks were laid up. Ordinary mortar is made by mixing *hydrated lime* with sand and water. Upon standing, the water evaporates and the calcium hydroxide reacts with carbon dioxide of the air to form calcium carbonate. The surface becomes very hard and strong with age. Today cement is being used in some cases to replace the lime.

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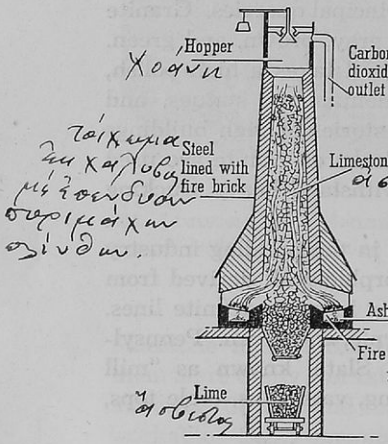
Lime is also used in the making of some plasters, stuccoes, and finishing coats.

How lime is produced. Many references have been made to the uses of lime. It is said that lime burning is one of the oldest industries of mankind. Lime made by heating a charge of limestone and coke in a limekiln (similar to a blast furnace) is known under various names as quicklime, live lime, or caustic lime.



This is a common type of limekiln. Limestone is fed into the kiln from the top. Fire is kept in the firebox and the heat rises through the limestone. This heat causes the decomposition of the limestone into lime (CaO) and carbon dioxide. The carbon dioxide passes out at the top, and the lime collects at the bottom from which it can be removed. Coal, gas, or oil may be used as fuel.

205. VERTICAL LIMEKILN

Figure 205 gives a diagram of a modern limekiln of the vertical shaft type. In some kilns of this type, limestone of fairly uniform size is charged in at the top of the furnace. Coke is frequently used as fuel although gas, oil, or pulverized coal may be used. Air is admitted from the bottom, at the center, and sides of the kiln. The burning coke produces heat to decompose the limestone to calcium oxide and carbon dioxide. The point of greatest heat (1050° C.) is about one-fourth of the distance from the point where air is admitted. Carbon dioxide is withdrawn from the top at a temperature of 80 to 90° C., and the lime is removed at the base at a

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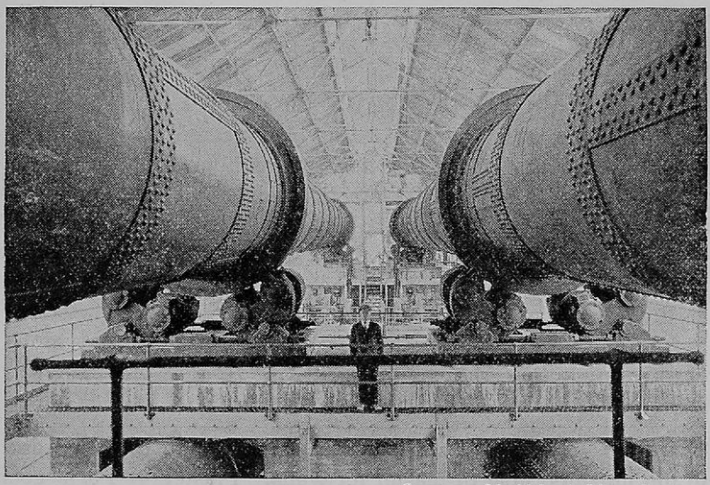

Courtesy, Marblehead Lime Company

206. ROTARY LIMEKILNS. Limestone is fed into the upper end of each cylinder. An intense flame enters at the other end. As the kiln rotates, the limestone moves along the cylinder and is converted into lime.

temperature around 45 to 55° C. In some cases the gases are taken from the kiln at considerably higher temperatures.

Many conditions may arise to cause "overburned" or partially "burned" lime. These conditions affect the yield of carbon dioxide gas. A rotary type kiln similar to the cement kiln (page 641) can utilize a poorer and finer grade of limestone. It uses oil, producer gas, or pulverized coal as fuel. In both types of kilns, a waste-heat boiler is often installed to recover the heat of the burned gases.

The equation for the "burning" or calcination of limestone is:

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

This reaction would be reversible but the carbon dioxide is removed by the forced draft as fast as it is formed.

What are CaO and $Ca(OH)_2$ like? As its various common names imply, we may expect calcium oxide (CaO) to be lumpy and caustic. It is generally white and porous. It reacts with

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water and produces so much heat that steam is given off:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat}$$

Calcium hydroxide [$Ca(OH)_2$], the product of the reaction shown above, goes under the name of hydrated lime, builders' lime, milk of lime when sufficient water is present to make a paste, or air-slaked lime if the action takes place slowly in the air. In the latter case, some calcium carbonate is formed because of the action of carbon dioxide on the calcium oxide or calcium hydroxide. A great deal of the lime today is hydrated at the time of calcination and bagged at once for the trade. In the building industry, hydrated lime has replaced much of the quick lime which, according to former practice, was slaked at the time it was needed.

The good earth supplies the plaster of Paris used in stucco and in the finishing coat of plaster for walls. Plaster of Paris gets its name from its first preparation near Paris. It is used in the finishing coat of plaster for walls, in stucco, and in the various finishes about a building, such as baseboards, molding, and wall decorations.

Plaster of Paris is also used to hold broken bones in place and in surgical bandages where movable parts must be held rigidly in place. Molds of plaster of Paris are used as the foundation in the making of many vases, pieces of statuary, and the like.

Plaster of Paris [$(CaSO_4)_2 \cdot H_2O$] is prepared from calcium sulfate which occurs in nature as gypsum. Gypsum is usually a hydrate with the formula $CaSO_4 \cdot (H_2O)_2$. In order to prepare plaster of Paris, gypsum is heated and three-fourths of the water is driven off:

$$2\ CaSO_4 \cdot (H_2O)_2 \rightarrow (CaSO_4)_2 \cdot H_2O + 3\ H_2O$$

When this partially dehydrated plaster of Paris is mixed with water, it sets to a white solid with the formation of a hydrate, similar to the original one.

$$(CaSO_4)_2 \cdot H_2O + 3\ H_2O \rightarrow 2\ CaSO_4 \cdot (H_2O)_2$$

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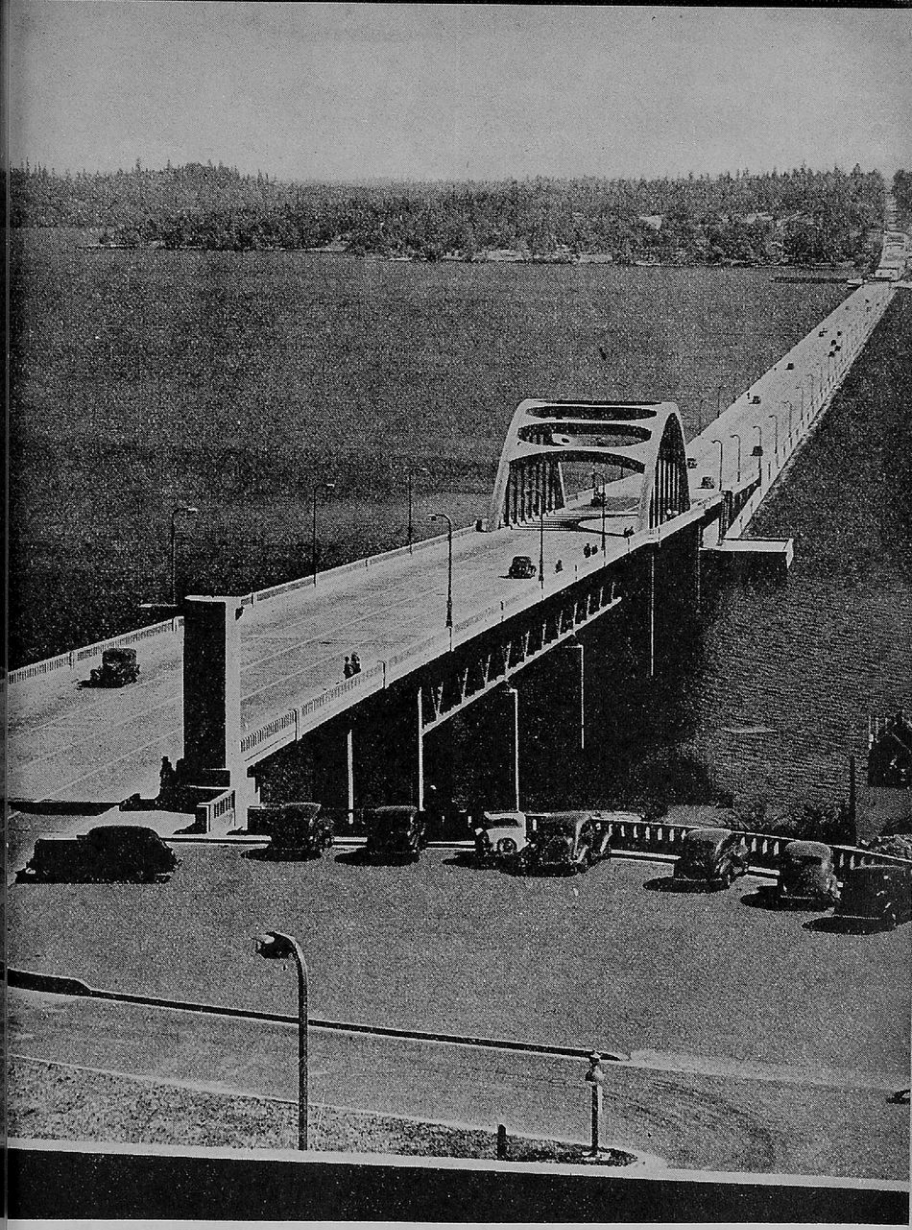

Courtesy, Washington State Highway Dept.

A Floating Cement Bridge. The most common way of making a pontoon bridge is to use wooden boats, large casks, or inflated rubber. Here is a pontoon bridge made of concrete, anchored in place over Lake Washington near Seattle.

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Courtesy, Warner Bros.

A Plaster of Paris Likeness of an Actress. First a special preparation is put on the skin so the hardened plaster can be removed. Then the plaster, reinforced with fabric, is smeared on to make the mold. Finally a cast is made from the mold giving a strikingly lifelike likeness of Ann Sheridan.

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Is the building industry standing still? There are many homes and buildings in the United States which are not up-to-date in construction. For modernizing these and for new construction work, there are many materials on the market under various trade names which are the product of the modern chemist. Asbestos shingles have largely replaced wooden and slate shingles on many homes. "Rubberoid" shingles are used to cover old siding in order "to keep out the cold." Rock wool, a fibrous product, and other materials are used to insulate walls, thereby keeping *in* the heat in the winter and keeping *out* the heat in the summer. Many grades of wall board under various trade names such as Celotex have been devised. Metal lath, metal window frames, and other metal features add to the permanence of buildings.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XVIII, pp. 225-230, "Lime."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XXXI, pp. 353-361, "The House of the Future."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XII, pp. 352-362, "Lime and Mortar"; Chap. XII, pp. 374-378, "Gypsum."

Applying in Life What You Have Learned in Chemistry

A thoughtful but not too well informed student tried to substitute "magnesia water" [$Mg(OH)_2$] for limewater in making the carbon dioxide test. What do you think the result was? Try it.

You are the chemical engineer for a lime manufacturer. You decide to try to hasten the production of lime by blowing very hot air through the kiln. How could this plan help the chemical action?

A student wanted to prepare in the laboratory some ammonia for a special purpose. He used slaked lime from a can that had stood open for a long time. Account for any difficulty he may have had.

In the cold season "hoboes" are apt to sleep near an operating limekiln for warmth. Fatalities may result in what way?

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Suppose you are carrying a bag of quicklime on your shoulder and get caught in a thunderstorm. The bag gets too hot to carry. Will you put water on the bag to cool it off? Explain.

Putting Chemistry to Work

A

(1) Why does the air in a newly plastered room seem damp? (2) Why does mortar not harden under water? (3) In winter, fires are sometimes built in open stoves in freshly plastered rooms to keep the plaster from freezing before it sets. In what two ways does this hasten the setting? (4) Suggest a reason why the plaster in Egyptian pyramids is so much harder than that in our modern buildings. (5) Sandstone is sand cemented together by some sort of natural cement. The most common are silicic acid and calcium carbonate. What chemical test will distinguish between the two? (6) The city of Philadelphia brings large granite bricks from Maine to pave some of its busiest streets. What is your idea of their permanence? (7) In the New England states one finds homes 300 years old in a better state of preservation than some modern homes only 15 years old. Can you suggest reasons?

B

(8) Present arguments for and against the continued use of wood as the chief material for house construction. (9) How has the chemist helped to lengthen the life of wood used in constructions? (10) What difference in composition is there between calcium sulfate, gypsum, plaster of Paris, and plaster of Paris casts? (11) List the so-called building stones; give their general composition and particular advantages. (12) How do you account for the widely different colors of marble quarried in different localities? (13) How is plaster of Paris used in making casts to support a broken leg or to form lifelike reproductions of one's facial features? (14) By means of equations show the chemical changes from limestone to the plaster on a wall. (15) What is the meaning of the term "burning" applied to lime production?

Research and Activities That You Will Enjoy

A practical report: After outside preparation, make a report on the source, composition, refining, and uses of asphalt. How does it differ from tar? (Ask your lumber dealer or write to Barber Asphalt Corporation, Philadelphia for information.) From local builders or builders' supply companies learn about other modern

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building materials. Ask about their general composition, their trade names, and uses. Report to the class anything of special interest.

A geological report: After outside preparation, tell the class more about the various minerals mentioned in this problem. Ask your instructor about specimens of minerals and, if possible, show them to the class.

An interview: Talk with a plasterer or bricklayer to learn how he makes mortar now as compared with ways used in the past twenty-five years. Also ask a builder to explain to you the material known as "masonite."

An exhibit: Collect and show to the class as many natural and artificial calcium materials as you can find. (Do not fail to include various forms of calcium carbonate and calcium sulfate.) Tell what you can about the composition, properties, and uses of each.

Problem 66

HOW DOES INDUSTRY GET SOME OF ITS MOST NEEDED CHEMICALS FROM THE GOOD EARTH?

In earlier units you found how nature has provided man with many useful chemicals. Among these have been sodium chloride, sodium nitrate, sulfur, carbon, petroleum, and natural gas. You have observed that man has been obliged to convert natural products into many other forms for his use.

How borax occurs in nature. American industries have apparently unlimited quantities of borax in the deposits of colemanite [$Ca_2B_6O_{11} \cdot (H_2O)_5$], borax [$Na_2B_4O_7 \cdot (H_2O)_{10}$], and rasorite [$Na_2B_4O_7 \cdot (H_2O)_4$] all found in the immediate region around Death Valley in southern California. Early transportation of borax from this region required a long haul over desert territory by mule teams, hence the famous trade name "20 mule team borax." Today the rasorite, or kernite, deposits in the Mojave Desert are the most used source. The borax is dissolved in water and purified by recrystallization. The successful recovery of borax and other chemicals in this desert region is one of the triumphs of modern engineering.

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Borax is used as a water softener and a cleansing agent—what other important uses has it? Borax is used as a water softener and a cleansing agent in the majority of homes in our country. It is used directly as borax or as an ingredient of cleansing agents under various trade names. Its use as a water softener is due to its reaction with calcium and magnesium ions forming insoluble borates that precipitate.

Much borax is used as a flux in soldering. Here it may be considered as a combination of the basic and acidic anhydrides, $Na_2O \cdot (B_2O_3)_2$. When melted on the metal to be welded or soldered, the metallic oxides (rust or corrosion products) react with the acidic anhydride B_2O_3 to form fusible slags which are easily removed, leaving the surface of the metal clean for welding.

Borax is also used in the making of enamels, glass, soap, and pottery; also as a preservative, as an antiseptic, and in borax bead tests for the metals.

Boric acid (H_3BO_3), commonly called boracic acid, is perhaps known to you as an eyewash. It is a very weak acid and has an antiseptic action. It imparts a green color to a gas flame or to an alcohol flame.

The asbestos used for making "fireproof" shingles and fireproof stage curtains is a magnesium compound—what other magnesium products are in common use? Natural magnesium compounds are either simple or complex. Examples of the simple compounds are the carbonate, the chloride, and the sulfate. Examples of complex magnesium compounds are the silicates, meerschaum, serpentine, soapstone or talc, asbestos, and the double carbonate, dolomite ($MgCO_3 \cdot CaCO_3$). Since fifteen per cent of the soluble salts in ocean water is either magnesium chloride or magnesium sulfate, the supply is apparently inexhaustible.

Magnesium oxide (MgO), or magnesia as it is called, is prepared by heating the carbonate:

$$MgCO_3 \rightarrow MgO + CO_2$$

Magnesium oxide is a light, flocculent, white powder, capable

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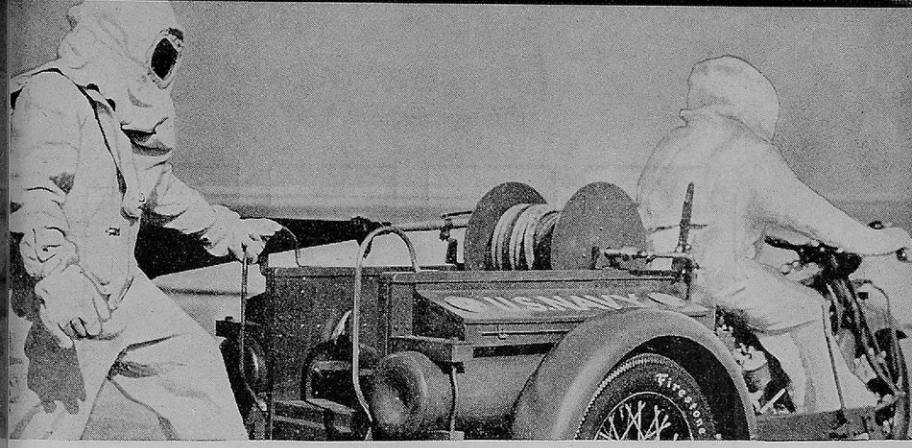

Courtesy, Johns-Manville

207. Asbestos Furnishes a Mineral Fiber. Asbestos suits protect men who fight very hot flames.

of being sintered in an electric furnace at high temperature to a dense, hard clinker. Mixed with a suitable binder, such as clay, magnesium oxide is molded into magnesia brick, used in furnace linings.

Magnesium oxide combines with water to form the hydroxide $[Mg(OH)_2]$ or *milk of magnesia.*

Magnesium oxide is also treated with a saturated solution of magnesium chloride, which resembles plaster of Paris and is used in wall plasters, floorings, and stucco.

Heat insulation is directly connected with magnesium compounds either through the use of asbestos alone, or through the use of "85% magnesia" or "magnesia pipe covering," which is a mixture of asbestos and 4 $MgCO_3 \cdot Mg(OH)_2 \cdot (H_2O)_5$.

Magnesium carbonate may occur alone as magnesite ($MgCO_3$) or as the double salt dolomite ($MgCO_3 \cdot CaCO_3$) in which the percentage of each carbonate may vary greatly. The greatest uses of dolomite or dolomitic limestone are as crushed rock for road building and as a refractory lining for furnaces. Dolomite is very plentiful in some localities, whole mountain ranges being composed of this substance.

Magnesium sulfate $[MgSO_4 \cdot (H_2O)_7]$ is commonly called Epsom salts because it occurs naturally in the waters of Epsom Springs, England. It is valuable in medicine, in dyeing, tanning, and as a filler for cotton goods.

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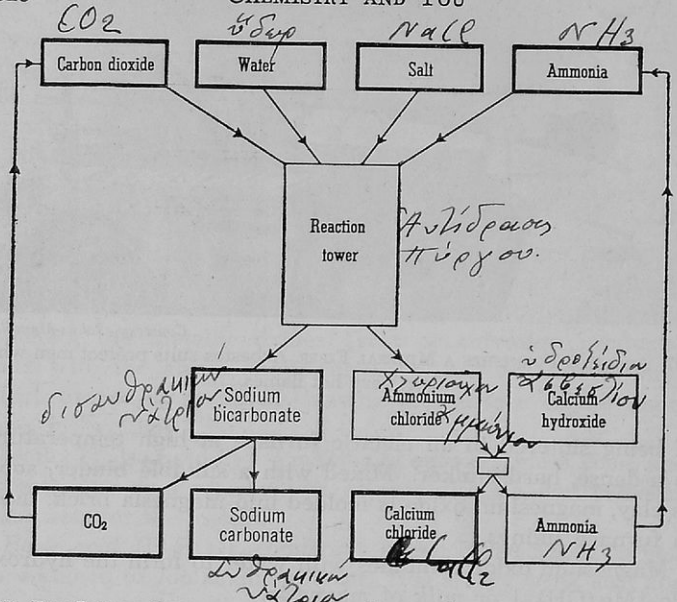

207. THE SOLVAY PROCESS OF PREPARING SODIUM CARBONATE. Salt dissolved in water reacts with ammonia and carbon dioxide in the gaseous state to form sodium bicarbonate and ammonium chloride. When the sodium bicarbonate is heated, it yields sodium carbonate and carbon dioxide which can be used in the reaction. The ammonia can be recovered from the ammonium chloride and used again.

Tons of washing soda and baking soda are used each year—how are these materials produced? Washing soda, also known as sal soda, and soda ash, is sodium carbonate (Na_2CO_3). Baking soda or sodium bicarbonate is sodium hydrogen carbonate ($NaHCO_3$). Often either form is spoken of as soda. Natural deposits of soda are so scarce, so far distant from market, and so impure that industry has had to devise ways to make these products. Today nearly all sodium carbonate and sodium bicarbonate are made by the Solvay process. Fig. 207 shows a "flow" diagram of the Solvay process.

How is sodium carbonate manufactured by the Solvay process? In order to understand the Solvay process, note

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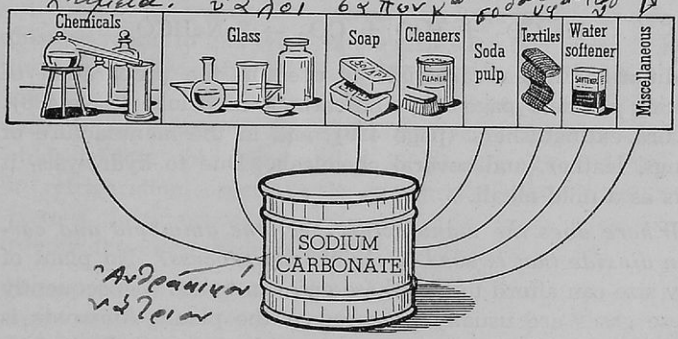
Fig. 207 carefully. The immediate raw materials are sodium chloride, carbon dioxide, and ammonia. The following reactions take place:

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3\downarrow$$

The sodium hydrogen carbonate is heated to form sodium carbonate:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\uparrow$$



208. HOW SODIUM CARBONATE IS USED. Next to sulfuric acid, sodium carbonate is the most important heavy chemical. This chart shows a few of its important industrial uses.

In actual practice ammonia gas is first passed into a saturated sodium chloride brine and then carbon dioxide enters this solution and reacts with ammonium hydroxide in the brine. The reaction is more complicated than these equations would indicate and requires extreme care in mechanical and chemical manipulation.

The sodium hydrogen carbonate solution becomes so concentrated that it crystallizes; the crystals are dried in a centrifugal drier. This crude sodium hydrogen carbonate is not the baking soda of commerce, however, as it contains considerable Na_2CO_3, NH_4HCO_3, and water.

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Sodium carbonate is prepared from the crude sodium hydrogen carbonate by heating. Carbon dioxide is driven off and recovered; the ammonium hydrogen carbonate volatilizes and the gases are recovered; the remaining sodium carbonate is over 99% pure. This soda ash is anhydrous and is now most popular with the trade. If the sal soda crystals [$Na_2CO_3 \cdot (H_2O)_{10}$] are desired, they are prepared by crystallization from concentrated solutions of the sodium carbonate.

How is baking soda prepared? Sodium hydrogen carbonate is prepared by treating solutions of the sodium carbonate with carbon dioxide.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2\ NaHCO_3$$

Sodium hydrogen carbonate is used in the preparation of baking powder (page 441) and carbonated drinks (page 438), in fire extinguishers (page 439), and in the manufacture of drugs, leather, and several chemicals. Due to hydrolysis, it acts as a mild alkali.

Where does the manufacturer get the ammonia and carbon dioxide that is used in the Solvay process? No plant of any size can afford to buy these gases in tanks. Consequently these gases are usually prepared at the plant. Ammonia is prepared by the direct combination of hydrogen and nitrogen (page 372) or in a by-product coke plant (page 428) which also furnishes valuable fuels for operation purposes. A limekiln (page 610) produces carbon dioxide and calcium oxide. The calcium oxide is then hydrated.

What happens to the ammonium chloride in the Solvay process? You will recall (page 619) that ammonium chloride is formed in the reaction:

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

Ammonia is very essential in this process so the ammonium chloride is treated with calcium hydroxide in order to release ammonia:

$$2\ NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2\ NH_3\uparrow + 2\ H_2O$$

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This ammonia and all the carbon dioxide formed in the process re-enter the system to form more NH_4HCO_3. (See Fig. 207.) The calcium chloride then is a real by-product of the process.

What is done with the calcium chloride in the Solvay process? More calcium chloride is produced than the trade requires. It is a by-product and is stored in large lakes adjacent to the plants. Its use is growing. It crystallizes from a water solution as white $CaCl_2 \cdot (H_2O)_6$. The porous, granular, and deliquescent form, that is so familiar in the laboratory for drying gases, is made by heating the crystalline form to drive out most of the water. The dehydrated form is also used to lay dust on roads, to mix with concrete in winter in order to keep the concrete work from freezing, and to place on finished concrete work in summer in order to prevent too rapid drying out of the concrete. Since a saturated solution of calcium chloride does not freeze until —48° C. is reached, it is used in refrigeration, especially in ammonia systems (page 374). Here a thirty per cent calcium chloride brine solution surrounds the pipes through which the ammonia passes.

Natural waters sometimes need treatment—how are hard waters made fit for use? Rain water is pure enough for industrial and home needs, but it usually is impractical to try to collect rain water for use. Once in the ground it starts dissolving soluble substances. Calcium carbonate (limestone) and magnesium carbonate are very common substances. They dissolve in water charged with carbon dioxide and form $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

$$MgCO_3 + H_2CO_3 \rightarrow Mg(HCO_3)_2$$

Water that contains these bicarbonates is said to have carbonate hardness, formerly called "temporary" hardness. Such hard water may be softened merely by boiling.

Natural waters are also apt to contain varying amounts of calcium sulfate and lesser amounts of magnesium sulfate,

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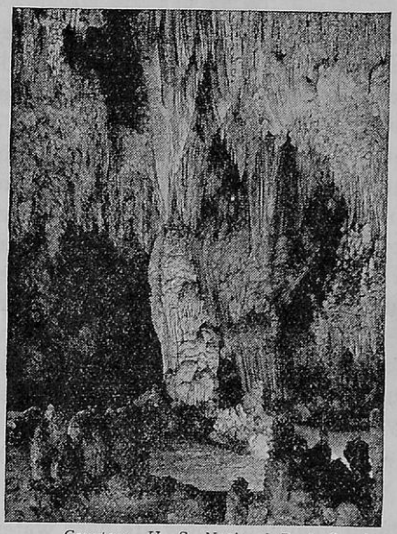
calcium chloride, and magnesium chloride. Water in which these chemicals are dissolved is said to have noncarbonate hardness, formerly known as "permanent" hardness.



Courtesy, U. S. National Park Service

Water containing carbon dioxide dissolves pure calcium carbonate. Where the bed rock is pure limestone, underground waters containing carbon dioxide dissolve the rock and leave great caverns. Carlsbad Cavern in New Mexico is one of the greatest of these. Where water drips from the roof of one of these caves, the loss of carbon dioxide may precipitate the dissolved limestone. This leads to the formation of icicle-like masses of stone called stalactites. Masses forming on the floor are called stalagmites.

209. CARLSBAD CAVERN

What are the disadvantages of hard water? A satisfactory water supply is so essential to some industrial concerns that the choice of a location is primarily based on the nature of the water supply. Wherever steam is necessary in the operation of industrial machinery, boiler scale is an enemy that must be given consideration. Salts which produce carbonate hardness [$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$] decompose upon being heated to form insoluble carbonates, as for example:

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

The calcium carbonate deposits in the boiler as a scale, similar to the deposit formed in most teakettles after continued use. Boiler scale lowers the efficiency because of its poor heat conductivity. When the layer of scale cracks, water may reach

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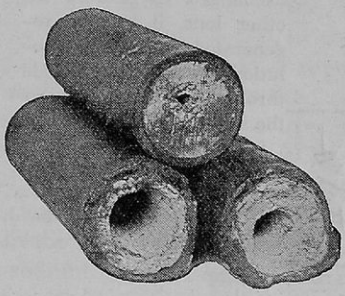
the overheated iron of the boiler and cause trouble since too rapid formation of steam and oxidation weakens the iron itself.

Calcium sulfate is the most common cause of noncarbonate hardness. It is increasingly less soluble in water above 35° C. and precipitates out as detrimental boiler scale. Hard water likewise deposits this scale even in water lines and eventually renders them useless.



This pipe was taken from a hot water heater in Chicago. The deposit of scale had almost closed the pipe. The scale is a poor conductor of heat. The outer surface of the pipe is covered with a scale of black iron oxide due to overheating.

210. SECTION OF A PIPE CONTAINING BOILER SCALE

Soap is generally a sodium salt of oleic, palmitic, or stearic acids (page 506). Soap reacts with hard water to form a so-called calcium soap:

$$2\ C_{17}H_{35}COONa + CaSO_4 \rightarrow (C_{17}H_{35}COO)_2\,Ca + Na_2SO_4$$

All calcium soaps are insoluble, sticky, and curdy. Clothes washed in hard water soon become gray and discolored. Since the cleansing action of soap does not begin until all the salt causing the hardness is removed by precipitation, the quantity of soap necessary to precipitate all the hardening agents makes the family soap bill very high. Hardness of water is measured in parts per million (p.p.m.) or in "degrees." One degree of hardness is considered as 1 grain per gallon, equivalent to 0.017 g per liter or 17 p.p.m.

How is water softened? There are three general methods in use for softening water: (1) the use of lime, (2) the use of lime and sodium carbonate, and (3) the use of zeolites.

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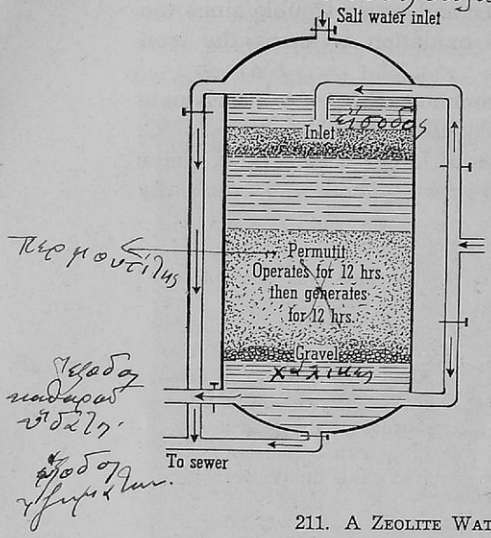

Hard water may be softened by flowing through a tank filled with the zeolite. Here the water exchanges calcium or magnesium ions, which make it hard, for sodium. When the zeolite has exchanged its sodium for other ions, it can be regenerated by pouring a solution of sodium chloride through it. This replaces the sodium and the softener is ready for use again.

211. A ZEOLITE WATER-SOFTENING PLANT

Lime [$Ca(OH)_2$] alone is satisfactory only in the case of water containing carbonate hardness. It reacts with the bicarbonate to precipitate insoluble compounds.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3\downarrow + 2\ H_2O$$

$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \rightarrow 2\,CaCO_3\downarrow + Mg(OH)_2\downarrow + 2\,H_2O$$

These insoluble substances are removed by sedimentation or sedimentation with filtration.

Lime and soda ash together are more effective because the salts causing both types of hardness are removed. Lime itself is not effective in removing calcium or magnesium sulfate. This action is best illustrated by an equation:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

Although more expensive, caustic soda, NaOH, will remove both the bicarbonates and sulfates:

$$Ca(HCO_3)_2 + 2\ NaOH \rightarrow CaCO_3\downarrow + Na_2CO_3 + 2\ H_2O$$

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The sodium carbonate, so formed, then precipitates the calcium sulfate as calcium carbonate as shown above. The sodium salts remaining in the water are usually not objectionable.

The *zeolites*, which are artificial products of the general formula $NaAlSiO_4$, will remove bicarbonates, sulfates, carbonates, chlorides, and other soluble salts of magnesium and calcium, as magnesium and calcium zeolites. Eventually the zeolite loses its ability to soften water; then the water-softening plant (Fig. 211) is withdrawn from operation and a solution of sodium chloride is put in the plant and allowed to stand for a time. The reaction is reversed and the zeolite is regenerated; the equipment is then ready for use again. The same charge of zeolite may be used many years. It is sold under such trade names as Permutit, Verdite, Crystolite, Delcaso, and Borromite. One disadvantage is that it is applicable only to clear waters.

In the laundry, soda, borax, trisodium phosphate (Na_3PO_4), or sodium hexametaphosphate ($Na_6P_6O_{18}$) are used to soften the water before the addition of soap.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry*. Chap. XVIII, pp. 233-236, "Magnesia."

REED, A. MAXWELL. *America's Treasures*. Chap. III, pp. 35-53, "Mercury and Borax"; Chap. VIII, pp. 122-138, "Phosphorus"; Chap. XX, pp. 291-307, "America Versus World Production."

TILDEN, SIR WILLIAM. *Chemical Discovery and Invention in the 20th Century*. Chap. XVI, pp. 251-256, "Water Softening."

Applying in Life What You Have Learned in Chemistry

Janet has learned enough chemistry to know that $NaHCO_3$ is an acid salt. She decides not to use baking soda with sour milk in making biscuits for fear of too much acid. What would you tell her?

The labels from bottles of sodium carbonate and sodium bicarbonate have been lost. How would you distinguish these substances by laboratory tests?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Why do washwomen sometimes put out tubs to catch water when it is raining?

Several persons lost their lives in California some time ago because a careless clerk used washing soda instead of baking soda. Can you explain why the mistake was fatal?

Putting Chemistry to Work

A

(1) The chief material in wood ashes is potassium carbonate. In what two ways can it improve the soil? (2) What property of magnesia makes it valuable in linings for furnaces? (3) Potassium bicarbonate is much more soluble than sodium bicarbonate. How does this prevent its being made by the Solvay process? (4) A precipitate appears and then disappears when carbon dioxide is passed through limewater for some time. Write equations for the two reactions. (5) A certain calcium compound causes carbonate ("temporary") hardness in water. Yet the hardness is removed by *adding* a calcium compound. How can this be? (6) Ammonium bicarbonate is frequently used in baking crackers. Why would you expect this to give a more porous product than sodium bicarbonate would? (See the equation.) (7) Show by equations how household ammonia may be used to remove hardness from water when both types of hardness are present. (8) How might a look into a teakettle suggest a possible problem of a neighboring industrial concern?

B

(9) Explain in detail why hard water is objectionable for laundry and industrial purposes. (10) How would you prepare each of the following from sodium chloride? Write equations for reactions involved: HCl, Na_2SO_4, Na_2CO_3, Na, NaOH, $NaHCO_3$. (11) The following terms are in more or less common use; tell what each means: soda, washing soda, sal soda, baking soda, bicarbonate of soda, soda lime, soda ash, soda water. (12) Write complete equations suggested by the following: $MgCO_3 \rightarrow MgO \rightarrow Mg(OH)_2 \rightarrow MgSO_4 \rightarrow MgCO_3 \rightarrow Mg(HCO_3)_2$. (13) Give equations to show five ways in which you might prepare magnesium chloride.

How Good Are You at Solving Problems?

(1) How many grams of magnesia can be prepared from 200 grams of magnesite? How many liters of carbon dioxide can be obtained from the reaction?

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(2) You have equal weights of sodium carbonate and sodium bicarbonate. From which can you obtain the larger volume of carbon dioxide?

(3) How much Epsom salt could be obtained from a solution made by treating 10 grams of magnesium oxide with sulfuric acid in excess?

(4) When you purchase 100 pounds of borax (hydrate) how much $Na_2B_4O_7$ are you getting?

(5) What weight of potassium carbonate is required to perform the same chemical work as one pound of sodium carbonate?

(6) What weight of potassium nitrate must be taken as a substitute for 50 grams of sodium nitrate?

(7) The analysis of a fertilizer shows: N, 2.8%; P, 7.4%; K, 3.6%. Express its composition on the $NH_3:P_2O_5:K_2O$ basis.

(8) Express the ratio composition of KNH_4HPO_4.

Research and Activities That You Will Enjoy

A proof of hardness: See if you can find a small section of an old steam pipe or water pipe with scale in it. Show the class and explain its cause. Test the scale for the presence of a carbonate.

A report: By outside study see what you can learn about the older Leblanc process for making sodium carbonate. Give a two-minute report on it.

Problem 67

SILICON IS THE GOOD EARTH'S SECOND MOST COMMON ELEMENT. WHAT SHOULD YOU KNOW ABOUT THIS ELEMENT AND ITS COMPOUNDS?

Silicon makes up more than one-fourth of the weight of the earth's crust. It occurs in nearly all of the rocks except limestone, marble and gypsum. Whole mountain ranges are made up of silicon dioxide in the form of quartz, and others are made up of silicates in the form of granite and slate and gneiss.

Silicon belongs to the carbon family of elements, but unlike carbon it never occurs free in nature. Carbon is the characteristic element in the world of plants and animals, while silicon

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

is the characteristic element in the mineral world. Both have a valence of four and form similar compounds with chlorine, hydrogen, and oxygen.

How may silicon be set free from its compounds? To prepare silicon, silicon dioxide is reduced with either magnesium or aluminum. When ground flint or fine sand is mixed with powdered magnesium and heated, a rather violent reaction takes place:

$$2\ Mg + SiO_2 \rightarrow Si + 2\ MgO$$

Some magnesium silicide is usually formed at the same time. The cooled mixture is treated with dilute acid to dissolve the magnesium oxide and the silicide, and the silicon is left.

Like carbon, silicon exists in several allotropic forms. Amorphous silicon is a brown powder; crystalline silicon is a steel-gray substance resembling graphite in appearance. Silicon is more reactive than carbon, reacting readily with hydrofluoric acid forming silicon tetrafluoride, and with active bases forming silicates. In its elemental state silicon has few uses, but its natural and artificial compounds have many uses. Primitive man used silicon dioxide in the form of flint to provide him with tools and weapons. Modern man uses silicon carbide (carborundum) in whetstones and polishing wheels. Men in all ages have used stone and brick, both silicates, as building materials to provide shelter. Glass in the form of lenses has made possible the telescope and the microscope which have enabled us to extend the range of our knowledge to the distant constellations and to the extremely small cells which make up all living matter.

The commonest compound of silicon masquerades in many forms. Silicon dioxide is the commonest compound of silicon. In its pure crystalline form it occurs as quartz in beautiful hexagonal crystals that terminate in hexagonal pyramids. When colored with iron and manganese, quartz is amethyst; when colored by organic matter, it is smoky quartz. Amor-

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212. THREE COMMON FORMS OF SILICON OXIDE. Quartz, sand, and flint are three of the many forms in which silicon oxide is found in nature.

phous forms, colored with various minerals, are agate, jasper, and onyx. When slightly hydrated, quartz is opal and flint. While silicon dioxide in no way resembles carbon dioxide in its physical characteristics, chemically it is quite similar. It is an acid oxide, combining readily with bases to form salts.

Quartz glass can be heated red-hot and plunged into cold water without cracking. Silicon dioxide, either in the form of quartz or sand, fuses at a very high temperature. The quartz glass thus formed has a very low coefficient of expansion. It can be heated red-hot and plunged into cold water without cracking. Test tubes, crucibles, ignition tubes for electric furnaces, and other pieces of laboratory ware are now made of this fused silica. Quartz glass also transmits ultraviolet light while ordinary window glass is almost opaque to it. The low heat expansion of quartz makes it valuable for telescope lenses. Such lenses cut from natural crystals are quite small. Lenses and telescope mirrors are now made from *fused* silica.

Many common rock-forming minerals are compounds of silicon. Many *silicates* occur as common rock-forming minerals. Mica, hornblende, feldspar, and kaolin are all silicates. They are the salts of the silicic acids which are all derived from orthosilicic acid (H_4SiO_4) by the loss of water. The formulas of a few of these minerals and the acids from which they are derived are given at the top of the next page.

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Mineral	*Formula*	*Acid*
Zircon	$ZrSiO_4$	H_4SiO_4
Mica	$KH_2Al_3(SiO_4)_3$	H_4SiO_4
Wollastonite	$CaSiO_3$	H_2SiO_3
Serpentine	$Mg_3Si_2O_7$	$H_6Si_2O_7$
Feldspar	$KAlSi_3O_8$	$H_4Si_3O_8$

A little study will show that when these are not salts of orthosilicic acid (H_4SiO_4), the acids may be derived from orthosilicic acid through loss of water:

$$H_4SiO_4 - H_2O \rightarrow H_2SiO_3 \quad \text{metasilicic acid}$$
$$2\ H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7 \quad \text{disilicic acid}$$
$$3\ H_4SiO_4 - 4\ H_2O \rightarrow H_4Si_3O_8 \quad \text{trisilicic acid}$$

Other silicic acids are similarly related to orthosilicic acid.

None of these acids have ever been isolated in a pure form. When hydrochloric acid is added to sodium silicate, a jelly-like precipitate of orthosilicic acid forms. It is colloidal (page 419) and can be separated from the dissolved salts in solution by dialysis. When attempts are made to separate the water from the acid, the acid loses combined water and is converted to silicon dioxide:

$$H_4SiO_4 - 2\ H_2O \rightarrow SiO_2$$

The silicates are all insoluble in water except those of the alkali metals. They are also insoluble in most acids except hydrofluoric. Hydrofluoric acid acts on them and the silicon passes off as silicon tetrafluoride, a gas. If calcium silicate is treated with hydrofluoric acid the reaction is as follows:

$$CaSiO_3 + 6\ HF \rightarrow CaF_2 + 3\ H_2O + SiF_4\uparrow$$

Thus by the use of hydrofluoric acid the insoluble silicates can be converted into soluble compounds for purposes of analysis.

Silicates are also acted upon by alkalies. They are quite readily soluble in melted sodium hydroxide or melted sodium carbonate. When a silicate is fused with sodium carbonate, sodium silicate and the carbonate of the metal are produced.

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WHAT ARE THE CHIEF ARTIFICIAL COMPOUNDS OF SILICON; HOW ARE THEY MADE?

Civilized man is quite dependent on several artificial compounds of silicon. Chief among these are glass and cement. By the use of glass you admit sunlight to your home but keep out the chill winds of winter. It graces your dinner table in the form of dishes and drinking glasses. In the form of lenses, glass corrects defects of vision. In the lenses of the microscope it brings to sight tiny forms of plant and animal life whose control is so important to your health and well-being. In the lenses of telescopes it brings to view far-distant objects, and thus "widens the universe."

It is hard to imagine how people in this modern age could get along without glass—what is glass? Glass is a mixture of silicates. Ordinary glass, such as is used in bottles and window panes, is a soda-lime glass. It is made by fusing together pure silica sand (silicon dioxide) with sodium carbonate and lime:

$$2\,SiO_2 + Na_2CO_3 + CaO \rightarrow CO_2\uparrow + \underbrace{Na_2SiO_3 + CaSiO_3}_{\text{Glass}}$$

The sodium carbonate serves as a source of sodium oxide (a basic oxide) which combines with the silicon dioxide (an acid oxide) to form the sodium silicate. This, mixed with the calcium silicate, constitutes soda-lime glass.

Other basic oxides may be substituted in whole or in part to produce glasses that have certain desirable properties. Potassium oxide may be substituted for sodium oxide; zinc oxide, lead oxide, aluminum oxide, magnesium oxide, arsenic trioxide, or barium oxide may be substituted for calcium oxide. By substituting boron trioxide (or less commonly, phosphorus pentoxide) for part of the silicon dioxide, other changes in properties may be obtained.

A lime-potash glass is hard, has a high melting point, and is quite resistant to chemical action. A lead-potash glass is heavy, has a low melting point, and a high index of refraction. Due to this last property, it is widely used for lenses for optical

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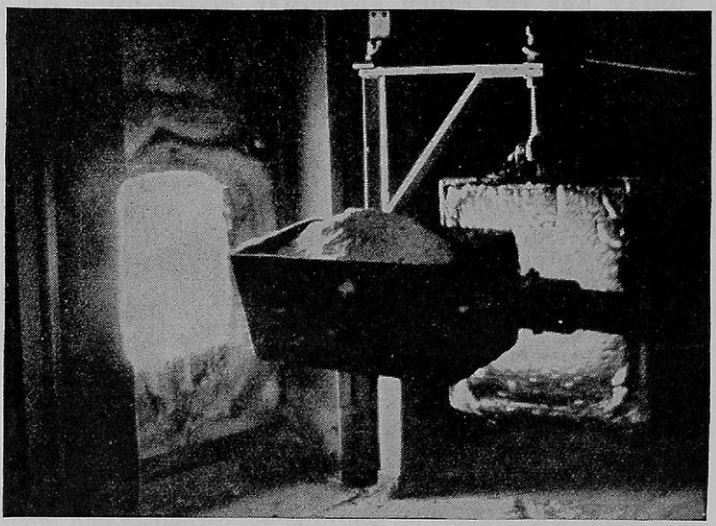

Courtesy, Corning Glass Works

213. A GLASS FURNACE. In this great furnace pure silica sand, lime, and soda combine to form glass.

instruments. A glass containing boron trioxide (in place of some of the silicon oxide) and aluminum oxide (in place of calcium oxide) shows a very low expansion when heated. The pyrex glass used in the laboratory is such a glass. It is a sodium aluminum boron silicate glass containing some arsenic trioxide.

How is glass made? After the chemist has determined the quantities of materials which are to enter into a "batch" of glass, the materials must be fused together. Two types of furnaces are used. For the finer grades of glass the raw materials are placed in large fire-clay pots and heated until fusion is complete. These pots are then removed from the furnace, and the glass is ready to be cast into any form desired.

Most glass, by far, is made in a tank furnace. This is a large rectangular box of firebrick. The mixed raw materials are fed in at one end. A gas flame plays across the surface

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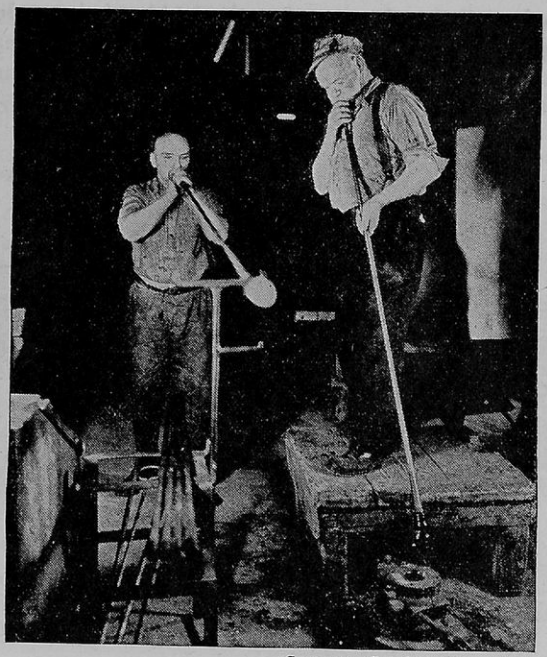


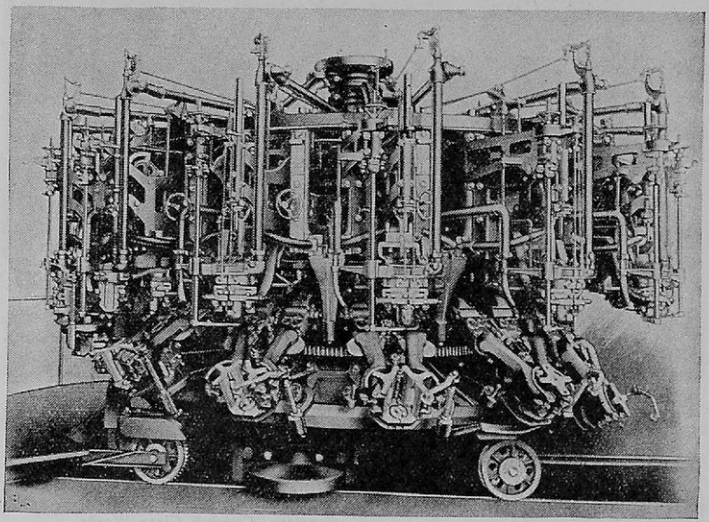
Courtesy, Corning Glass Works

214. GLASS BLOWERS. These men are making bottles. A portion of melted glass is taken up by the blowpipe, and a bubble is blown much as you would blow a soap bubble. This bubble is lowered into the bottle mold and blown until the glass fills the mold. After the bottle is taken from the mold, a different workman finishes the neck.

of the material and melts it. As it melts, it flows toward the front of the tank or the working end. At a little distance from the working end a curtain of firebrick dips into the molten glass. This prevents floating impurities reaching the parts from which the glass is withdrawn. A workman dips a long iron pipe into the molten mass and gets a lump of the melted glass on the end of the pipe. Withdrawing it from the furnace, he blows a bubble of the melted glass, much as you would blow a soap bubble. If glass bottles are being made, the bubble is lowered into an iron bottle-mold and the blowing

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

continued until the glass touches the inside of the mold. The bottle is removed from the mold, and another workman finishes the neck. After this, the ware is placed in a long oven where it is allowed to cool very slowly.



Courtesy, Owens-Illinois Glass Company

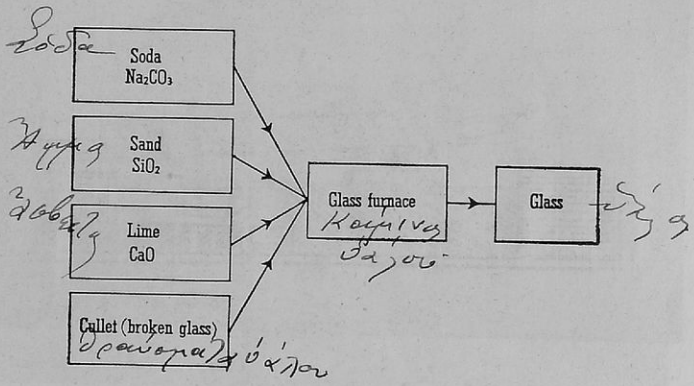
215. BOTTLE MAKING MACHINE. Many bottles are now made in great machines like this one. This machine does the work of many men.

In many factories this old process of bottle making is being replaced with a very complicated machine which does the work that formerly required many men. One of these machines makes over sixty bottles a minute.

Glassware, either blown or pressed, cools quite rapidly. In this condition it is hard and brittle. Due to unequal cooling, there is unequal contraction in the object; this causes strains in the glass. A slight shock or jar may cause the glass to fly to pieces. To prevent this, the glass is *annealed.* This is done by passing the glass through a long furnace where the glass is heated near the entrance and is cooled very gradually as it passes slowly through the furnace. This slow cooling makes

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

possible the molecular rearrangements which relieve the strain. Glass thus treated is tough and quite resistant to shock. This annealing process also serves to remove any strains caused by too rapid cooling.



216. How Common Glass Is Made. Pure silica sand, soda, lime, and cullet (broken glass) are heated in a glass furnace to form glass.

Many small dishes and other small articles, such as glass stoppers for bottles, are made from pressed glass. In this operation some plastic glass is pressed into a mold by a die. Cut glass articles are usually made of pressed glass. Later they are cut with grinding wheels and finally polished with some fine polishing powder such as rouge, a form of ferric oxide.

Window glass has changed dismal abodes to cheerful homes—how is window glass made? Common window glass is now made by dipping a blowpipe into a mass of melted glass and raising it slowly while air is blown into it. This produces a cylinder of glass about thirty feet long and about three feet in diameter. A longitudinal cut is made down one side, and the cylinder is cut into sections. These sections are placed in a furnace where they flatten out into sheets.

Window glass has added physical comforts to the home; it also has done much to improve working conditions in industrial plants.

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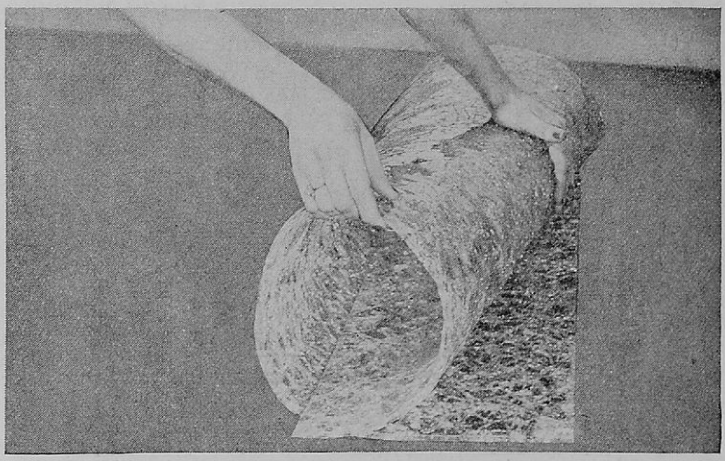

Courtesy, Monsanto Chemical Co.

217. ROLLING UP GLASS. This is a pane of safety plate glass which has been broken by hammer blows. It rolls up like a rug because the glass fragments adhere to the plastic binder used in making safety glass.

Plate glass is strong enough to be used in large store windows—how is plate glass made? Plate glass is made by pouring a pot of melted glass on a flat metal table and rolling it out while plastic, much as a piece of piecrust is rolled out. The surface of this is polished with rouge. This gives a sheet of glass of uniform thickness and with a highly polished surface. Recently a number of machines have been developed to produce a continuous sheet of window glass. The glass is melted in a tank furnace and allowed to flow out in a continuous stream between a pair of rollers. After passing through an annealing furnace it is cut to size and polished.

Safety glass used in automobiles helps to eliminate the danger of shattered glass—how is safety glass made? Safety glass is made by taking two sheets of thin plate glass and placing between them a sheet of celluloid. These thin sheets are firmly

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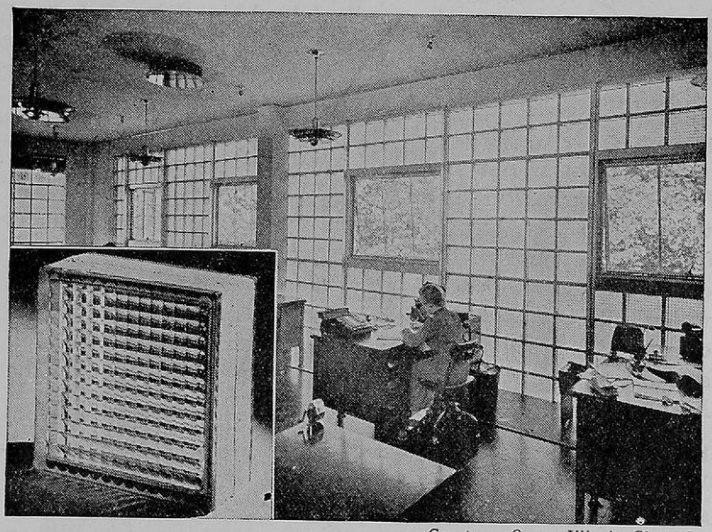

Courtesy, Owens-Illinois Glass Co.

218. GLASS BRICK IN USE. Glass bricks are now being used in the walls of buildings. This office shows the effect of using glass brick in the walls.

cemented together. When struck, the glass breaks but the flexible sheet of celluloid prevents the shattering or "slivering" of the glass. Wire glass, sometimes used as safety glass, contains wires or wire mesh that was rolled into the glass while it was plastic.

Beautiful colored glass is frequently used in church windows—how is colored glass made? Colored glass is made by adding metallic oxides to the glass. Cobalt oxide produces blue glass. Uranium produces yellow; chromium gives a green color. Manganese dioxide in large quantity is black; in smaller quantity it produces an amethyst color. Ferrous iron causes a green color. This color is often seen in cheap glassware due to the presence of iron in the sand. A comparatively small amount of ferric iron imparts a yellow tinge; a large amount produces a brown color. Red is produced by the

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presence of cuprous oxide or colloidal gold particles. Selenium also produces a very clear red glass; this glass is the one now commonly used for signal lights. Amber glass is colored by suspended particles of carbon. White glass or milk glass is made by adding cryolite or fluor spar to the bath.

Since glass is not a pure chemical substance, it does not have a sharp melting point. When heated, the components of the mixture that have the lowest melting points, melt first; other components remain suspended in the fluid mass. This causes the glass to soften so that it may be bent or shaped or welded. It makes possible the beautiful pieces of glass produced by the Bohemian and Venetian glass blowers, as well as some of the more intricate pieces of apparatus used in the laboratory.

Water glass—a glass that dissolves in water—how is it made? Water glass is a sodium silicate glass. It is prepared by fusing sodium carbonate and glass sand in a tank furnace. After it has cooled, it looks very much like ordinary glass. When heated with water under pressure, it dissolves forming a thick sirupy colloidal solution. In this form it is used to preserve eggs, in sizing paper, and in fireproofing wood and draperies. It is also used as a binder in cements and as an adhesive in manufacturing paper boxes and cardboard cartons. It is also used as a reagent in water softening and as a filler in some soaps.

WHAT IS CEMENT: HOW IS IT MADE?

The most common material used in modern building construction and engineering projects is Portland cement. Great dams such as Boulder Dam and Norris Dam, miles of cement highways, great bridges, and tunnels are all made possible by the use of this wonder working material. Its use has caused a revolution in modern building construction. Where a few years ago blocks of stone were laboriously cut to shape and built into a structure, now sand, gravel, cement, and water are mixed and poured into wooden forms. In a few days when

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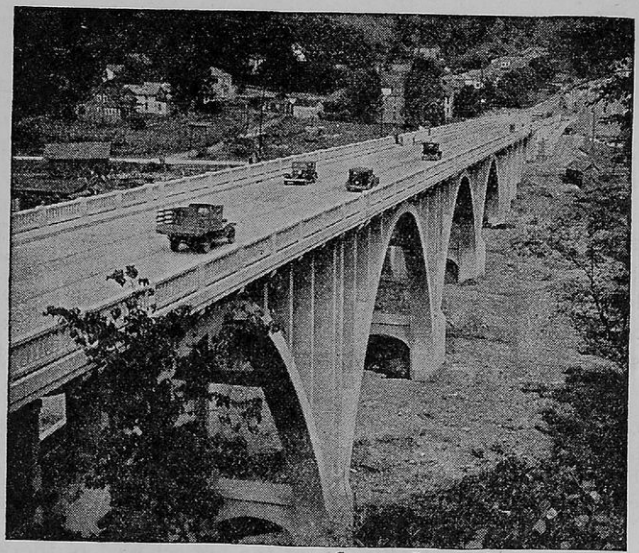

Courtesy, Portland Cement Association

219. ARCHES OF MEMORY. Belmont County, Ohio, cement was used in the building of this great memorial arch bridge.

the forms are removed, we find a hard stonelike mass which has the shape of the forms into which it was poured.

This product is the result of a long period of research; even yet there is much to learn about it.

How is cement made? The first step in the manufacture of cement is the selection of a good pure limestone and a good clay of uniform composition. These are pulverized and mixed in the proper proportions. The "burning" of the mixed materials is carried out in a cylinder kiln which is a long steel cylinder lined with firebrick and mounted on rollers. The kilns are from 100 to 200 feet long and from 6 to 10 feet in diameter. They are inclined slightly so that material fed in at one end will slowly travel down the kiln as it rotates. At the lower end a flame from burning powdered coal, fuel oil, or gas shoots about thirty or forty feet into the kiln. This produces a

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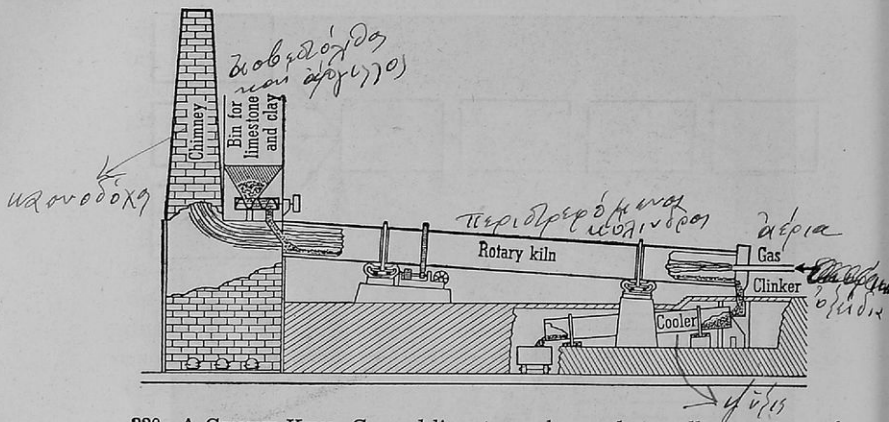

220. A CEMENT KILN. Ground limestone, clay, and a small percentage of gypsum are fed into the upper end of the large rotating cylinder. A blast of burning gas enters at the lower end. The limestone and clay are fused into a clinker-like mass which, on being finely ground, becomes cement.

temperature of about 1425° C. at the hottest part of the kiln. The high temperature causes the mixed limestone and clay to fuse into little lumps varying in size from one-quarter to one inch in diameter. The burned clinker is ground to a fine powder, and to this is added a small amount of gypsum which tends to regulate the time of setting. It is then ready for use.

• **What happens when cement hardens?** When cement is mixed with water, a hard mass is formed by the chemical action of the water and the components of the cement. The first change, the passing from the plastic state to the solid state, is called "setting." This requires only a short time. After the cement has set, there is a steady increase in the hardness and strength of the mass. During this time the cement is said to "harden." The hardening process may extend over a full year.

Each of the major components in cement acts in a different manner during these changes. When tricalcium aluminate is mixed with water, a gelatinous material forms which sets and hardens quite rapidly. Tricalcium silicate also sets and

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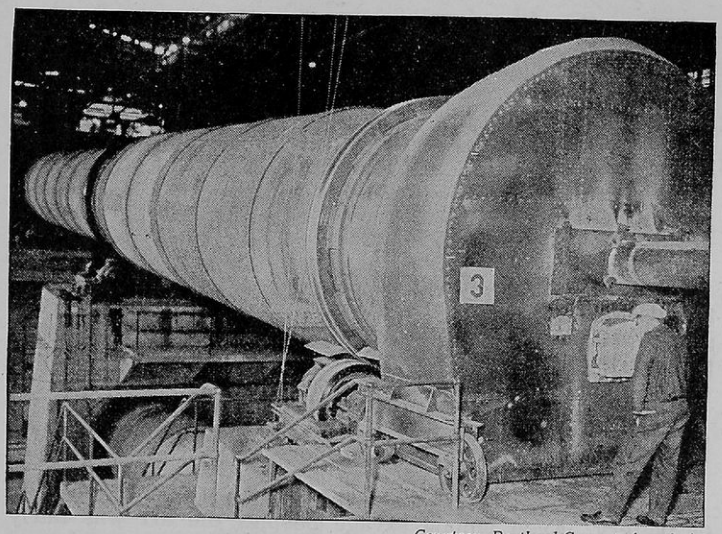

Courtesy, Portland Cement Association

221. A CEMENT KILN. This great cylinder, 120 feet long, rotates on rollers set on the pedestals at each end and the middle. Gaseous fuel enters through the pipe just above the workman's head. The mixture of clay and limestone enters at the other end. This mixture, after it is "burnt," forms cement.

hardens rather rapidly. In these cases the action is due to the formation of a gelatinous hydrated material which cements together the components of the mixture. Dicalcium silicate acts very much slower. In time this gelatinous material crystallizes in part.

The setting of Portland cement seems to be due to the hydration of the calcium aluminate, resulting in the formation of a gelatinous substance. The hardening action and strength are due to the cementing action of this material, and the increase in strength and hardness is due to the slower hydration of the other components of the cement. The tricalcium silicate is the best cementing material for it readily releases gelatinous silica when wet and forms the most insoluble compound in the cement.

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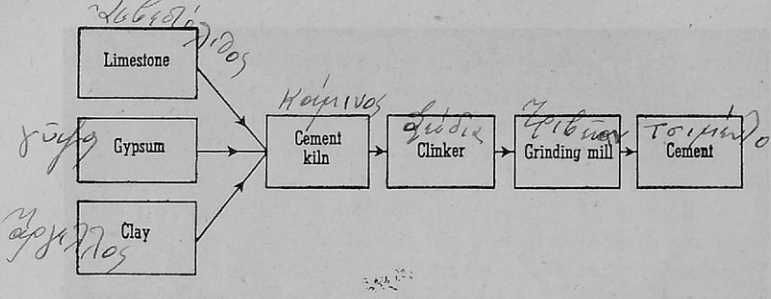

222. HOW CEMENT IS MADE. Limestone, clay, and a small percentage of gypsum are ground and mixed. As they pass through the cement kiln they are burned to a clinker. When this clinker is finely ground it becomes cement.

HOW ARE CLAY PRODUCTS PREPARED?

One of the earliest arts developed by man was the making of pottery. Even among savage peoples the art was fairly well developed. Long before the dawn of the period of written history, brick and tiles were used as building materials in the valley of the Tigris and Euphrates rivers. Some of these tablets with their cuneiform inscriptions form the earliest written records which we have.

What is clay? Clays differ widely in chemical composition and physical properties. They are mixtures of various substances, but the basic material in clay is kaolin, which is hydrated aluminum acid silicate ($Al_2H_2Si_2O_8 \cdot H_2O$). In addition to this, a good pottery clay contains ground feldspar and silica. Each of these plays an important part in pottery making. Kaolin is plastic but infusible; feldspar is not plastic, but easily fusible; and the silica reduces the shrinkage on "burning."

Clay which is formed by the decomposition of feldspar usually contains both kaolin and some unchanged feldspar. There is usually enough silica present as an impurity.

Ordinary brick is usually made from a single clay. After the clay is dug, it is ground and mixed with water and thor-

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oughly kneaded until the composition is uniform. The clay is then forced through a die, the cross section of which is one face of the brick. The clay bar thus formed passes onto a cutting table where it is cut by wires into the bricks. Some brickmaking machines have a capacity of 15,000 bricks per hour.

The bricks then pass into a dryer to remove the excess moisture, after which they are placed in a kiln to be "burned." The temperature and time of firing depend upon the kind of clay used and the hardness desired. Bricks used for paving are heated until the clay starts to fuse. This results in a hard "vitrified" brick which will not absorb water.

Most sewer pipes are made from shale clay which, after being ground, is mixed with water and shaped in a special press. They are dried and "burned" in a manner similar to that used for vitrified brick.

How were the dishes you used at dinner made? Pottery is a term used to include a variety of ware made from a single clay—or clays mixed with other substances.

Pottery made from mixed clays includes chinaware and porcelain. Chinaware has a porous body covered with a glaze; porcelain has a dense, hard, translucent, glassy body and is able to withstand high temperature.

White chinaware is made from such a typical clay mixture as this:

China clay (kaolin)	40 per cent
Ball clay	12 per cent
Powdered flint (silica)	33 per cent
Feldspar	15 per cent

The kaolin forms the main body of the ware and gives the white color. It is not sufficiently plastic to be worked properly, so the ball clay is added to give this desired plasticity and to make the body stick together. The flint makes the body porous and thus aids in the drying of the ware. The flint also reduces shrinkage during firing. The feldspar melts at high temperatures, and (by dissolving some of the flint and clay) cements the whole mass into a firm body. The temperature in

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the kiln is not high enough to cause complete fusion of the body, so unglazed chinaware is quite porous.

Porcelain is made from a mixture containing more feldspar and less ball clay and flint. It is fired to a higher temperature, so very complete fusion takes place. The resultant body is a translucent glassy mass and is not porous. A broken crucible will show the nature of this body.



By Ewing Galloway, N. Y.

223. THE POTTER'S WHEEL. The workman is shaping the plastic clay into a vase which rests upon a small revolving table called a "wheel." The shaping is done largely by the skillful use of the hands.

The making of pottery is one of the oldest known arts—how is pottery made? The American Indians made pottery by rolling moist clay out in long strips and coiling it in the desired shape. The coils were then worked together with the fingers. Very beautiful symmetrical bowls and bottles were made in this way. Commercial pottery is made on a potter's wheel, by casting in a plaster mold, or by a process known as "jiggering."

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By Ewing Galloway, N. Y.

224. MAKING POTTERY ON A JIGGER. This device consists of a mold on a rotating disk. A lump of clay is thrown into the mold. As the mold turns, a form having the profile of the inside of the dish is lowered. The clay is forced against the mold.

Pottery may be made on a potter's wheel. The potter's wheel is a horizontal disk that can be rotated. The potter throws a lump or clay on the center of the disk; as the wheel rotates, he shapes the piece with his hands. This work requires a high degree of skill, and since it is very difficult to duplicate exactly any piece of ware, it is not used much in large factories.

Pottery may be made by casting. In the casting process clay is mixed with water until it is about the consistency of a thick cream soup. This "slip," as it is called, is poured into a dry plaster mold, the mold having the shape of the piece to be made. The moisture in the slip near the surface of the mold is absorbed by the dry plaster, leaving a coating of clay on the

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inside of the mold. When this coating has reached the desired thickness, the excess slip is poured out and the mold is set to dry. In drying, the clay shrinks and the vessel can be easily separated from the mold.

Pottery may be made by jiggering. This process is in most common use in making tableware. A mold takes the place of the disk on a potter's wheel. This mold has the shape of one surface of the object to be made. A lump of very soft clay is thrown into the mold; as the mold rotates, a tool shaped to conform to the other surface of the object is lowered into the mold. This forces the clay into all parts of the mold and also removes all excess clay. The mold with the formed dish is then set to dry. This process is very rapid, and by its use exact duplicates for sets of dishes are easily made.

Pottery is made durable and beautiful by firing—how is pottery fired? Most pottery is given two firings. The first firing is called the biscuit firing. In this, the thoroughly dried clayware is placed in fire-clay boxes called saggers. These saggers protect the ware from the flames and keep the ware on the bottom of the kiln from being deformed by the weight of the ware above it. A large pottery kiln takes about 60 hours to fire and about 48 hours to cool off.

The second firing takes place after the biscuit ware is glazed. Glazes are colorless glasses having a coefficient of expansion the same as that of the body. The ingredients in the glaze are in the form of a thick suspension in water. The glaze is either applied by dipping the biscuit ware into it or by spraying with an airbrush. After the glaze is dry, the ware is again placed in saggers. This time great care must be taken so that the ware does not come in contact with another piece, or with the bottom of the kiln, for the glaze on melting would cause the pieces to stick together. The second firing takes about 36 hours and is carried on at temperatures varying from 1150° C. to 1350° C. depending on the composition of the glaze.

Tunnel kilns where the ware is placed on cars which very slowly move through the kiln are now coming into use. Here the process is continuous and the kiln does not have to cool off to remove the ware.

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Pottery is usually covered with a glaze that protects its surface and makes it beautiful—how are glazes prepared? Glazes are glasses which fuse at a comparatively low temperature. The raw materials which enter into a glaze must be insoluble in water and of a density low enough to remain in suspension for some time.

A typical glaze may be made by grinding in water the following substances in the proportions by weight as indicated:

White lead	155	Source of PbO
Whiting	30	Source of CaO
Feldspar	56	Source of K_2O, Al_2O_3, SiO_2
Kaolin	26	Source of Al_2O_3, SiO_2
Flint	48	Source of SiO_2

This mixture provides basic and acid oxides in such proportion that, when fused, they form a clear glaze.

White lead, a basic carbonate of lead, is used instead of lead oxide because of its lower density and because it is more easily ground to a fine powder. Whiting ($CaCO_3$) is used instead of calcium oxide because it does not react with water and is less soluble. Flint is used instead of quartz or sand as a source of silicon dioxide because it is more easily ground and has a lower density.

To change the properties of the glaze (such as melting point or coefficient of expansion), other basic oxides may be substituted for those in the formula, or the proportions may be varied, or boron trioxide may be substituted for part of the silicon dioxide. Any soluble substance which is to be used in a glaze must be made insoluble by fusing it into a glassy insoluble mass. This process is called "fritting," and the insoluble product is called a "frit." Borax as a source of boron trioxide is introduced into a glaze in this manner.

Matt glazes are used to give a soft dull finish to art pottery. This effect is produced by using an excess of aluminum oxide in the formula or an excess of silica. The alumina is believed to aid in the formation of compounds in the finished glaze which gives the desired effect.

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Burnt clayware is one of the most permanent substances we have. The first historical records preserved by man were made on clay tiles in the Tigris and Euphrates valleys. From them we can get a picture of civilizations which have completely disappeared. Brick and terra cotta furnish pleasing and permanent building materials. Chinaware and porcelain provide us with beautiful and sanitary tableware which is easily cleaned. Pottery is one of the oldest arts known to man, but it is only recently that the chemist has made a science of pottery making.

Readings for Pleasure and Profit

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XVII, pp. 214-224, "Sand and Clay."

DARROW, F. L. *The Story of Chemistry.* Chap. XII, pp. 423-428, "American Glass."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XIX, pp. 308-316, "Pottery and China"; pp. 316-322, "Glass Manufacture—Varieties of Glass."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 26, pp. 177-186, "Glass, an Indispensable Factor in Modern Civilization."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XXVI, pp. 298-304, "Windows toward Heaven"; Chap. XXVIII, pp. 316-325, "What Transportation Owes to the Chemist."

HOWE, H. E. *Chemistry in Industry.* Vol. I, Chap. X, pp. 130-146, "Glass, One of Man's Blessings"; Vol. II, Chap. VI, pp. 95-109, "Earthenware and Pottery"; Chap. XV, pp. 261-278, "Portland Cement"; Chap. XVI, pp. 279-291, "Chemistry, Radio, and Incandescent Lamps."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XII, pp. 363-373, "Portland Cement"; Chap. XIII, pp. 381-401, "Clay, Brick, and Pottery"; Chap. XIV, pp. 405-444, "Glass."

Applying in Life What You Have Learned in Chemistry

The glass in the front of an ultraviolet lamp was broken. It was replaced with window glass. How did this affect the efficiency of the lamp?

What is the advantage of using window glass rich in quartz in sun rooms?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

An unknowing student obtained a new silica crucible from the stock room and started heating sodium carbonate in it.

Imagine his surprise when the bottom dropped out!

What happened? Why are we instructed not to heat washing soda in silica dishes? Chemical facts confront us everywhere. If we *know* about them, we can use materials to advantage without loss.

How could you distinguish between a quartz crystal, a diamond, and a piece of polished glass?

Putting Chemistry to Work

A

(1) Why are theater curtains often made of asbestos? (2) Bottles used for solutions of sodium hydroxide or ammonium hydroxide often become etched on the inside. Account for this action. (3) Acidproof iron, like duriron, contains silicon (about 15 per cent). Would such iron resist the action of strong alkalies? (4) Would it be any advantage to you to have a test tube of quartz glass to use? Why are such test tubes not usually supplied to students in the laboratory?

(5) Why is glass not made from sand and sodium carbonate only? from sand alone? (6) What properties does chemical glassware need that window glass does not need? (7) What properties does glass used for lenses need that chemical glass does not need? (8) Account for the pale green color often seen in cheap glass jars and bottles. What can be done about it? (9) The firebricks used in a glass furnace wear out rapidly. Account for this action. (Hint: The bricks are silicates.) (10) Would you favor glazing sewer pipe? drainage tile? Explain each case.

B

(11) Account for the fact that glass tubes and rods can be bent when heated. (12) In making glass what substances may furnish the acid oxides? the basic oxides? (13) In what way does silicon resemble carbon? How does it differ? (14) Show how the acid, $H_2Si_2O_5$, is derived from orthosilicic acid. (15) Distinguish the meaning of these words: silicon, silica, silicide, and silicate. (16) Why are several months spent in cooling the glass poured for lenses for large telescopes? (17) Show by equations how SiO_2 can be prepared from water glass. (18) Write the formulas for silicon hydride (silane), silicon tetrachloride (tetra-chloro-silane), and silicon

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

chloroform (tri-chloro-silane). To what carbon compounds are they analogous? (19) Make a list of products made in the electric furnace. Make a brief statement about each.

Research and Activities That You Will Enjoy

A paper: Prepare a brief report on natural and artificial "Precious Stones" and present it to the class. (See "Man-Made Gems," by Frank B. Wade, in *J. Chem. Ed., 8,* 1015-26, June, 1931.)

A report: The use of activated silica gel as an adsorbing agent.

Interesting topics: (a) Carborundum (b) Products of the electric furnace (c) Index of refraction (d) Silicates as fireproofing and heat-resisting materials.

Looking Back into Unit 15

Be sure you know the purpose of this unit. Read again the material on page 590, "Looking Ahead into Unit 15." Then study the following Summary Test.

Summary Test

1. *How can the good earth continue to feed you well?*
   (a) What is soil?
      (1) Where do soils come from?
      (2) What are the different kinds of soils?
   (b) On what does a plant feed?
   (c) How can a farmer keep his soil producing?
      (1) What fertilizers are added to soils?
      (2) What plant foods are supplied by commercial fertilizers?
   (d) How can a farmer control plant diseases and insect pests?
2. *How does the good earth supply the building industry with its materials?*
   (a) What are the common construction materials?
   (b) How is lime produced and used?
   (c) How is plaster of Paris produced and used?
3. *How does industry get some of its most needed chemicals?*
   (a) What boron compounds are obtained and used? How are they used?
   (b) What magnesium compounds are obtained and used? How are they used?

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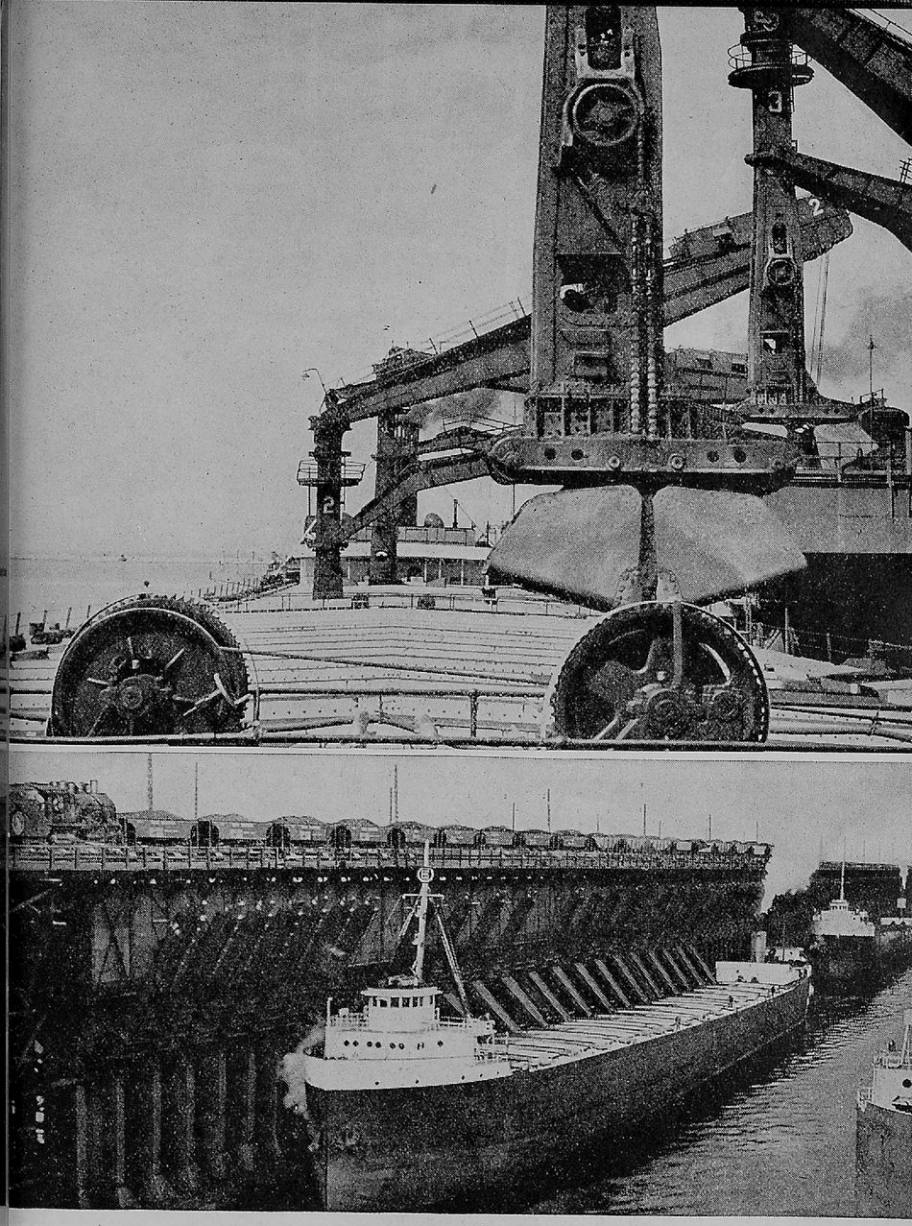

Courtesy, United States Steel Corp.

LOADING AND UNLOADING AN ORE BOAT. In the bottom picture the ore-carrying boat is lying alongside an ore dock from which it will be loaded in a surprisingly short time. Ore is brought in from the mines by the train on the dock. The ore is then dumped into "pockets" in the dock and delivered aboard the boat by means of the chutes. In the top picture steam shovels scoop up great loads of ore.

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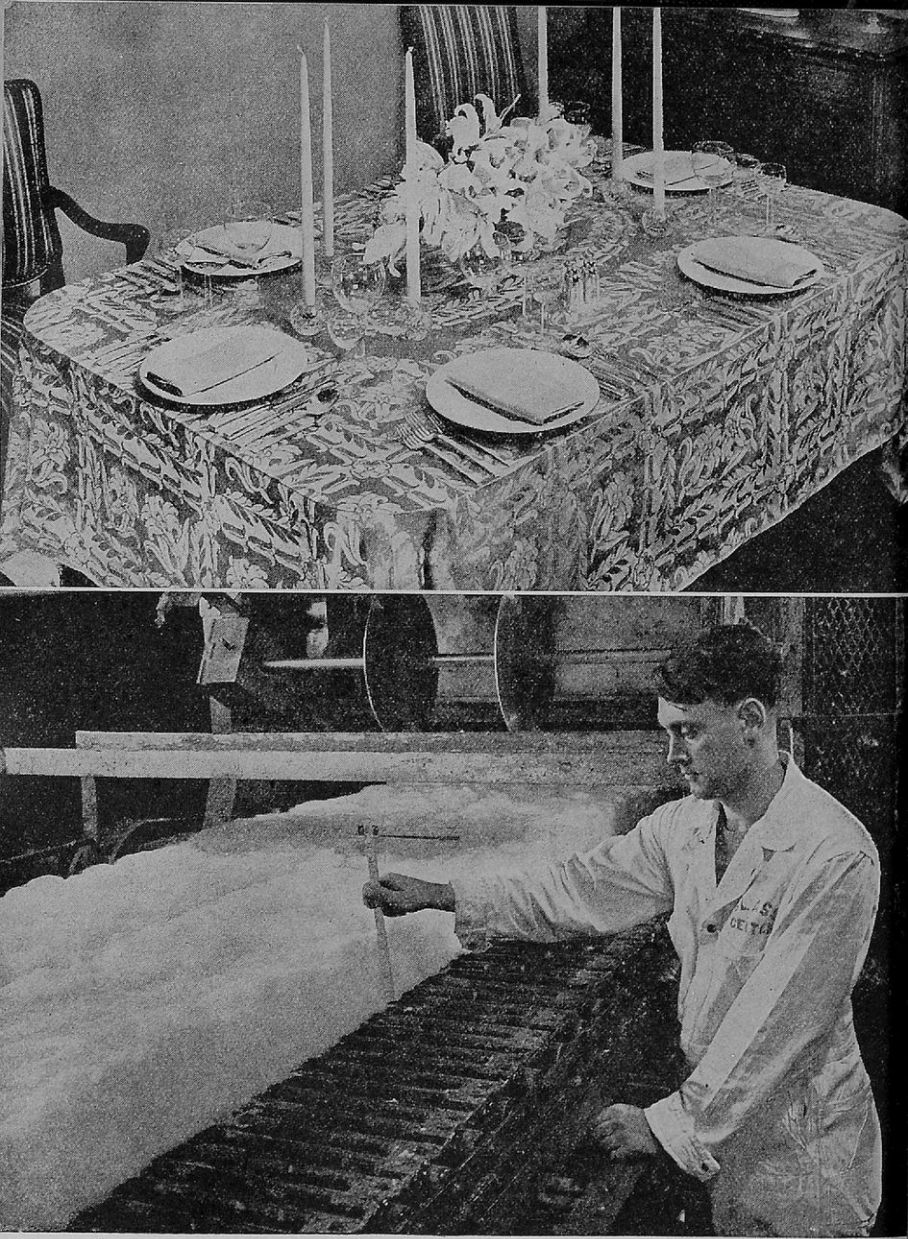

Courtesy, Owens-Corning Fiberglas Corporation

GLASS FIBERS. When molten glass is formed into a very fine fiber, it is elastic, yet strong. It also is fire-proof, moth-proof, rot-proof, and mildew-proof. It may be used for heat insulation and sound-proofing. The tablecloth shown in the picture offers no laundry problem. Water will wash it clean. Cigarettes will not harm it. The colors are fast.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

(c) How are baking soda and washing soda produced?
(d) What are the disadvantages of hard water?
(1) What is hard water? What are the different types of hard water? What dissolved substances cause hardness in water?
(2) What chemicals are used to soften water? Explain why they are used?

4. *What natural and artificial silicon compounds are useful?*
(a) How does silica masquerade in many forms?
(b) How are many common rock-forming minerals related to silicon?
(c) How is glass made?
(1) What is glass?
(2) What different kinds of glass are used? How are they used?
(3) How are colors put into glass?
(d) How is cement produced and used?
(e) What clay products are useful and ornamental?
(1) What is clay?
(2) How is clay made into chinaware?
(3) How is clay made into pottery?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

Great demands are being made upon the "*good earth.*" It has been good in that it has yielded the essential requirements of man—*food, shelter,* and the *raw chemicals* for his complex civilization. But successful *agriculture* requires man's co-operation in returning to the soil the nitrogen, phosphorus, potassium, and other elements that crops remove, and in combating plant diseases and insects.

Man has been using the materials furnished him by the "*good earth*" for a long, long time. But today there is *one great difference.* No longer is the *rule of thumb* method predominant. The *scientific method* of study of these materials is used today. Chemistry, with its basic conceptions of matter, and its laws, enables the people of today to use these materials more effectively.

Do you have an appreciation of your advantage over people of previous generations?

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Looking Ahead into

Unit Sixteen

"Today, as never before, the mineral resources of a nation are recognized as one of its foundations of power," write Kraus and Hunt in their book on mineralogy.

Metals are the servants of industry. They do the heavy industrial work. But they also serve in many other capacities as well. Today, due to the efforts of chemists and metallurgists, scores of metals and combinations of metals are available for a great variety of purposes.

Strangely enough, the choice of a metal for some special purpose almost always depends upon its physical properties. Only one chemical property usually is important if the metal is chosen for a permanent purpose. The metal must either be able to resist the oxidizing action of the air or be capable of taking a protective coating—to protect its surface.

As you well know, paint serves as a protective coating for metal surfaces and other surfaces, but there are other means of protection which you will learn as you proceed with this unit on winning metals from nature, fashioning them for a variety of uses, and saving them against corrosion.

Problem 68. *How Are Metals Freed from Their Ores?*

Problem 69. *How Is Iron Produced and Made into the Strong "Sinews of Industry"?*

Problem 70. *How Is Copper Produced and Used as the "Nerves" of Industry?*

Problem 71. *How Has Aluminum Become an Industrial and Household Servant?*

Problem 72. *How Are Alloys Prepared—Why Are They More Common Than Pure Metals?*

Problem 73. *How Is It Possible to Save Metal Surfaces?*

Problem 74. *What Is in Paint to Give It Its Protective Qualities?*

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Metallurgy: How Metals Are Won from Nature—How Metal Surfaces and Other Surfaces Are Protected.

Problem 68

HOW ARE METALS FREED FROM THEIR ORES?

Have you ever thought of what would happen to you if mankind were suddenly deprived of metals? All modern methods of transportation would disappear, for without steel and aluminum there could be no railroads, airplanes, automobiles, or steamships. Without copper there could be no modern methods of communication—no telephones, no telegraph instruments, no radios. Without metals the many tools and machines that lighten labor and provide leisure would vanish, and mankind would be forced to carry on the work of the world by tedious physical labor. Without metals there could be no type to print newspapers, books, or magazines. In fact, without the use of metals you and your friends would be reduced to the condition of savages.

Metals are elements that will form bases—how can you recognize metals? Probably no one would ever have much difficulty in recognizing the common metals because of their "metallic luster" and their ability to conduct heat and electricity well. They are malleable and ductile. Most metals are more or less silvery, although some are bluish or gray. The only common, colored metals are gold and copper. In general, metals are rather heavy—usually having densities that are between 7 and 14; however, potassium, sodium, and lithium are lighter than water, and magnesium and aluminum have densities of only 1.74 and 2.7 respectively. Gold (density: 19.3) and platinum (density: 21.4) are very heavy metals.

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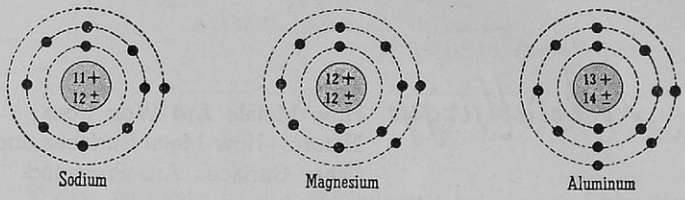

225. ELECTRONIC STRUCTURE OF THREE TYPICAL METALS. Metallic elements have but few electrons in their outermost shells. They readily lose these electrons to form positive ions.

None of the metals are soluble in any ordinary solvents without chemical change.

From a chemical standpoint, metals are elements whose atoms lose electrons and form positive ions. (Fig. 225.) The hydroxides of metals are bases, while those of nonmetals are acids. Therefore, metals are base-forming elements; nonmetals are acid-formers. However, there is no sharp dividing line between the metallic and the nonmetallic elements. Some are on the border line, having both base-forming and acid-forming properties.

The gold obtained during the great Alaskan gold rush of 1898 was free gold—how do metals occur in nature? Metals are found either free or combined. Any metal below hydrogen in the activity series (page 659) may occur in the uncombined state. The gold obtained in the great Alaskan gold rush of 1898 was free gold. In the combined state metals occur in *minerals* which are natural substances having a fairly definite composition. A mineral from which a metal can be extracted profitably is called an *ore*.

Most metals react readily with sulfur or with oxygen, especially at higher temperatures, and many metallic oxides react easily with carbon dioxide to form carbonates. Since sulfur, oxygen, and carbon dioxide are naturally present in large quantities in the air or earth's crust, many of the ores of the common metals are found as sulfides, oxides, or carbonates. A list of the minerals which are ores of these metals follows.

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ORES OF COMMON METALS

Metal	*Mineral*	*Formula of Mineral*
Aluminum	Bauxite	$Al_2O_3 + H_2O$
Antimony	Stibnite	Sb_2S_3
Arsenic	Orpiment	As_2S_3
Calcium	Limestone	$CaCO_3$
Copper	Copper glance	Cu_2S
	Chalcopyrite	$CuFeS_2$
	Cuprite	Cu_2O
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
Iron	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
Lead	Galena	PbS
	Cerussite	$PbCO_3$
Magnesium	Magnesite	$MgCO_3$
Manganese	Pyrolusite	MnO_2
Mercury	Cinnabar	HgS
Nickel	Nickel pyrites	NiS
Silver	Silver glance	Ag_2S
	Horn silver	AgCl
Tin	Cassiterite	SnO_2
Zinc	Zinc blend	ZnS
	Smithsonite	$ZnCO_3$

In the preceding table note that with but one exception all these ores are sulfides, oxides, or carbonates. While this list includes all the common metals, a few less familiar ones such as sodium, potassium, and magnesium are found combined in chlorides. Cobalt and nickel also occur as arsenides, while magnesium and calcium are sometimes found as sulfates.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Although it is 47 per cent iron, iron pyrite is used very little as an ore—why are some "rich" minerals not ores? Many minerals, rich in metals, are not used as ores because of the difficulty of obtaining the metals in sufficiently pure form. For example, iron pyrites (FeS_2) contains about 47 per cent of iron, but the difficulties of removing the last traces of the sulfur from the iron make it of little value as an iron ore. Again, ordinary clay is a mineral containing about 20 per cent of its weight in aluminum, but no way has yet been found to extract this aluminum profitably. For this reason, clay is not at present an ore of aluminum.

Without metals modern civilization would be impossible—how are metals freed from their compounds by metallurgy? Metallurgy is the science of extracting metals from their ores and making them available for use. Most metallurgical processes are chemical reactions; but unless the ores are rich in metals, they are first purified or *concentrated* by physical means. By this preliminary treatment much of the worthless material is rejected. If the ores are sulfides or carbonates, they are *roasted* (heated in air) which changes them to the corresponding oxides. In the case of a sulfide, sufficient oxygen is supplied to convert both the metal and the sulfur to oxides:

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2\uparrow$$

A carbonate, when heated (calcined), loses carbon dioxide and becomes the oxide:

$$PbCO_3 \rightarrow PbO + CO_2\uparrow$$

The oxide is then *reduced,* which releases the metal from chemical combination. Most frequently this is accomplished by heating the oxide with carbon in the form of coke. But all metals cannot be reduced by this smelting process, so other means must be employed. Since the method of reduction depends on the chemical properties of the metal, this most important step in metallurgy is discussed more in detail in the next few paragraphs. The more active metals can be set free only by electrolysis.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

In order to obtain a metal from its ore, you must give back to the metal the electrons it lost when it went into combination. The atoms of uncombined metals contain relatively few electrons in their outer shells. (Fig. 225.) When they combine with other elements, metals lose electrons to form the metallic ions in the compounds. In other words during combination, metals are oxidized. In order to liberate the metals from combination, these electrons must be returned. Any method of reducing a metallic ore consists in returning electrons to the ions of the combined metals.

The activity of a metal determines the method of reducing its ore. The chemical properties of a metal, especially its activity, determine, to a large extent, the methods of winning it from its ores. If a metal is high in the activity series it forms stable compounds. (See chart, page 659.) This means that an active metal loses electrons easily when combining with other elements. Consequently, these electrons are difficult to replace and the metal is difficult to reduce. An electric current is the only practical means of supplying the needed electrons for reducing the ores of the most active metals.

The alkali metals are freed from their ores by electrolysis. Reduction by electrolysis is employed with ores of the alkali metals (Na, K, Li, etc.), alkali-earth metals (Ca, Ba, Mg, etc.), and aluminum. Since these active metals, with but one exception, react with water, electrolysis must be carried out in the absence of water; that is, in their melted compounds. The chlorides are usually the substances used. In the case of aluminum, aluminum oxide (purified bauxite) is dissolved in melted cryolite (Na_3AlF_6). During electrolysis the reduction occurs at the cathode where the metallic ions gain the electrons needed to become atoms.

The metals below aluminum in the activity series can be freed from their ores by the use of aluminum. In the *thermite process* (Goldschmidt's process) of reduction, powdered aluminum is mixed with an oxide of the metal desired, and the aluminum is ignited. In the violent reaction which follows, the aluminum

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

vigorously withdraws the oxygen from the oxide, thus liberating the metal. In the extraction of iron by this process the reaction is:

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

In the above reaction, aluminum is the reducing agent or the substance which supplies the electrons to the iron which is reduced. So much heat is released in this process that the metal is melted. The thermite reaction is frequently employed in welding steel objects which cannot be moved, such as steel rails or the propellor shaft of a ship.

The most common means of winning metals from their ores is through the use of ordinary reducing agents such as carbon, carbon monoxide, or even hydrogen. This type of reduction is used with the less active metals such as zinc, iron, lead, and copper. (Refer to page 659 again.) Oxide ores (also the oxides produced by roasting sulfides or carbonates) are heated with coke in a blast furnace (page 664). Although several fairly definite changes occur during this smelting process, the main change is that the metallic oxide loses its oxygen to the carbon or carbon monoxide:

$$2\ PbO + C \rightarrow 2\ Pb + CO_2$$

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Ores are not pure chemical compounds. They often contain earthy impurities and sand (SiO_2), so it is necessary to remove these undesirable materials during the smelting operation. This is accomplished by adding to the furnace charge a *flux* ("a flow"), which converts impurities to compounds that melt easily. When the impurities are of an acidic nature, consisting largely of silica (sand) and silicates, the flux most often employed is limestone ($CaCO_3$). At the temperature of the furnace the limestone loses carbon dioxide and becomes lime (CaO). This basic oxide combines with the acidic impurities, forming a glassy fluid *slag*, calcium silicate:

$$CaO + SiO_2 \rightarrow CaSiO_3$$

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If the ore contains basic impurities, silica is added as a flux. Since they are lighter than the metal, the slags thus formed separate from the metal; they also protect the metal from being re-oxidized.

The following chart shows how several metals occur in nature and summarizes methods of freeing them from their ores. The method used to free a metal from its ore depends upon the chemical activity of the metal.

ACTIVITY CHART OF METALS

Occurrence	*Activity*	*METAL*	*Ease of Reduction*	*Reduced by*
In Combined Form Only	ACTIVITY DECREASING	Potassium Sodium Calcium Magnesium Aluminum	Very Difficult	Electrolysis
		Manganese Zinc Chromium Iron Cadmium Cobalt Nickel	Difficult	Carbon with Diminishing Difficulty
		Tin Lead	Easy	Carbon
		HYDROGEN		
Free and Combined		Antimony Bismuth Arsenic Copper		
		Mercury Silver	Very Easy	Heat from Oxides
Free		Platinum Gold	Easiest	All Compounds Decomposed by Heat

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Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. XIII, pp. 244-252, "Historical Description of Use of Metals."

DARROW, F. L. *The Story of Chemistry.* Chap. X, pp. 329-362, "The Age of Metals."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XVII, pp. 272-286, "Metals and Metallurgy."

HOLMES, HARRY N. *Out of the Test Tube.* Chap. XXIX, pp. 326-340, "Minerals and World Power."

REED, A. MAXWELL. *America's Treasures.* Chap. I, pp. 3-18, "A Molten Earth and a Frozen Crust"; Chap. II, pp. 19-34, "How the Metals Come."

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. XIV, pp. 263-296, "Metals Old and New."

Applying in Life What You Have Learned in Chemistry

When a young boy, who had a hobby of playing with chemicals, placed a strip of iron in a solution of blue vitriol, he thought that the iron had changed to copper. What justification do you see for his error?

After noting that mercury can be obtained by merely roasting cinnabar (HgS), a student reasoned that this plan would also work with zinc blende (ZnS). Predict whether or not his plan would be successful and offer an explanation.

Putting Chemistry to Work

A

(1) In what ways do the popular ideas of a metal differ from those of a chemist? (2) If you wished to prepare iron, free from carbon, how would you proceed? (3) Since aluminum is much more expensive than carbon, why is it used instead of carbon to release some metals from their compounds? (4) After studying the activity series, point out the metals which you think would be most likely to corrode or tarnish. (5) The red color of many bricks shows that the clay from which they were made contains iron compounds. Why is this clay not used as an ore of iron? (6) Hydrogen can be used to reduce copper oxide. Why can it not be used to reduce calcium oxide? (7) Prepare to explain to a friend who has not studied chemistry how you recognize metals. (8) Why is it not possible to prepare metallic sodium or calcium by the electrolysis of their salt solutions?

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

(9) How do the properties of calcium limit its use in the uncombined state?

B

(10) Define concisely the terms *mineral* and *ore* so as to show the difference between them. (11) How do you account for the fact that many ores are oxides and carbonates? (12) Hydrogen is similar to metals in what two respects? (13) Consult the periodic chart (page 339) to learn whether metals or nonmetals are more numerous. Make a list of all the common metals and nonmetals with their symbols. (14) Give an example to illustrate each of the following: (a) a metal so light that it floats on water; (b) a metal which is liquid at ordinary temperatures; (c) a metal that tarnishes easily in air; (d) a metal that releases hydrogen from water; (e) one that releases hydrogen from hydrochloric acid but not from cold water; (f) a metal that does not tarnish in air; (g) a metal that tarnishes in sulfur fumes but not in air; (h) a metal that does not release hydrogen from acids. (15) Platinum and gold occur free in nature. What does this show concerning the activity of these metals?

(16) Write equations to illustrate how metals are won from different types of ores such as oxides, sulfides, and carbonates. (17) Write equations for the reduction of ores by different means, showing electron transferences. (See pages 301-305.)

Research and Activities That You Will Enjoy

A guest speaker: Invite an industrial chemist to develop in his own way the topic, "The Chemistry of Metallurgical Operations"; or visit him and ask him about his experiences. Report to the class anything that you think would interest them.

A helpful chart: Make a large, complete chart contrasting the physical and chemical properties of metals and nonmetals.

A demonstration: After consulting your instructor, arrange to demonstrate the thermite reaction for the class. Point out the advantages of this method of reduction. Write and explain the thermal equation for the reaction.

A display: Arrange the ores of the common metals in different groups on the basis of their similar metallurgy.

A collection: How many ores can you collect from your friends and classmates to show the various types from which our metals are obtained?

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Problem 69

HOW IS IRON PRODUCED AND MADE INTO THE STRONG "SINEWS OF INDUSTRY?"

During the centuries since some Bronze-age investigator first discovered iron, this metal has become the foundation of our material civilization. It is the best all-purpose metal. It is not the most plentiful metal, or the easiest to refine, or the easiest to work. Iron is not the most resistant metal to corrosion; neither is it the hardest, nor the lightest. Its value depends upon the fact that it has all of these valuable properties to a rather high degree. Furthermore, these valuable properties can be altered to fit specific needs by controlling the amount of carbon and other elements added and by proper heat treatment. Iron in the form of steel plays such an essential part in our industrial and economic life, that it has shaped to a large extent our present civilization.

Iron is rarely found in uncombined form except in meteorites—how iron occurs in nature. Since iron is rather easily corroded (oxidized), it is rarely found free except in meteorites. The common ores of iron are oxides and a carbonate:

CHIEF ORES OF IRON

Name of ore	*Formula*	*Ideal percentage of iron*[1]
Hematite	Fe_2O_3	70%
Limonite	$Fe_2O_3 \cdot (H_2O)_3$	59.9%
Magnetite	Fe_3O_4	72.4%
Siderite	$FeCO_3$	48.3%

Great quantities of iron are found in the form of the sulfide, iron pyrites (FeS_2). But this mineral has only limited use as an iron ore because of the difficulty of removing the last traces of sulfur from the iron.

[1] A considerable quantity of earthy and sandy material is always found mixed with these ores.

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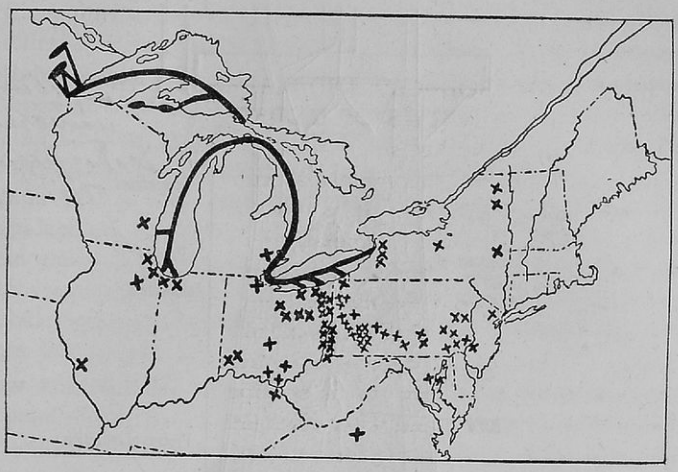

226. THE LOCATION OF STEEL MILLS IN EASTERN UNITED STATES. The greatest concentration of steel mills in this country is in western Pennsylvania and eastern Ohio. This is known as the Pittsburgh district. Other centers are around Detroit and around the lower end of Lake Michigan from Chicago to Gary, Indiana. The routes over which the ore travels to its final destination are shown on the map. Steel mills are also located in Provo, Utah; Torrence, California; and Birmingham, Alabama.

About fifty miles northwest of Duluth are the greatest known deposits of iron ore—how this ore is mined and transported. The greatest deposits of iron ore that are being worked at present are those in the Lake Superior district which include mines in the states of Minnesota, Wisconsin, and Michigan, and the Province of Ontario, Canada. In parts of this district are deposits of hematite and limonite covered over with thin layers of glacial drift. This top soil is removed with steam shovels and the ore, after being broken up by explosives, is loaded into trains by gigantic steam shovels. The trains carry the ore to lake ports where it is dumped into great ore-carrying boats which have been especially developed for this work. They are approximately 600 feet long

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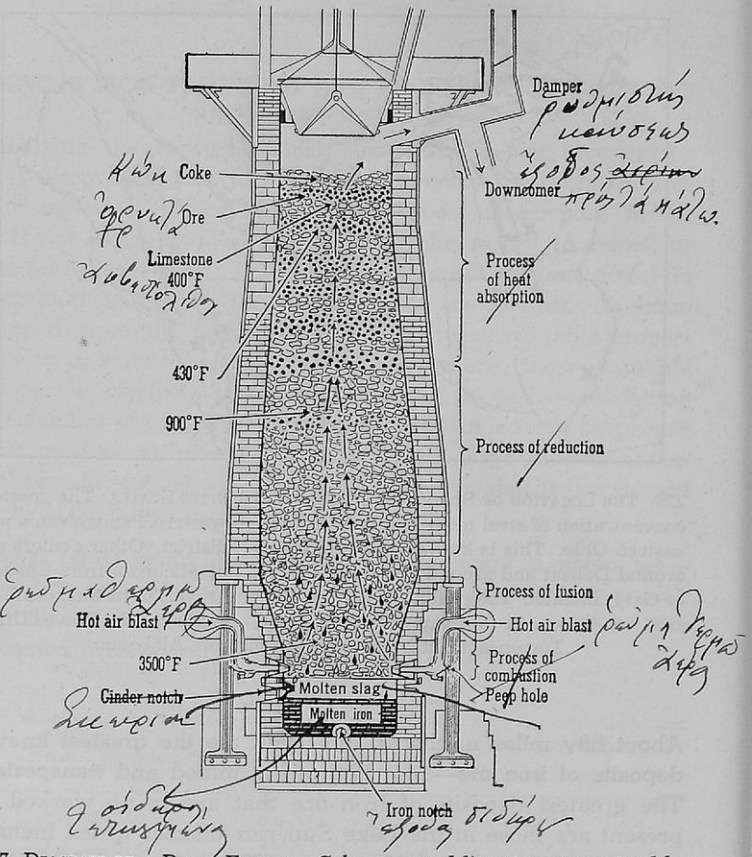

227. DIAGRAM OF A BLAST FURNACE. Coke, ore, and limestone are mixed by feeding them into the furnace through the double bell gate at the top. A hot air blast enters at the bottom. The ore is reduced and the impurities combine with the limestone to form slag. Iron and slag are drawn off through tap holes at the bottom of the furnace.

and carry about 10,000 tons of ore. When the boats arrive at their destinations, they are emptied by mechanical unloaders and the ore is transported to blast furnaces where its reduction to iron takes place.

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Since navigation on Lake Superior is closed from about the first of December to about the first of May, there is intense activity both at the mines and on the lake during the season of open navigation. All the ore that is used in the steel mills in the Chicago and Pittsburgh district must come down the lakes during the season of open navigation.

Iron ore is also found in smaller amounts all along the Appalachian Highland from New York to Alabama. The steel mills of Birmingham, Alabama use ore from mines in Alabama and Georgia. Large deposits of ore are also found in Cuba. Some of the mills along the Eastern seaboard use ore from this source.

How iron is freed from its ore by huge blast furnaces. Iron is smelted in a blast furnace, which is a giant cylindrical structure approximately 80 to 100 feet high. It is about 24 feet in diameter at its widest part, tapering slightly both above and below this greatest width. It is lined throughout with firebrick that can withstand the tremendous temperature produced in the furnace. A furious blast of air, already heated to about 2000°F. (1090°C.) by being passed through a series of huge stoves filled with red-hot bricks, is blown into the lower part of the furnace through a series of pipes called *tuyères*. Quantities of iron ore, coke, and limestone, carefully calculated in amount, are fed in at the top.

The chemistry of this enormous operation is relatively simple. The iron ore, coke, and limestone are dropped into the furnace; the heated air is blown through the mixture. The coke burns forming carbon dioxide which, in turn, is reduced to carbon monoxide as it rises through the hot coke. This hot carbon monoxide reduces the iron oxide ore and forms free iron and carbon dioxide. The heated limestone loses carbon dioxide and becomes calcium oxide, which combines with the impurities (mainly silica) in the ore and forms low-melting, lava-like slag. These two products, the iron and the slag, collect on the bottom of the furnace. The slag, being lighter, floats on top of the iron. The slag and the iron are drawn off through separate openings.

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The carbon dioxide produced by the reduction of the ore is reduced to carbon monoxide by passing through the hot coke. This gas, mixed with the nitrogen from the air which was blown into the furnace, passes out near the top into pipes which carry it to gasholders. It is used to run the blowing engines and to heat the stoves which preheat the blast. The nitrogen is of no value in the operation of the blast furnace. In fact it acts as a thief in stealing heat which is needed in the reduction of the ore. The nitrogen passes through the furnace unchanged and lowers the value of the carbon monoxide fuel.

The quantities of the materials used and produced in a blast furnace may give you a better idea of how enormous this undertaking is. The following chart shows *tons* of materials handled *each day.*

Raw materials that go into a blast furnace		*Products that come out of a blast furnace*
2000 tons iron ore		1000 tons iron
1000 tons coke		500 tons slag
500 tons limestone		6000 tons gases
4000 tons air		

What are the chemical reactions in the blast furnace? The equations for the chemical changes that occur in a blast furnace are relatively simple. As you study these reactions, refer at each step to the diagram in Fig. 227 to see about where in the furnace each change occurs.

A. *Burning the coke:* $C + O_2 \rightarrow CO_2$

B. *Reduction of CO_2:* $CO_2 + C \rightarrow 2\ CO$

C. *Reduction of ore:*
$$\begin{cases} Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2 \\ Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO \end{cases}$$

D. *Formation of slag:*
$$\begin{cases} CaCO_3 \rightarrow CaO + CO_2 \\ CaO + SiO_2 \rightarrow CaSiO_3 \end{cases}$$

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

The blast furnace produces an impure form of iron called pig iron. Iron that has come from a blast furnace is known as pig iron because the "old-time" molds for the hot metal looked somewhat like a litter of feeding pigs. Pig iron can be made into a firebox for your furnace by pouring the hot metal into a mold, sometimes called a *cast*. For this reason pig iron is also called *cast iron*.

Pig iron or cast iron contains from 2 to 4.5 per cent of carbon. Some of this carbon may be chemically combined with iron forming iron carbide (Fe_3C). The rest of the carbon that is in pig iron is dissolved in the iron; molten iron is a good solvent for carbon. As molten iron cools, however, some of the carbon that is dissolved "precipitates out" as graphite and floats about in the air or settles about the container that holds the metal.

Sulfur, phosphorus, silicon, and manganese are also present in pig iron since small amounts of these elements are found in American iron ores or in the coke that is used in the blast furnace. These impurities make pig iron very brittle—it cannot be welded; it is easily broken when hit by a sharp blow.

How pig iron is made into a most useful form—steel. From pins to battleships there is hardly a product or a structure that does not involve directly or indirectly the use of some kind of steel. Some steels may be drawn into wire and formed into such common articles as pins and nails, while others may be rolled into massive naval armor plates so hard and tough that they will turn aside or flatten out steel-tipped projectiles.

Steel is iron containing small but fairly definite amounts of other elements to make the product tough, strong, and hard. Steel making consists of removing impurities from pig iron as completely as possible and then adding the required "impurities," whose amounts in this way are *controlled*. It is remarkable that the various steels have relatively only slight differences in compositions, yet they can be used for such a wide variety of purposes. All steels can be welded and machined. Three common processes to produce steel are the following.

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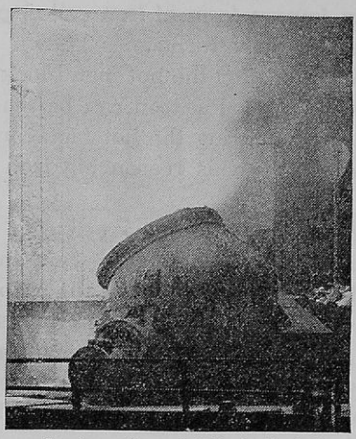

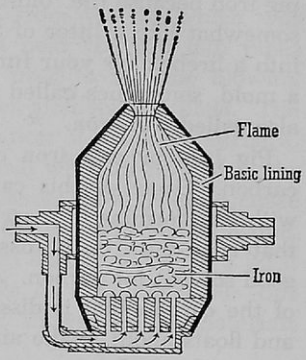

Courtesy, Carnegie-Illinois Steel Corp.

230. BESSEMER CONVERTER. A spectacular operation.

How steel is made by the Bessemer process. In the Bessemer process a blast of hot air is used to oxidize the impurities that are still in the molten pig iron which comes from the blast furnace. Molten iron from the blast furnace is poured into a "Bessemer converter," which is an egg-shaped vessel about fifteen feet high and eight to ten feet in diameter. It has a capacity of from 15–20 tons of the molten iron; this would make a cube about 4.35 ft. on an edge.

Through a series of holes in the bottom of this converter, hot compressed air is blown. The air gushes and hisses to the top of the converter, churning the molten iron as it goes and furnishing plenty of oxygen to oxidize impurities.

The chief impurities in the molten iron are carbon, silicon, manganese, sulfur, and phosphorus. The sulfur and phosphorus are not eliminated by the ordinary Bessemer process as is shown in the following table. For this reason the Bessemer process for making steel in this country is used only with pig iron having a low phosphorus and a low sulfur content. This process requires pig iron obtained from high-grade ore; it has the advantage of giving a large output of low-cost steel.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

REMOVAL OF NONFERROUS IMPURITIES BY BESSEMER PROCESS

Name of Element	*Per cent of Element in Pig Iron before "Blowing"*	*Per cent of Element in Iron after "Blowing" for the Number of Minutes Shown Below:*				
		2	*3½*	*6*	*8⅙*	*10*
Carbon	4.30	3.90	3.75	2.10	0.60	0.03
Silicon	1.25	0.70	0.38	0.03	0.03	0.005
Manganese	0.40	0.10	0.04	0.03	0.01	0.01
Phosphorus	0.085	0.088	0.09	0.092	0.094	0.096
Sulfur	0.035	0.035	0.036	0.037	0.038	0.039

The silicon and manganese impurities in the molten iron are oxidized early in the "blowing" process and are converted into ferrous silicates or manganese silicates, which are eliminated in the form of a scum called slag.

The carbon in the iron is oxidized to carbon monoxide, which then burns with a long yellow flame to give the Bessemer its spectacular "Fourth-of-July" appearance. This burning of the carbon requires the full blowing time, and the suddenly decreased length of the flame when the carbon is burned out indicates that impurities have been removed—the job is done.

During the Bessemer process, some of the molten iron is also oxidized; the resulting iron oxides dissolve in the molten metal. To remove these dissolved oxides, the Bessemer operator adds some "deoxidizers"[1] after the blast of air has stopped. At the same time the proper percentages of carbon and manganese are adjusted in order to produce the type of steel desired. If a special steel alloy is desired, proper amounts of copper, nickel, ferro-chrome, or other alloying elements may be added. The molten product is now poured into a large ladle and thence into molds where the metal cools into thick ingots.

After the operation of the Bessemer process once starts, there is no control of the process until the end. There is also no opportunity to use scrap steel as in the open-hearth process.

[1] Such as *ferromanganese:*
Fe, 13.0%; C, 6.8%; Mn, 79.4%; P, 0.16%; Si, 0.7%
or *spiegel:* Fe, 75.7%; C, 4.4%; Mn, 19.1%; P, 0.05%; Si, 0.7%; S, 0.3%

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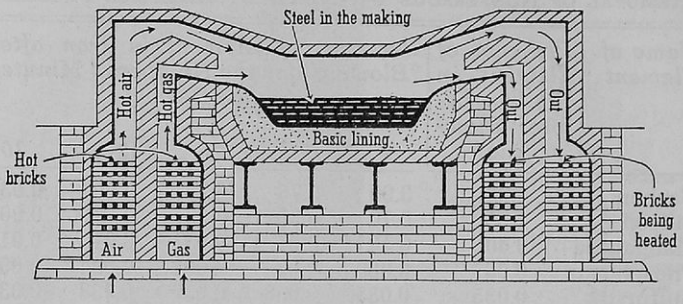

231. AN OPEN-HEARTH FURNACE.

How steel is made by the open-hearth process. An open-hearth furnace looks somewhat like a huge bakery oven; it really might be called an oven to burn the impurities that are in pig iron. After these impurities have been removed, more "impurities" are put back into the iron, but in measured quantities which produce the mixture that is called steel.

An open-hearth furnace consists of a rather shallow pan with a stone lining. Before the hot pig iron is poured into this pan, some limestone, some scrap steel, and sometimes some iron oxides (Fe_3O_4 or Fe_2O_3) are inserted and heated for about two or three hours until the mixture is almost all melted. Then into it is poured molten pig iron from the blast furnace.

As the heat is applied, the carbon in the pig iron is burned and the resulting carbon dioxide escapes as a gas. In a similar manner another impurity, sulfur, is burned, and some of the resulting sulfur dioxide also escapes as a gas.

In American ores phosphorus and silicon are also common impurities. When these two elements burn, the resulting oxides are not gases, and consequently they need "help" in order to escape from the molten iron. As a matter of fact, after the phosphorus and silicon are burned, the resulting oxides are still dissolved in the iron. How can they be gotten out? Fortunately they unite chemically with part of the stone

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

lining of the furnace and with the limestone thus forming phosphates and silicates which float to the top as slag. They can then be removed from the batch of iron. The iron oxides, inserted into the furnace before the pig iron was added, are used as oxidizing agents to help convert the phosphorus and the silicon to their oxides so they can be removed from the iron.

How an open-hearth furnace is operated. The open-hearth furnace is usually heated with a gaseous or liquid fuel. Before the gas is burned, it is preheated to about 800°C. by passing it through a chamber containing red-hot bricks. Air is also preheated in the same way. When the hot air and the hot gas combine, they produce a tremendous flame which is deflected across the surface of the melted metal. Then the "burned" gases rush out at the other end of the furnace, through bricks which absorb the great heat and become red hot.

Every few minutes the direction of the flame is reversed. In this manner heat, that otherwise would be wasted, is continually being *absorbed* on one side of the furnace and *used* on the other side of the furnace to preheat more fuel gas and more air. When liquid fuels are used, they are sprayed into the preheated air.

The operation in the open-hearth furnace requires a whole working day, and more—approximately eight to twelve hours. Toward the end of the operation, samples are taken from the furnace and analyzed in the laboratory to see that the impurities have been oxidized. The molten metal is then poured into an immense ladle where the proper amount of ferro-manganese, ferro-silicon, and (or) aluminum are added as needed for "deoxidizing" purposes as in the Bessemer process. Suitable materials are added to make the kind of steel that is desired.

The steel is poured from the ladle into molds where the metal cools into steel "ingots."

From 50 to 300 tons of steel are made at one time in a single open-hearth furnace.

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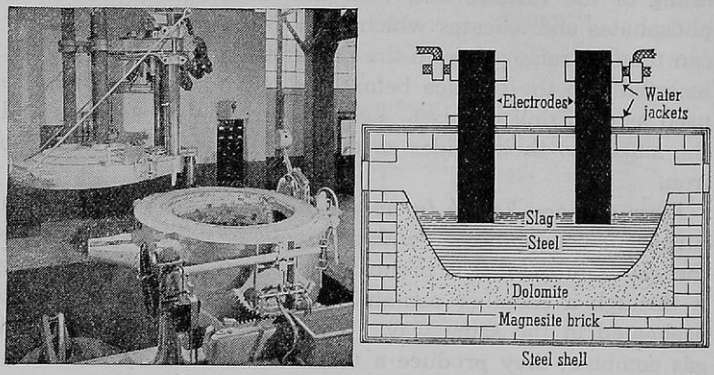

232. THE ELECTRIC FURNACE. The electric furnace is the newest type of furnace in the steel industry. Pure alloy steels free from sulfur and phosphorus can be made in the electric furnace for there is no chance of contamination from the impurities found in fuels.

Advantages of using an open-hearth furnace. A lower grade of ore can be used for the open-hearth process than can be used for the Bessemer process; vast amounts of scrap iron and scrap steel are used; at the same time a high-grade product of uniform composition is produced. The open-hearth process has largely replaced the Bessemer process in this country except that some steel mills now use a "duplex" process in which iron from the blast furnace is first treated in the Bessemer converter and then transferred to the open-hearth furnace. This cuts down considerably on the time required for open-hearth treatment.

How steel is made in an electric furnace. An electric furnace produces high-grade steels that are used in good tools, automobile parts, airplane parts, and stainless steel. An electric furnace uses steel that already has gone through a Bessemer converter or through an open-hearth; it also uses cold steel scrap.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

One of the common types of electric furnace is known as the arc resistance type. In this type an electric current passes from a carbon electrode through the molten iron and slag into another carbon electrode. The slag blanket offers resistance to the electric current and causes enough heat to keep the metal in a molten condition until the removal of the impurities is complete.

The first reaction is oxidation; the resulting silicon and phosphorus oxides become a part of the slag and are "raked off" from the furnace. Then quicklime, sand, fluor spar (CaF_2), and coke are added; the iron in the iron sulfide impurity is thus reduced and the sulfur is burned to SO_2 which escapes as gas.

How the steel in razor blades and skates is made hard by tempering. Iron exists in several allotropic modifications. *Alpha iron,* stable below 768° C., is magnetic and cannot hold much carbon in solution. *Beta iron,* stable between 768° C. and 900° C., is nonmagnetic and tough. *Gamma iron,* stable between 900° and 1400°, takes up carbon in the form of iron carbide. When this is cooled suddenly, by quenching in water or oil, the carbide that is dissolved in the iron gives the steel great hardness, but it also makes the steel quite brittle. If the steel is heated above 900° and allowed to cool slowly, the iron changes to the beta form, the carbon comes out of solution, and the steel becomes soft but tough. If this cooling is done slowly the change proceeds slowly. When this cooling process has proceeded far enough to give both the desired hardness and toughness, the steel is again quenched. By these processes steel is tempered.

How steel is "case hardened." When steel metal is to be exposed to shock (for example, the steel used in gears), it is frequently prepared by a process known as case hardening. In this process steel or high-grade iron is packed in carbon or carbonaceous material and heated until some of the carbon has penetrated the surface of the metal. This produces steel which has a tough *center* and a hard, wear-resisting *surface.*

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

How different kinds of steel are made to serve many different purposes. Six elements—iron, carbon, manganese, sulfur, phosphorus, and silicon—are common to all steels. Iron and carbon are essential; phosphorus and sulfur are unavoidable evils; manganese and silicon are necessary "deoxidizers." By varying only the carbon content, a wide range of physical properties may be obtained. In addition, the physical properties of steel may be greatly altered by adding other metals or nonmetals to it. The various kinds of steels, which are almost "made to order," are important in our national life.

TYPES OF STEEL

Types	*Characteristics*	*Uses*
Plain carbon steel	malleable, can be welded carbon 0.05 to 0.25%	boiler plates, sheet steel, structural work, bridges
	carbon 0.25 to 0.75%	axles, pistons, rods, rails, projectiles
	carbon 0.8 to 1.2%	springs, drills, lathe tools, axes, knives
Alloy Steels—		
Chrome	Cr less than 3%	files, gears, axles, projectiles
Chrome-tungsten	C 0.25 to 1% W 4 to 25% Cr 2 to 10%	high speed tools—may be run at 500° to 600° without losing edge
Manganese	Mn 6 to 15% C 1.0 to 1.4%	burglarproof safes, railroad frogs and switches, helmets

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

TYPES OF STEEL—CONTINUED

Types	*Characteristics*	*Uses*
Nickel-chromium	Ni 1 to 4% Cr 0.5 to 2%	tools, axles, drive shafts, gears—auto parts
Silicon	Si less than 5%	dynamo construction
	Si 16%	acid-proof chemical ware and plumbing
Stainless steel	Cr 13 to 20% Ni 8%	cutlery—containers for corrosives

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. XIV, pp. 262-280, "Iron and Steel."

CLARKE, BEVERLY L. *Marvels of Modern Chemistry.* Chap. XIX, pp. 238-251, "Iron and Steel."

DARROW, F. L. *The Story of Chemistry.* Chap. X, pp. 329-344, "Iron and Steel."

FOSTER, WILLIAM. *The Romance of Chemistry.* Chap. XVIII, pp. 287-307, "Story of Iron and Steel."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry.* Art. 29, A, pp. 202-206, "The Story of Steel"; B, pp. 207-212.

REED, A. MAXWELL. *America's Treasures.* pp. 84-109, "Iron."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XX, pp. 542-557, "Metallurgy of Iron and Steel."

Putting Chemistry to Work

A

(1) What is meant by tool steels? How do they differ from steel used in building construction? (2) Why is steel made by the open-hearth process usually superior to steel made by the Bessemer process? (3) Why is ore shipped from Minnesota to Pittsburgh instead of coal or coke being shipped to Minnesota? (4) In making steel an attempt is made to remove most of the carbon, yet carbon is then added. Why? (5) Name four elements as "impurities"

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

in cast iron that are removed in making steel. Tell in detail how this is accomplished. (6) Name one element in each case that you associate with steel having the following properties: (a) stainless; (b) very hard; (c) retains cutting edge when hot; (d) resists acid corrosion. (7) Show what would happen in a blast furnace if its operation were not continuous. (8) Under what conditions would it be necessary to add sand instead of limestone as a flux in the blast furnace?

B

(9) How can steel be made rustproof? (10) What advantages does the open-hearth process have over the Bessemer process? (11) Under what conditions would no flux be necessary in a blast furnace? (12) Iron is not the most common metallic element, yet it is our most common metal. Why? (13) Point out clearly how pig iron and steel are different in composition and properties. (14) What purpose is served by the electric current in the electric steelmaking process? (15) Calculate the percentage of carbon in a sample of cast iron if the combustion of 1.000 gram of the iron produces enough carbon dioxide to increase the weight of the potash-absorbing bulb 0.147 gram.

(16) How many pounds of iron are present in a short ton of hematite ore which is 80% pure? (17) Calculate the weight of coke that would be required to reduce the ore. (Assume that the coke is pure carbon and that only carbon monoxide is formed.) (18) How many pounds of carbon monoxide will be formed by the reduction of the ore? (19) If the only impurity in the ore is sand, how many pounds of limestone (assume it is pure $CaCO_3$) will be required as a flux? (20) How many pounds of slag will result?

Research and Activities That You Will Enjoy

Sponge iron. See if you can find what sponge iron is, how it may be made and the advantages of its use.

A worthy project: Plan and construct a model of a blast furnace.

A useful chart: Prepare a carefully constructed and complete chart to show the differences between the Bessemer and the open-hearth process for making steel.

Bessemer and Kelly. The stories of the achievements and disappointments of Henry Bessemer and William Kelly in perfecting the steel converter are typical of many parallel but independent discoveries and developments. Read and report the story of achievement for one and disappointment for the other.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Problem 70

HOW IS COPPER PRODUCED AND USED AS THE "NERVES" OF INDUSTRY?

Copper was probably the first metallic element known to man. Long before the period of written history, primitive man had found native copper in surface deposits and had fashioned it into crude tools. Soon he found that other metals mixed with the copper made a harder substance and bronze tools came into use. Modern man still uses copper in the alloys (brass and bronze) but it is more important to him in the electrical industries. Without it the great dynamos in the huge power plants of the country would not exist. Copper is the foundation metal upon which all of our systems of communication depend. Without it, there would be no telephones, telegraph systems, or radios. The electric current which lights your home, runs the vacuum cleaner, and toasts your bread enters your home through copper wires. It is difficult to imagine how the many modern conveniences of an industrial age could exist without this valuable metal.

How copper is found in nature. In a few places on the earth's surface, copper is found free. In northern Michigan it occurs mixed with beds of eruptive rocks. Here it is quite pure, running slightly above 99.9 per cent copper with traces of silver, iron, nickel, and arsenic. A single mass found in a Michigan mine weighed over 500 tons. However, most of the copper used in industry comes from ores in which copper is found in combined form.

Copper occurs in nature chiefly as sulfide and oxide ores. The common sulfide ores are the minerals chalcocite (Cu_2S) and chalcopyrite ($CuFeS_2$). Other ores are cuprite (Cu_2O) and malachite [$CuCO_3 \cdot Cu(OH)_2$].

Cuprite and malachite are formed from sulfide ores by the action of oxygen and carbon dioxide on the sulfide. Since they are the result of the action of the air, they are always found near the surface of the earth.

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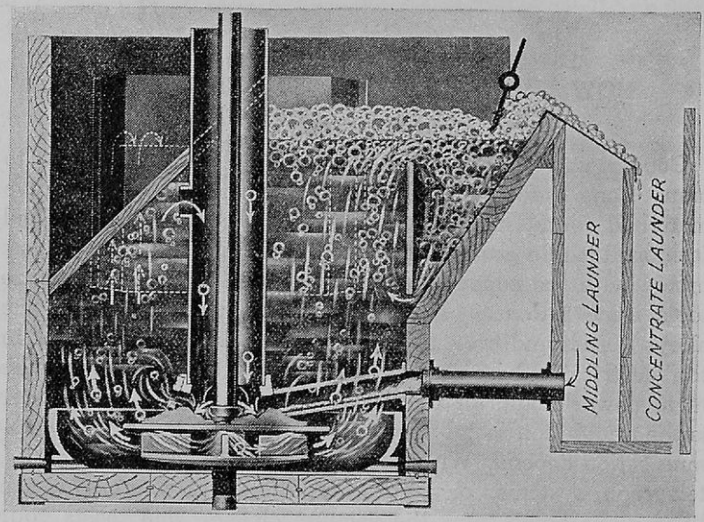

Courtesy, Denver Equipment Company

233. AN ORE FLOTATION UNIT. In this piece of apparatus, sulfide ores can be separated from rock. The separation is based on the fact that the ore adheres to bubbles of foam while the rock does not. Rapid stirring produces foam which rises to the top of the liquid carrying the ore, which can be floated off from the liquid and thus separated from the rock.

How copper is extracted from its sulfide ores. The metallurgy of copper is somewhat more complicated than the metallurgy of iron. Since the most important copper ores are sulfides, we shall consider them first. The complete metallurgy is indicated briefly in the following steps: (1) Low-grade sulfide ores are concentrated by flotation. (2) A part of the sulfur is removed by roasting. (3) The nonmetallic earthly impurities are removed as slag, and the "*matte*" (a mixture of sulfides) is formed. (4) The matte is converted to impure copper. (5) The impure copper is refined by electrolysis.

How copper sulfide ores are concentrated by flotation. In the flotation process, the sulfide ores are crushed and ground to a fine powder before they enter the flotation ma-

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

chine. Here they are mixed with water and oil and are vigorously agitated. This beats air into the mixture, and a frothy mass of oil rises to the surface. The oils used in the process adhere to the metallic sulfides, but not to the non-metallic rock. In this manner the froth, bearing the sulfide content of the ore, flows out of the tank and leaves the non-metallic residue behind. After the froth subsides, the sulfides are removed by mechanical filters, and are ready for the roasting process.

How copper sulfide ores are roasted. The object of the roasting operation is to burn out part of the sulfur and to oxidize part of the iron sulfide, which is present, to iron oxide. This iron oxide mixes with the slag and is removed with it in the next operation. In the roasting furnaces the copper sulfide ore is heated to red heat. This decreases the sulfur content to about 10%.

How the "matte" is formed. The product from the roasters consists of a mixture of copper and iron sulfides, together with some silica and lime. It is heated with powdered coal or oil in large reverberatory furnaces. The silica forms a slag with any iron oxide that is present, and the lime makes the slag more fusible. This operation removes a considerable quantity of the iron.

The other product formed in the reverberatory furnaces is "matte." It is an artificial sulfide containing from 23 to 25 per cent sulfur, combined with copper and some iron. Any gold or silver which may be present is also in the matte. The copper content of the matte is about 40%.

How the "matte" is converted to impure copper. In order to obtain metallic copper, the matte is heated in a converter similar to the one used in the Bessemer steel process. It consists of a large cylinder about 15 feet in diameter and 10 feet high, topped with a truncated cone open at the top. About 65 tons of matte from the reverberatory furnace are poured in, together with some raw ore, and hot compressed air is blown in through the bottom of the liquid mass. This burns the sulfur to sulfur dioxide and the iron to iron oxide. The iron oxide

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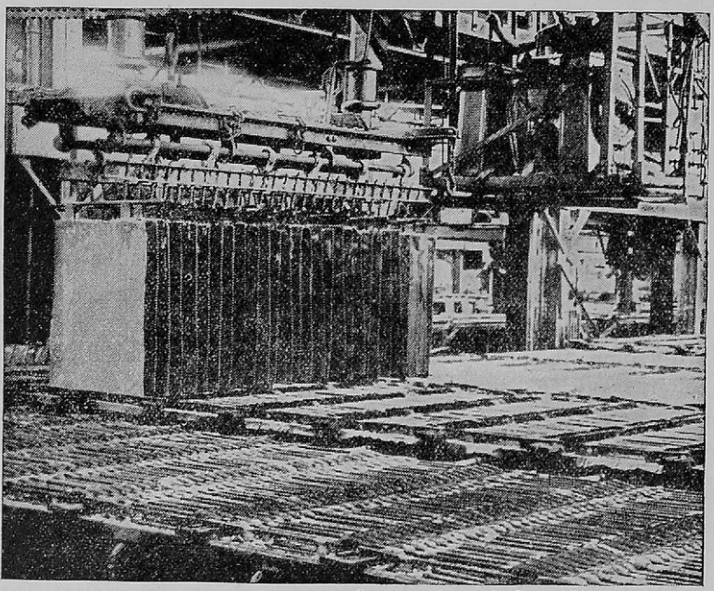
combines with the silica of the raw ore to form a slag. Flames of many colors pour from the throat of the converter. They finally change to a blue color as the iron oxidizes. It takes about three hours to burn off the iron and another two hours to convert the copper sulfide to copper. The sulfur is never completely removed.



Courtesy, Anaconda Copper Mining Company

234. REFINING COPPER BY ELECTROLYSIS. Slabs of impure copper are immersed in dilute sulfuric acid and are used as anodes. The pure copper is plated on the cathode. A crane has just lifted a group of these pure copper sheets from one of the cells like those shown in the lower foreground.

Since it is impossible to separate completely the copper and the slag in the converter, further refining is carried out in a small reverberatory furnace. Air is blown through the molten metal to oxidize any unoxidized iron. Any oxides of sulfur, arsenic, zinc, or antimony which may be present are

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

vaporized and passed off. During this operation some copper is also oxidized. This is reduced back to the metallic state by forcing poles of green wood below the surface of the melted metal. When the reducing action is complete, the metal is cast into slabs about 36 inches long, 30 inches wide and 2 inches thick. This metal contains about 99.3 per cent copper, 0.2 per cent silver, and small amounts of gold, arsenic, and antimony.

How copper is refined by electrolysis. Electrolytic refining is used to get the pure copper. The cast slabs of impure copper are used as anodes in an electrolyte containing about 10 per cent sulfuric acid and 3 or 4 per cent copper sulfate (Fig. 234). The cathode is a thin sheet of pure rolled copper. As a heavy electric current passes through the solution, copper is dissolved from the anode and deposited on the cathode. This deposit is almost chemically pure copper. Impurities present in the anode, together with a small amount of copper, collect as a muddy deposit on the bottom of the tank. This sludge is treated to extract its content of gold, silver, copper, and other metals.

How copper is extracted from its oxide ores. Rich copper oxide ores are sometimes smelted with coke in a blast furnace, similar to the method used in smelting iron oxides. More often they are mixed with sulfide ores and treated as sulfides. Since many of these oxide ores are quite low in copper content, various methods have been used to dissolve out the copper with sulfuric acid and then precipitate the copper by displacement with iron; or the copper may be recovered electrolytically. The flotation process does not work with oxide ores, so it is very difficult to concentrate these ores.

Copper is the only common metal with a red color—what are other characteristics of copper? The specific gravity of copper is 8.9. It melts at 1083° C. It is easily rolled into sheets, drawn into wire, and hammered into thin foil. Hammering or rolling copper causes it to become hard and brittle, but heating it to 500 to 700° C. softens it again. Next to silver, copper is the

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

best conductor of heat and electricity, though small amounts of impurities greatly diminish its electrical conductivity. As little as 0.03 per cent of arsenic in copper lowers its conductivity about 14 per cent, and less than 0.5 per cent of silicon has about the same effect.

Copper occurs just below hydrogen in the replacement series, so this metal does not liberate hydrogen from acids. Strong oxidizing acids, such as nitric acid, hot concentrated sulfuric acid, and aqua regia, easily react with it. Iron and other active metals displace copper from solutions of its salts.

$$CuSO_4 + Fe \rightarrow Cu + FeSO_4$$

Copper is not acted upon by dry air. But in moist air a thin layer of cuprous oxide (Cu_2O) forms on it. Carbon dioxide and water convert the oxide into a green coating of basic copper carbonate [$CuCO_3 \cdot Cu(OH)_2$]. This coating acts as a protective layer to prevent further corrosion. It is often seen on copper roofs and bronze statues.

Copper wires conduct electricity to the homes and commercial houses in your city—in what other important ways is copper used? Because of its inactivity with acids, water, and steam, copper is used in many manufacturing industries. Bottoms of ships are coated with it. The poisonous copper compounds, which form on its surface, prevent the growth of barnacles and other marine organisms. In regions where the water is soft, water pipes of copper or brass (an alloy of copper) are employed in houses to prevent the contamination of the water which might otherwise occur through the corrosion of lead or iron pipes.

Because of its high conductivity and ductility, copper is widely used in electrical work. The coils in the electromagnets of dynamos, motors, telegraph instruments, telephones, and radio sets are made of copper. Most of our transmission lines are also copper.

Many copper alloys are in use. No other metal enters into so many alloys as copper. A few of these, which are in common use, are listed on the next page.

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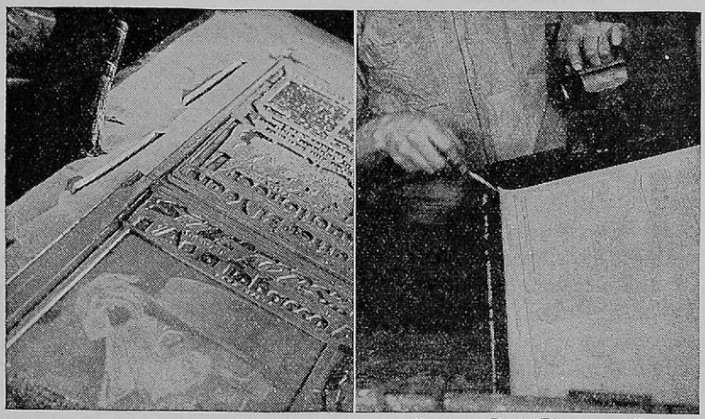
Alloy	*Composition*	
Coin silver	Copper 10%	Silver 90%
Nickel coin	Copper 75%	Nickel 25%
Coinage bronze (cent)	Copper 95%	Tin 3% Zinc 2%
Brass	Copper 66—73%	Zinc 27—34%
Bronze	Copper 89%	Tin 11%
German silver	Copper 57%	Zn 19% Ni 24%
Aluminum bronze	Copper 90%	Al 10%
Bell metal	Copper 75—80%	Tin 20—25%
	(sometimes silver, nickel, or other metals also)	



Courtesy, Rapid Electrotype Company

235. MAKING ELECTROPLATES. After the type for this book was set, an impression was made in wax. Such a wax impression is shown at the left. This is dusted with graphite and made the cathode in an electrolyte of copper sulfate. The copper shell thus formed is backed with type metal. The pages of this book were printed by means of plates of this kind.

Copper was used in the printing of this book—how? The use of copper in electrotyping is important and interesting. When large editions of a newspaper or book are to be printed, the type is first set by machine or by hand in the usual way. This

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

type is soft and would wear down very rapidly. A wax impression is made of this, and the wax is smoothly and evenly coated with powdered graphite. Then it is made the cathode in an electroplating solution containing copper sulfate. A coating of copper is soon plated on the graphite surface. When the deposit is thick enough, the wax is melted off and the copper shell is backed up with type metal to make a plate strong enough to print two or three hundred thousand copies.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. XIII, pp. 252-261, "Copper."

MORRISON, A. CRESSY. *Man in a Chemical World.* Chap. VIII, pp. 202-229, "Serving Industry."

REED, A. MAXWELL. *America's Treasures.* Chap. IV, pp. 54-72, "Copper, Lead and Silver."

Putting Chemistry to Work

A

(1) Why is copper instead of iron preferred for window screens, eave troughs, and spouts? (2) Explain the statement: "The flotation process has made available large quantities of copper which otherwise might never have been recovered." (3) Many copper-covered roofs turn green in a few months. Explain this. (4) Account for the large number of electrochemical works located at Niagara Falls. (5) Draw a diagram of an electrolytic cell for the refining of copper. Label all parts and explain in detail how pure copper is obtained by the process.

B

(6) What reason do you see for the fact that copper was one of the earliest metals known to man? (7) Why is pure copper needed in the electrical industries? (8) What products other than copper may be recovered at a copper smelter? (9) List three uses of copper, each of which depends on a different property. (10) Write equations for: (a) roasting copper sulfide (Cu_2S); (b) reduction of cuprous oxide with carbon (c) action of concentrated nitric acid on copper; (d) replacement of copper from a solution of copper sulfate by zinc; (e) heating solid copper nitrate.

(11) In a recent year the three states Arizona, Montana, and Utah produced 365,000 tons of copper. Assuming that the ore used was

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Cu_2S, show how much sulfuric acid could have been prepared as a by-product. How does this compare with the world's consumption of sulfuric acid?

Research and Activities That You Will Enjoy

A display: Bring together all the alloys of copper you can find. Show the composition and an important use of each.

A forum: Develop the following topic: "What copper means to communication."

A project: Try copper plating some object. Study the conditions necessary for a smooth deposit and see how good a job you can do.

An advanced project: One type of "homemade" photoelectric cell can be made by suspending in a solution of a lead salt one plate of lead and, very close to it, another plate of copper on which is an extremely thin layer of cuprous oxide. Are you interested? Get more facts before trying it.

Problem 71

HOW HAS ALUMINUM BECOME AN INDUSTRIAL AND HOUSEHOLD SERVANT?

"There is so much aluminum in the earth it ought to be dirt cheap." This statement is frequently heard. Aluminum is the most abundant and the most widely distributed metallic element in the earth's crust, but it is far from being the most common metal in use. There is aluminum in all common clay—where it is present in the mineral *kaolin,* a rather complex silicate of aluminum.

Until about 1880 aluminum was a rare metal because of the difficulty of separating it from the complex compounds in which it is found. Aluminum oxide is more stable than carbon dioxide, for aluminum gives up its electrons more easily than carbon. Consequently, carbon does not reduce aluminum oxide as it does iron oxide in the production of iron in the blast furnace.

You have learned that hydrogen is a powerful reducing agent, but it is not active enough to reduce aluminum oxide, so the electrolytic process must be used.

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Common clay contains a wealth of aluminum, but this wealth is too difficult to free—what substance is used as the source of aluminum? Aluminum is produced commercially from *bauxite* which is an impure hydrated oxide [$Al_2O_3 \cdot (H_2O)_2$]. This ore contains as impurities, ferric oxide (Fe_2O_3), titanium oxide (TiO_2), and silica (SiO_2). From this mixture the aluminum compound is dissolved by treatment with sodium carbonate. Next the aluminum hydroxide is separated from solution by precipitation and filtration. Upon being heated, the hydroxide loses water and pure aluminum oxide is formed. Metallic aluminum is prepared from this purified oxide by electrolysis.

Icy Greenland furnishes cryolite which makes it possible to free aluminum from aluminum oxide by electrolysis. Aluminum oxide must be reduced in order to free its aluminum. But the problem of reducing aluminum oxide was a difficult one—even by electrolysis. Before any substance can be reduced by electrolysis, it must be melted or dissolved so its ions are free to "carry" an electric current. However, aluminum oxide cannot be melted easily; its melting point is about 2000° C. Neither can it be dissolved sufficiently when water is used as the solvent.

What solvent can be used to dissolve aluminum oxide? This part of the problem of producing aluminum was solved when it was found that molten *cryolite* is an excellent solvent for aluminum oxide and has a low melting point. Cryolite is a double fluoride of sodium and aluminum (Na_3AlF_6) which is found plentifully in Greenland. It is the most important export from Greenland.

The apparatus used is a rectangular iron box with a heavy lining of baked-in carbon, which is used as the negative electrode. The anodes are heavy carbon rods, suspended in the tank (Fig. 236). A mixture of cryolite and fluor spar (CaF_2) is used as the solvent. Because of its low melting point, the cryolite is easily kept in a melted condition. After the purified aluminum oxide is dissolved in the melted cryolite, an electric current is passed through the cell. The aluminum

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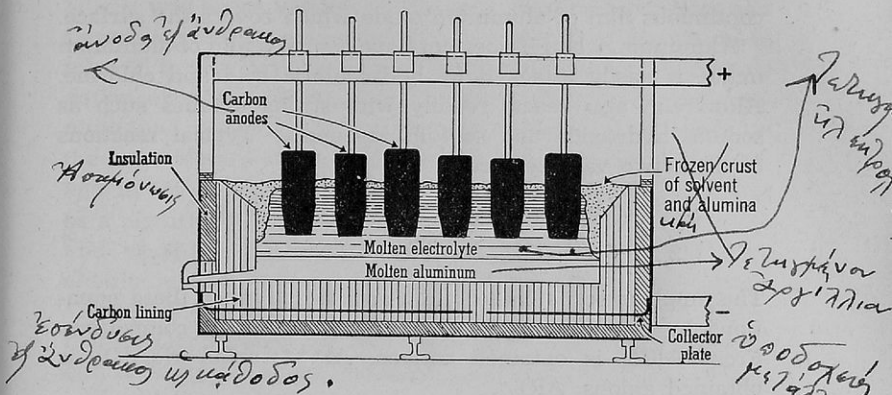


236. COMMERCIAL PREPARATION OF ALUMINUM. Purified aluminum oxide dissolved in molten cryolite is electrolyzed. Metallic aluminum is deposited on the carbon lining which forms the cathode. The heat produced in the operation is sufficient to keep the aluminum in a melted condition.

collects on the bottom of the cell—while the oxygen goes to the carbon anodes, combines with the carbon, and comes off as carbon dioxide. The aluminum thus prepared is drawn off from time to time. It is usually about 99 per cent pure.

This electrolytic process for the extraction of aluminum was worked out by Charles Martin Hall in the family woodshed just after he had graduated from Oberlin College. The Hall process lowered the production cost of aluminum to about twenty-five cents a pound, and changed it from a rare metal to a common one. The comparative cheapness of aluminum is emphasized by the fact that because of its natural lightness one pound of aluminum is about three times the size of one pound of almost any other common metal.

Aluminum is a white metal, capable of taking a high polish—what other properties does it have? The specific gravity of aluminum is 2.7. It melts at 659° C. While it is an active metal, high in the replacement series, it is quite resistant to corrosion and to the action of strong oxidizing acids. Its resistance to atmospheric corrosion is due to the formation of a tough

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

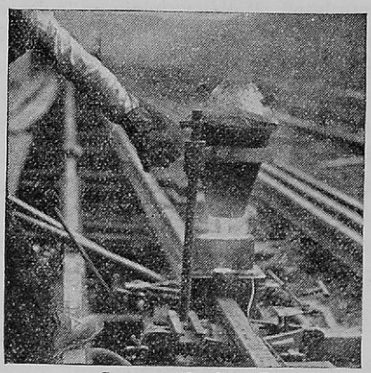
continuous film of aluminum oxide which covers the surface.

Aluminum, when it does not have over it a film of aluminum oxide, is easily attacked by hydrochloric acid and chlorine. Aluminum also reacts readily with strong alkalies such as sodium hydroxide and sodium carbonate. Typical reactions of these two varieties are:

$$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2\uparrow$$

$$2\ Al + 2\ NaOH + 2\ H_2O \rightarrow 2\ NaAlO_2 + 3\ H_2\uparrow$$

The amphoteric nature of aluminum is shown in these equations by the fact that it forms two classes of compounds. From $AlCl_3$ is obtained cations, Al^{+++}; from $NaAlO_2$ is obtained anions, AlO_2^-.



Courtesy, Metal and Thermit Corp.

237. WELDING BY THE USE OF THERMITE. Thermite is a mixture of powdered aluminum and iron oxide. When it is ignited, a violent displacement reaction takes place liberating iron. The temperature of the iron is far above its melting point. This molten iron flows into the mold around the rail joint and welds the rail.

Aluminum is one of the most important of the metals—how is it used? Although aluminum is a comparatively new metal, it probably is the third most important commercial metal. The world's annual production in the years previous to World

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

War II was about 400 million pounds. The United States and Germany were leading producers. Commercial aluminum is from 98 to 99.5 per cent pure. Its chief uses are in the deoxidation of metals (such as steel, chromium, manganese, uranium, and titanium) by the thermite process (page 688), in the manufacture of cooking utensils and chemical apparatus, and in the electrical industry. Powdered aluminum is used as a pigment in paint. Most of the "silver paper" which you find wrapped around your candy bars is a thin sheet of aluminum foil. Aluminum foil also is used in flash lamps.

The use of aluminum in the electrical field depends on the fact that its conductivity is about 60 per cent of that of copper, and its weight is about one-third. However, since its strength is less than one-half that of copper, aluminum wire in cable form is usually stranded about a steel core to give it strength. In this form many miles of it are used to carry high voltage electric currents.

The alloys of aluminum are numerous and useful. They are discussed in the next problem.

Aluminum has become the "housemaid" of the metals. The use of aluminum in cooking utensils is based on the fact that it is light and durable. It is an excellent conductor of heat. Its oxide film of tarnish is almost invisible, and this thin coating of oxide makes it easy to clean. The freedom of aluminum from corrosion has enabled it to replace iron and copper in cooking utensils. Aluminum has become the "housemaid" of the metals.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff*. Chap. XIX, pp. 367-382, "Aluminum—Lightweight Champion of the Metals."

DARROW, F. L. *The Story of Chemistry*. Chap. X, pp. 344-349, "Aluminum."

GOLDBLATT, L. A. *Collateral Readings in Inorganic Chemistry*. Art. 27, A, pp. 187-192, "Award of the Perkin Medal to Chas. M. Hall"; B, pp. 193-199, "Economics of the Aluminum Industry."

HOLMES, HARRY N. *Out of the Test Tube*. Chap. XXX, pp. 341-352, "Three Light Metals."

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REED, A. MAXWELL. *America's Treasures.* Chap. VII, pp. 110-121, "Aluminum."

WEEKS, MARY ELVIRA. *The Discovery of the Elements.* Chap. XII, pp. 163-177, "Aluminum."

Applying in Life What You Have Learned in Chemistry

Helen was helping her mother can some peaches. Grandmother was looking on.

"When I was a girl," said Grandmother, "we always used a copper kettle at canning time. Now you are using an aluminum one."

Why didn't Grandmother use an aluminum kettle?

Mary was making fudge when the telephone rang. It was Bob and he wanted to talk over plans for the next week-end picnic. When he finally hung up, Mary found the fudge burned to a cinder.

Since it was in their best aluminum pan, Mary was anxious to clean it before her mother arrived home. Scouring helped little. Finally, in desperation she thought of her chemistry book, and to her relief found that concentrated nitric acid had little effect on aluminum.

She found the nitric acid in her brother's lab, tried it, and it worked!

Aluminum is an active metal and nitric acid is a strong acid. Can you explain why Mary did not ruin the aluminum pan? Would HCl do as well? Would you use *Drano* (lye) to clean aluminum?

Comment on Ostwald's remark: "Dr. Hans Goldschmidt has given the industrial world a blast furnace and smithy for the waistcoat pocket."

Putting Chemistry to Work

A

(1) How do you account for the fact that although aluminum is the most common metallic element, it has only comparatively recently come into general use? (2) Justify the statement: "The cost of aluminum depends largely on the cost of electricity." (3) Although aluminum is high in the activity series, it does not corrode as easily as iron. Account for this fact. (4) If grease is burned onto an aluminum frying pan, should it be cleaned with lye, washing soda, strong soap? Explain your answer. (5) What factors enter into the cost of producing a metal? Illustrate with Fe, Al, Au.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

B

(6) In the production of aluminum, what is the use of the cryolite, the carbon coating on the inside of the cell, and the aluminum oxide? (7) Why is the natural bauxite not used in the electrolytic cell? (8) Make a list of all the elements that are obtained by the use of electrical energy. (9) Although aluminum is the most abundant metallic element, it was not discovered until 1827. Why? (10) How would you proceed to prepare pure manganese from manganese dioxide?

Research and Activities That You Will Enjoy

A resumé: Prepare and present to the class a brief summary of Professor Holmes' pamphlet, "Fifty Years of Aluminum." (A copy of this historical sketch may be secured by writing Oberlin College.)

A forum: Develop the topic: "How aluminum has fostered aviation."

A report: Although you may think of aluminum most frequently in connection with cooking utensils and lightweight aviation alloys, its oxide is known in several varieties of natural and artificial gems. Report to the class all you can learn about aluminum-oxide gems.

Interesting topics: See what you can learn about any of these topics and report to the class what you have learned: (a) Use of aluminum foil for heat insulation (b) How Christmas tree tinsel is made (c) The manufacture of aluminum powder and its use in thermite welding and in paint (d) The use of aluminum in the 200-inch telescope at Mt. Palomar, California.

Problem 72

HOW ARE ALLOYS PREPARED—WHY ARE THEY MORE COMMON THAN PURE METALS?

Pure metals are almost chemical curiosities. In general metals are mixed with other substances to form alloys. Thus gold, silver, and nickel coins contain copper. Tool steels contain tungsten, manganese, and chromium—in addition to carbon. The lead sheath around telephone cables contains antimony. The "copper" cents which you use to pay for a newspaper are made of an alloy of copper, tin, and zinc. The

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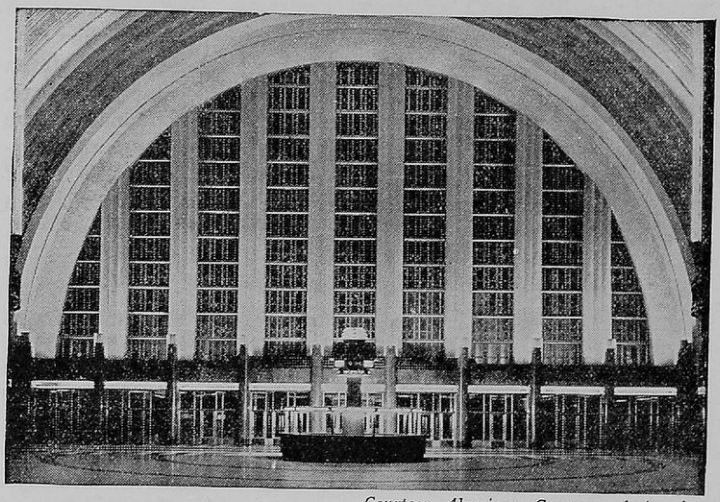

Courtesy, Aluminum Company of America

238. THE USE OF ALUMINUM ALLOYS IN ARCHITECTURE. Aluminum alloys are being used more and more in architectural design. Here is a great arch and a window made of some of these beautiful alloys.

brass door knob, which you grasp when you enter a room, is an alloy of copper and zinc. The stainless steel knife blade is an alloy of iron, chromium, and nickel. Nearly all the metal articles which you buy are alloys. The number of alloys produced for various uses is very large, and new ones are constantly being prepared and put to use.

How are alloys prepared? Alloys are usually prepared by melting together the metals which compose them until a uniform mixture is produced. In many cases the mixtures seem to be solutions of one metal in another. This variety includes by far the greater number of technically important alloys. Steel, brasses, and bronzes belong to this group. In other alloys, some of the metals seem to combine to form definite compounds which do not agree with our ideas of valence. We have, for example, such "compounds" as $NaZn_{11}$, Fe_3C,

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Cu_5Sn_2, and Cu_2Zn_3. These "compounds" occur as small crystalline masses in solid solution of one metal in another, or the solid solution of compounds of metals in one or more of the metals. Some metals are miscible in all proportions, like alcohol and water. Examples are gold and copper. Others have only a limited solubility in one another.

The melting point of an alloy is lower than that of any of its component metals. This fact does not seem so strange when you realize that alloys are solutions (page 112). In the case of some of the alloys of bismuth, the melting point is even below the boiling point of water. Wood's metal, which consists of one part each of tin and cadmium and two parts of lead dissolved in four parts of bismuth, melts at 65° C.

An alloy is usually harder than the metals which compose it. Copper is added to gold to harden it for use in coins and jewelry. Brass is also much harder than either copper or zinc.

An alloy is usually a poorer conductor of electricity and heat than the pure metals which compose it. German silver (an alloy of copper, zinc, and nickel) is used as resistance wire, and nichrome (an alloy of nickel and chromium) is used for the heating units of electric toasters and electric furnaces.

The physical properties of many alloys are greatly influenced by the size of the crystalline particles in the alloy. This fact makes it necessary to "heat treat" metals in order to get crystals of the proper size to give the desired properties. If the alloy cools slowly, the crystalline grains are large, just as the crystals that form from ordinary solutions during slow crystallization are larger than those that form during rapid crystallization. By heating and cooling an alloy under carefully controlled conditions, the size of the crystalline grains can be controlled and through this the physical properties can be altered to a considerable extent.

How are alloys used? Alloys of different metals are numerous and new ones are frequently developed. A few alloys of technical importance are given in the following table.

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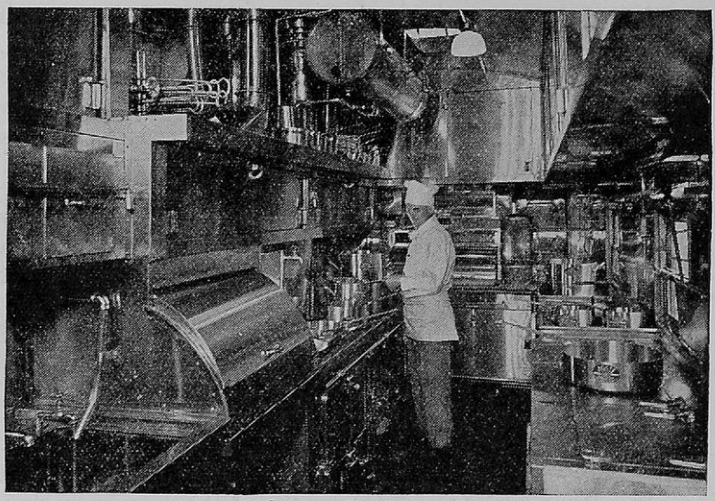

Courtesy, The Atchison, Topeka and Santa Fe Railway Co.

239. A NICKEL ALLOY IN USE. This view of the kitchen of a dining car shows its entire interior made up of monel metal, an alloy of nickel and copper containing a little iron. Monel metal does not tarnish and is easy to keep clean.

SOME IMPORTANT ALLOYS AND THEIR USES

Alloys	*Properties*	*Uses*
ALUMINUM–copper (8%)	High tensile strength, light	Automobile parts—crankcases, step plates—heavy cooking utensils
ALUMINUM–zinc	High tensile strength, heavier than copper alloys, more easily corroded than copper alloys	Somewhat limited use due to properties
ALUMINUM–silicon (5 to 15%)	Tough, noncorrosive, lighter and stronger than the commoner aluminum copper alloys	Used in chemical industries

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Alloys	*Properties*	*Uses*
ALUMINUM – small amount of copper, nickel, and magnesium	Strong even when subjected to high temperature	Pistons for gas engines, other engine parts
ALUMINUM – copper (4%)–magnesium (1%)–manganese (6%). Known as "Duralumin"	About as strong as steel but only about one-third as heavy	Dirigibles, and metal airplanes, automobile parts
COPPER – tin (up to 12%). Known as bronze	Good-wearing properties	Making "copper" coins and medals (4 to 8% tin), English gear bronze (11% tin) for heavy gears
COPPER–zinc (up to 50%). Known as brass	Gold colored. Dutch metal brass is very malleable, sturdy brass; has high tensile strength and is very ductile. Brasses containing more zinc have less tensile strength and are more brittle.	Cheap jewelry (up to 20% zinc), Dutch metal (20-25% zinc) is a substitute for gold leaf.
LEAD–tin (50%). Known as solder	Low melting point, adheres to metal.	Soldering metals
LEAD–tin–antimony	Does not contract when it solidifies. Antimony expands when solidifying.	Type metal
TIN–antimony (7.5%), copper (3.5%). Known as Babbitt metal.	Very low coefficient of friction with steel	Used in bearings
BISMUTH–tin (24%), lead (27%)	Low melting point, melts at 95° C. Almost any desired point can be obtained by varying composition.	Electrical fuses, plugs in sprinkler system

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Applying in Life What You have Learned in Chemistry

"Here is a brand new uncirculated nickel I just got from the bank," said Fred. "I've been wanting a piece of pure nickel to put into my collection of elements and now I have it."

"But it isn't pure nickel at all," replied Tom. "It's an alloy."

Who was right? How can you prove your answer? Do the 5-cent pieces that were made in 1943 contain nickel?

Susan learned in chemistry that tarnished silver could be brightened by immersing it in a dilute solution of salt and baking soda in an aluminum pan. She tried it on an old spoon which was badly blackened and was amazed at the result.

Can you explain, from the activity series, why aluminum is necessary, and why a gold dish cannot be substituted? Do you recall what substance is most frequently responsible for blackened silver? Can you suggest what may have happened to this element when Susan tried her experiment?

Putting Chemistry to Work

A

(**1**) What is the advantage of using alloys instead of the pure metals in gold and silver coins? (**2**) What advantages has duralumin over aluminum in airplane construction? (**3**) How do you account for the fact that solder has a lower melting point than either tin or lead? (**4**) Would you expect the silver on a silver-plated spoon to be harder or softer than the silver in a sterling silver spoon? (**5**) How do alloys protect your electric house circuits from the danger of overheating? (**6**) How do alloys help protect many department stores and office buildings from fire? (**7**) Why is brass better than copper for screws? Why is it better for a door handle? (**8**) A highly magnetic alloy is known as *Alnico*. What three metals would you expect to find in it? What metals would you expect to find in nichrome? magnalium? palau? chromel?

B

(**9**) Name five alloys that you may see today and tell what each contains. (**10**) Primitive man made axes and other tools from bronze. Why were they better than tools made from copper? (**11**) Point out several ways in which the properties of alloys differ from the properties of pure metals. In each case cite an example of an alloy whose use depends in part on these differences. (**12**) Sodium melts

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

at 97° C.; potassium, at 67° C. If an alloy were made of these two metals, would you expect its melting point to be above that of sodium, below that of potassium, or between the two? Why? (13) Tell what is meant by each of the following terms and give at least one example to illustrate each: brasses, bronzes, jewelry metals, coinage metals, fusible alloys, lightweight alloys, antifriction alloys, amalgams, pyrophoric alloys.

Research and Activities That You Will Enjoy

Chemical magic—the melting spoon: Obtain some Wood's metal or prepare it as follows: In a crucible melt 20 grams of bismuth, 10 grams of lead, 5 grams of tin, and 5 grams of cadmium. Stir with an iron wire until well mixed.

Mold it into the form of a stirring rod or spoon. Stir some boiling water with it. Note what happens and explain. The alloy may be used again.

How could you determine the melting point of Wood's metal?

A collection: Make a collection of samples of alloys which you use most often. Label each with its composition. Show your interesting display to the class.

A problem: How could you distinguish gold from brass?

Problem 73

HOW IS IT POSSIBLE TO SAVE METAL SURFACES?

Whenever a piece of metal or of wood is left exposed to the weather, it undergoes change. The combined action of oxygen, water, and carbon dioxide causes the exposed surface to deteriorate. Wood or other organic material may change in a more complicated manner due to the action of molds and bacteria. When oils or acid solutions are transported through pipes, the question of corrosion of the metal is a troublesome and expensive problem. If metal is continuously exposed to high temperatures, as in furnaces and pipe stills in an oil refinery, the rate of corrosion of the metal may be a measure of the life of a still or furnace. This steady deterioration of metals in use costs industry millions of dollars each year.

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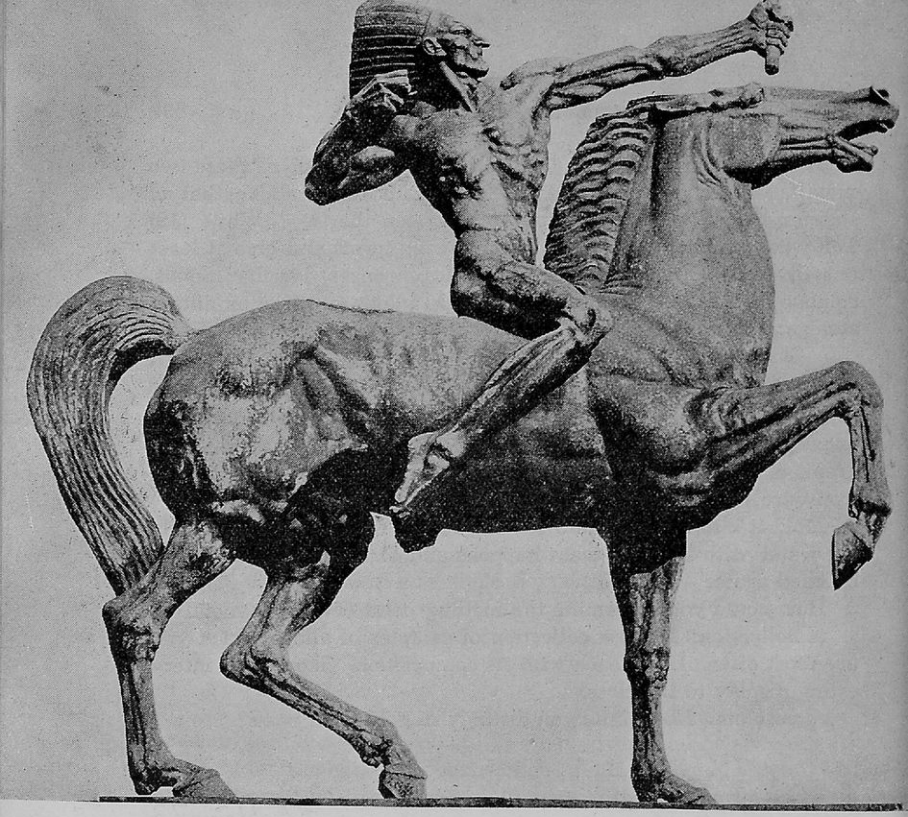

Kaufmann & Fabry Co.

240. Bronze Statues. These famous statues of American Indians are made of bronze.

Some metals protect themselves against corrosion by forming a thin protective layer over their surfaces. Some metals provide their own protection against the ravages of corrosion. Aluminum is an active metal, high in the activity series. In general such active metals react with water and are easily oxidized. When a fresh surface of aluminum is exposed to the air, it quickly becomes coated with a thin continuous film of aluminum oxide, which acts as a protective coating to prevent any further action. It has been estimated that this film is about one ten-millionth of a millimeter thick. It covers the metal like a

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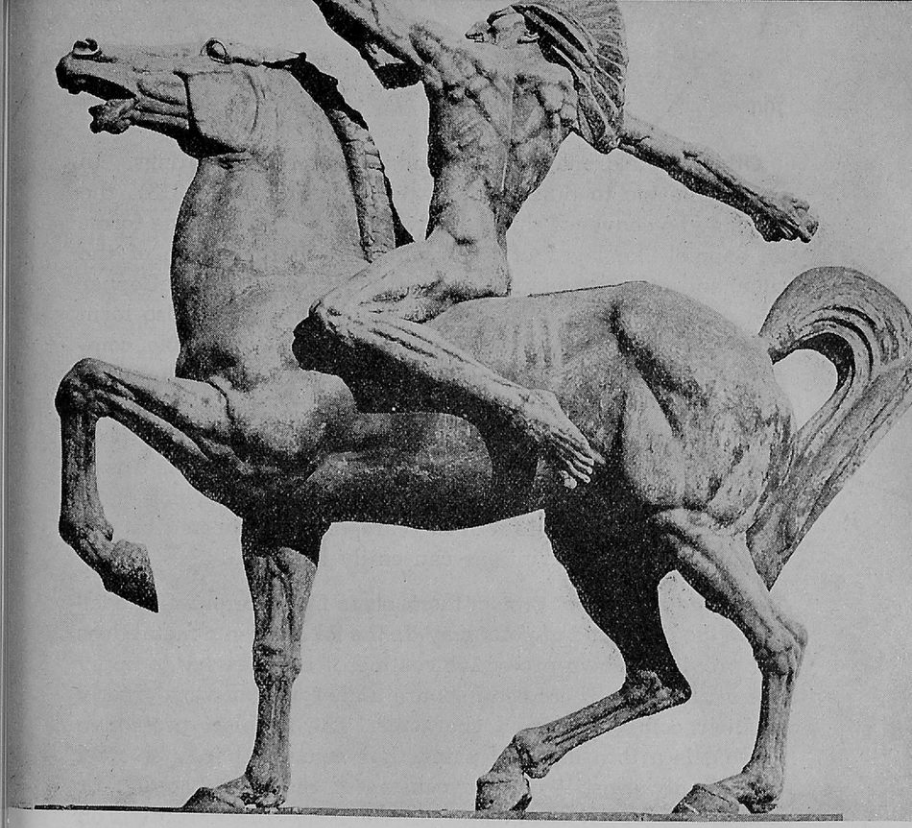

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241. Bronze Statues. The bronze of these statues has become covered with a beautiful protective coating.

thin film of varnish. It is an almost insoluble substance, and as long as it remains, the metal is protected. Likewise, the active metal zinc soon becomes coated with a film of zinc oxide when exposed to the weather. These are *self-protective* metals.

In a similar manner, chromium provides its own protective coating. The brilliant luster of chromium-plated articles and of tools made from stainless steel is due to the thin transparent film of chromium oxide. Like aluminum oxide film, it is almost insoluble, and gives the metal surface under it a nearly perfect protection against further corrosion.

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Other metals may form similar protective coatings. In using chlorine to purify city water supplies (page 318), the gas may be conveyed through silver tubes. The chlorine forms an enamel-like layer of silver chloride on the inside of the tube, and this protects the metal from further action. Copper and many copper alloys, such as bronze and brass, also form protective coatings. These have a somewhat variable composition, but in general consist of an enamel-like coating made up largely of copper carbonate, which gives the metal the beautiful gray-green color so often found on old bronze statues. The "patina" found on ancient bronze coins is a protective layer of this sort. Roman bronze coins, which have been buried in the soil for 1800 years, are so protected by this coating that the inscriptions can easily be read.

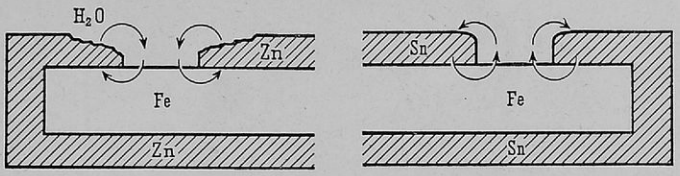
When metals cannot protect themselves from corrosion, a coating of the right kind of paint may do the job. When a metal does not provide its own protective coating, it is necessary to apply one artificially. These coatings are numerous and vary greatly in their composition and character. The simplest protective coating is a thin layer of paint. For structural iron or steel this usually consists of a suspension of red lead (Pb_3O_4) or iron oxide (Fe_2O_3) in linseed oil. Such coverings are used on steel skeletons for large buildings, bridges, and steel tanks. Paints used as protective coatings on iron and steel must contain no substance of an acid nature, or no substance which will act as a catalyst to aid corrosion.

Galvanized iron is iron covered with a thin layer of zinc; the zinc protects the iron. Galvanizing has long been used to protect metal surfaces. In galvanizing, a thin layer of zinc is applied to the metal surface. This may be done electrically on most articles. Here a thin coating of zinc is plated on to the surface of the metal. For sheet metal, wire, and some forms of light structural steel, the scale is first removed by "pickling" in sulfuric acid, after which the metal is washed to free it from acid. It is then drawn through a bath of melted zinc. A thin layer of zinc, about 0.0025 cm thick, clings to the metal

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

A third method of applying a zinc coating is a process known as *sherardizing,* in which the articles to be coated are packed in zinc dust and heated to about 300° C. Although this temperature is below the melting point of the zinc, a metallic coating of zinc adheres to the steel.

Zinc is more electropositive (active) than iron. When a portion of iron that is under a zinc coating becomes exposed to the atmosphere, you have all of the conditions necessary for a small primary electric cell. Here the chemical action results in the corrosion of the zinc instead of the iron. The iron is protected at the expense of the zinc, which is soon coated with a thin layer of zinc oxide.



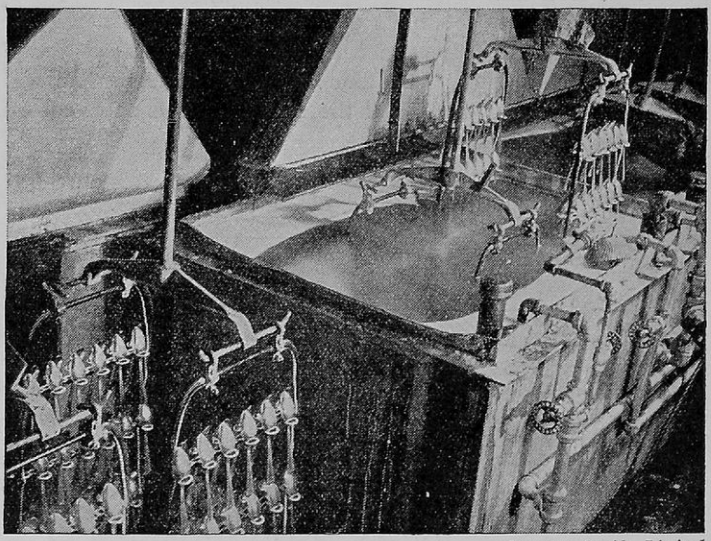
242. CORROSION MAY BE AN ELECTROLYTIC PROCESS. When two dissimilar metals are immersed in a solution, small electric currents are produced. The arrows show the direction of the current. When zinc is the protective coating, the iron is protected at the expense of the zinc. When tin is the coating, the iron being the more active metal rusts rapidly after the coating is broken.

"Tin" cans are made of iron covered with tin; the tin protects the iron. Tin also has long been used as a protective coating on iron. The tin is applied to the clean iron or steel by dipping it into a bath of melted tin, after which it is run through rolls which press a very thin coating of the tin firmly upon the metal. The result is a firm, smooth, bright coat which furnishes excellent protection. Tin plate is of especial value in making cans for the storage of food. Tin is less active than many metals, so it withstands the action of the organic acids found in canned foods to a very considerable extent.

Since tin is less electropositive than iron, if any of the iron is exposed, local action sets in and the iron is corroded more

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

rapidly than the tin (Fig. 242). This accounts for the fact that a tin can exposed to the weather rusts much faster than a piece of galvanized iron under the same conditions. It is now quite common practice to coat the inside of cans, to be used for storing food, with a thin layer of enamel, which keeps the food from contact with any metal whatever.



Courtesy, Oneida, Limited

243. PLATED ARTICLES AND ELECTROPLATING. Protective coatings of the less active metals are applied to more active metals by electrolysis. The article to be plated is made the cathode and the metal to be plated is the anode. Here spoons are supported on racks which form the cathode and are lowered into a tank containing a solution of silver salts.

The silver on plated silverware is deposited by electrolysis. Many protective coatings are plated on metals electrolytically. This is done by making the article to be plated the negative electrode and suspending it in a solution containing ions of the metal to be deposited. Coatings of nickel, chromium, cadmium, gold, silver, and other metals are applied, which

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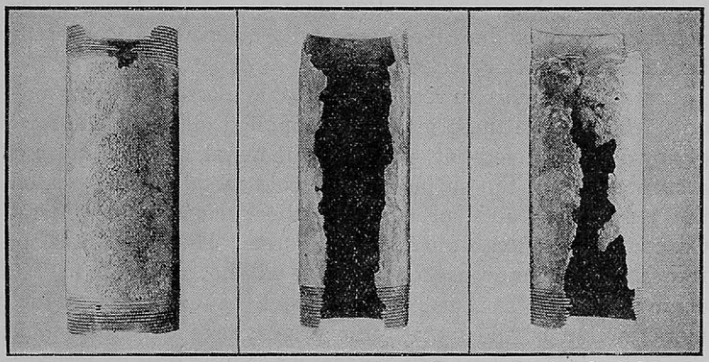
improve the beauty and the wear-resistant qualities. Recently rubber has been plated on metal from solutions of latex. By a nonelectrolytic process rubber is precipitated from latex onto large surfaces. Tank cars are now frequently rubber lined by this process. Such cars are used to carry hydrochloric acid and other corrosive liquids.



Courtesy, Republic Steel Company

244. CORROSION OF IRON PIPE. These are pieces of pipe taken from a drain carrying corrosive liquids. Such corrosion causes a loss of millions of dollars each year.

Pipes for use in the large stills in oil refineries may be coated with a layer of stainless steel. In the stills of oil refineries, the high temperatures used and the flow of oil through the pipes cause very rapid corrosion. To avoid this, tubes may be made of stainless steel—an alloy of iron, chromium, and nickel. This is very expensive. Consequently tubes recently have been made with a layer of stainless steel on the inside and outside. They are made by rolling together slabs of stainless steel on each side of an ingot of ordinary steel. This process produces thin sheets of metal with a thin layer of stainless steel on each side of a core of ordinary steel. The tubes for the pipe stills are formed from these sheets. Nickel-clad and and aluminum-clad steel equipment is also used. These "metal-clad" sheets are finding wide use in the chemical industries,

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where corrosive liquids are stored, or where the product might be contaminated by the presence of iron.

The stove in your kitchen may be protected from corrosion by a coating of enamel. The use of enamel as a protective coating on steel is increasing. When properly applied, enamels not only offer almost perfect protection, but also add greatly to the beauty of the coated article because of the many colors possible. Enameled surfaces are easily cleaned and can easily be kept in a sanitary condition.

Enamels are more or less easily fusible glasses. The ingredients which make these glasses are applied either in the form of powder to the red-hot surface of the metal, or in the form of a suspension on the surface of the cold metal. When heated, the glaze fuses and spreads over the surface of the metal. On cooling, a smooth even surface forms. The metal must be free from scale or grease, or the glaze will not adhere to it. The enamel must also have a coefficient of expansion which matches that of the metal, otherwise cracks will develop in the glaze and its value as a protective coating will be lost.

Glass-lined tanks are sometimes used in chemical industry. These are tanks lined with a layer of clear, glassy enamel. Special acid-resisting enamels have been developed which not only serve to protect the metal surface, but also serve to keep the contents of the tank from contamination.

Applying in Life What You Have Learned in Chemistry

A state highway commission asked for bids on painting a new bridge. One contractor submitted a low bid. He explained that he would omit the usual "priming" coat of red lead oxide before putting on the black carbon paint. Should he be given the contract? Why? (Hint: Carbon is less electropositive than iron.)

Two boys were waiting at a railroad crossing while some freight cars were being switched into the yard of a large manufacturing plant. A large tank car went slowly past. On a card was a label reading, "Sulfuric Acid—Handle with Care."

One boy said, "That can't be so. Sulfuric acid dissolves iron."

Yet, it *was* sulfuric acid. How can you explain it? (See page 296.)

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Putting Chemistry to Work

A

(1) What advantages do you see in nickel plating and chromium plating for bathroom fixtures? (2) Why does tinware rust so readily as soon as a little of the iron is exposed? (3) Account for the fact that although aluminum is an active metal, cooking utensils made of it show little sign of wear or corrosion over long periods of use. (4) What kind of protection against corrosion would you use on the steelwork on a bridge? (5) Why is a tin can better for canning tomato juice than one made of galvanized iron? (6) Why does the sheet-iron flue leading from a household furnace usually corrode more during the summer months than during the winter months when in use?

B

(7) Give several reasons why lead was formerly used for water pipes; why bronze is taking the place of iron. (8) Do the terms *rusting* and *corrosion* mean the same thing? Explain. (9) What makes "stainless" steel stainless? (10) Make a list of metals that (a) do not tarnish in air (b) are self-protective (c) corrode easily. (11) How can the corrosion of metals be used to give color to artistic metal wares? Give an example.

Research and Activities That You Will Enjoy

A report: Find out all you can about the composition, properties, and uses of monel metal, allegheny metal, duriron, and tantiron. Report your findings to the class.

A reported interview: Talk with an electroplater to see what you can learn about chromium plating. Bring back to the class any interesting or valuable information you gain.

An advanced topic: One of the newer features in protective coatings is the use of resins. Can you see any advantage in a resin-lined airplane gas tank in the event of a "crack-up"? See what more you can learn about this use and other uses of resins and report to the class.

A guest speaker: Ask a lawyer to visit your class to explain the nature and importance of patents in industrial chemistry, or interview him and report to the class all the interesting information you gain. If neither of the above plans is possible, summarize for the class the results of your outside reading in Riegel, *Industrial Chemistry,* Chap. 40, or in other similar books.

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Problem 74

WHAT IS IN PAINT TO GIVE IT ITS PROTECTIVE QUALITIES?

The surfaces of wood, metal, or other materials used in construction, are usually covered with paint. Paint serves two purposes. It completely covers the surface with an elastic, impervious, protective layer and at the same time provides beauty and color. Paints are applied in thin layers in a liquid state; they change into elastic protective films.

What makes up a paint? Paint consists of different classes of materials: the *vehicle* or liquid part, the *pigment* which consists of the suspended solids, the *drier*, and sometimes a *"filler."* Each of these ingredients plays an important part in making the paint act as it should when it is applied as a protective coating.

What oils are used in paint? The liquid part of paint is usually *linseed oil* which comes from the seeds of the flax plant. When the plant ripens, the seed contains from 36 to 40 per cent of its weight in oil. The oil is pressed out of the seed and purified. Raw linseed oil has a pleasant odor and is used for food in some European countries. Its value in the paint industry lies in the fact that when thin films of it are exposed to the air, they undergo chemical changes which result in the formation of a tough resistant material called *linoxyn*. While this action is referred to as "drying," it is not drying due to evaporation.

Like other vegetable oils and fats, linseed oil is a mixture of glycerol esters of fatty organic acids, most of which are esters of linoleic and linolenic acids (page 505). These are unsaturated acids, and the addition of oxygen to the unsaturated carbon atom is the chief cause of the "drying" action of the oil in the formation of the linoxyn. The "drying" of paint is therefore mostly oxidation rather than real drying. The "drying action" of linseed oil can be hastened by the use of catalysts. These are called "driers." They are usually

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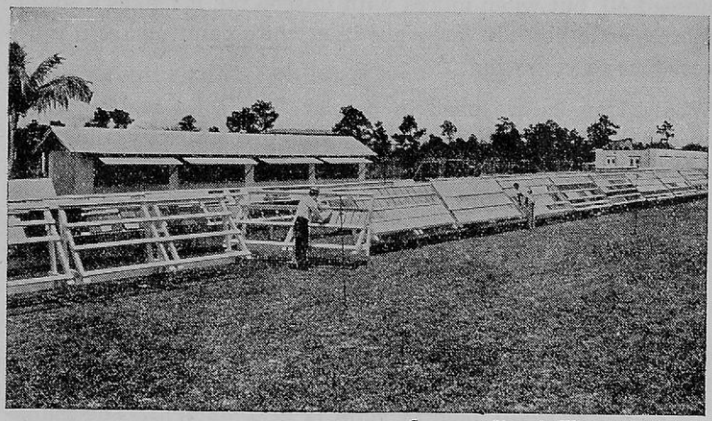

Courtesy, Sherwin-Williams Company

245. PAINT TESTING RACKS. Samples of paint spread on various surfaces are exposed to the action of the weather to test their value as protective coatings.

compounds of lead, cobalt, manganese, or iron with organic acids. They are used only in small amounts.

Linseed oil is used not only in paints but also in the manufacture of linoleum. Here the linoxyn is mixed with powdered cork and coloring matter and pressed into a burlap base while heated. The linoleum, thus produced, makes a fine resilient floor covering which is easily kept clean.

Tung oil, or China wood oil, is the oil pressed from the seeds of the tung tree, a native of China. This tree has been introduced into our southern states, and thousands of acres are now being grown there. The raw oil is of little value in paints because it dries white. However, by heating it with driers, this fault is overcome. Tung oil is widely used in all types of paints and varnishes.

Soy bean oil is also used in paints. It is found in the soya bean now widely cultivated in the United States. This plant is also an importation from China where it has been grown for centuries. The oil is not as good a drying oil as

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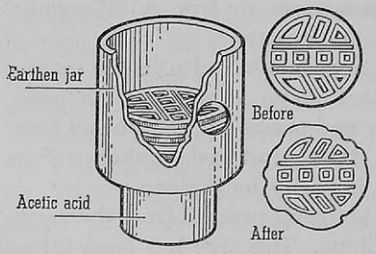
linseed oil, but when mixed with linseed oil, it makes a softer, more elastic film. Its presence in a white paint makes it more resistant to yellowing.

What pigments are used in paints? The solid matter which enters the paint is the pigment. This gives opacity and color to the product. There are not many substances that are used for this purpose. With the exception of white lead, they are of comparatively recent origin. *White lead* is a basic lead carbonate [$Pb(OH)_2 \cdot 2PbCO_3$]. *Zinc white* is zinc oxide (ZnO). *Lithopone* is a white mixture of barium sulfate ($BaSO_4$) and zinc sulfide (ZnS). *Titanium white* is titanium dioxide (TiO_2). These are the materials now generally used to give the body to paint.

The use of white lead in paint is very ancient. The manufacture of white lead was known to the early Greeks and was described by Theophrastus about 300 B.C. The Dutch process is a development of the methods used in Europe for over a thousand years. This process is described beside Figure 246.



246. WHITE LEAD POT AND BUCKLES

In the Dutch process perforated disks of lead are placed in earthen jars which contain some acetic acid in the bottom. The jars are placed in stacks and covered with spent tanbark which ferments, producing carbon dioxide. The lead unites with the acetic acid vapor and the carbon dioxide combines with acetic acid vapor to produce basic lead carbonate which is called white lead.

In the Carter process fine lead pellets known as "atomized lead" are revolved in large wooden cylinders with dilute acetic acid and carbon dioxide.

In these processes the essential chemical reaction is one in which lead reacts with acetic acid to form basic lead acetate and then with carbon dioxide to form the basic lead carbonate, called white lead, $Pb(OH)_2 \cdot 2PbCO_3$.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Zinc white is a common ingredient in paints. Zinc oxide was first used as a paint base in France about the middle of the last century. Its use has increased greatly. Mixed with white lead it is a common ingredient in most ready-made paints.

A paint consisting only of white lead in linseed oil has long been used for exterior work. With the increased use of soft coal as a fuel and the resultant production of hydrogen sulfide, these paints darken, due to the formation of lead sulfide. When a lead paint gets old, it may crumble to a powder. A paint with a zinc oxide base in linseed oil dries to a hard smooth finish. Its color is not affected by sulfur gases, but in time this hard coat may crack and peel. If the surface is to be repainted, the old paint must all be removed before a smooth finish can be obtained. By mixing white lead and zinc white, the advantages of each may be obtained. The zinc white gives whiteness, durability, and smoothness; the white lead gives a good covering and a good surface for repainting later.

Zinc oxide is also used in high-grade enamels.

Lithopone is a comparatively new paint material. Unlike white lead, the stable white pigment called lithopone is not acted upon by sulfur gases. It does not turn yellow with age, and it has a high light-reflecting value. It is used extensively in making interior wall paints, enamels, lacquers, oilcloth, and linoleum. It also is used in the rubber industry in the manufacture of white rubber goods. Lithopone is not used much for exterior work since it shows a tendency to darken under ultraviolet light. Chemists are attempting to overcome this difficulty.

The manufacture of lithopone in the United States began about 1900 and the growth of the industry has been phenomenal. Lithopone is prepared by the double precipitation of zinc sulfide and barium sulfate from solutions of zinc sulfate and barium sulfide. The average composition of lithopone is about 71–73% barium sulfate and 29–27% zinc sulfate with less than 2% zinc oxide.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Titanium dioxide is one of the latest additions to the family of paint materials. Titanium dioxide is a pure white substance of permanent color and great stability. Its covering power is about three times that of pure white lead, and it is not affected by sulfur gases. It has the advantage also of being light in weight, nonpoisonous, resistant to high temperatures, and easy to apply in a smooth coat. Its use as a paint pigment is rapidly increasing. It frequently is mixed with lithopone, barium sulfate, and zinc white.

Titanium dioxide is used mostly in white paints since colored titanium paints fade. It also is not extensively used for exterior work since titanium dioxide paints grow powdery with age when exposed to the weather. New developments and discoveries are tending to overcome this difficulty.

The chief native compounds of titanium are rutile (TiO_2) and ilmenite ($FeTiO_3$). American production has come chiefly from Virginia, Oklahoma, and California. Importations from India, Australia, and Brazil have increased substantially. Most titanium paint material comes from ilmenite.

Paints from milk are growing in popularity. Paints manufactured from casein (Kem-tone) are now being used because of their low cost, easy application, freedom from "paint odors," soft colors in pastel tints, and pleasing reflection of light.

Aluminum paints contain powdered aluminum suspended in a suitable liquid. Because of their bright metallic appearance, paints of this type are good reflectors of heat. For this reason aluminum paints are used to paint some tank cars and oil tanks. Recent experiments show that aluminum paint is quite valuable for use as a priming coat for other paints.

Many paints contain inert materials known as fillers or extenders. Fillers or extenders consist of such substances as barium sulfate, gypsum, clay, whiting ($CaCO_3$), silica, and talc. They are not to be considered as adulterants or cheap substitutes for the more expensive pigments. They modify the pigments that are too light or too bulky or too expensive to be used alone. Because of their relatively coarse grain, they adhere

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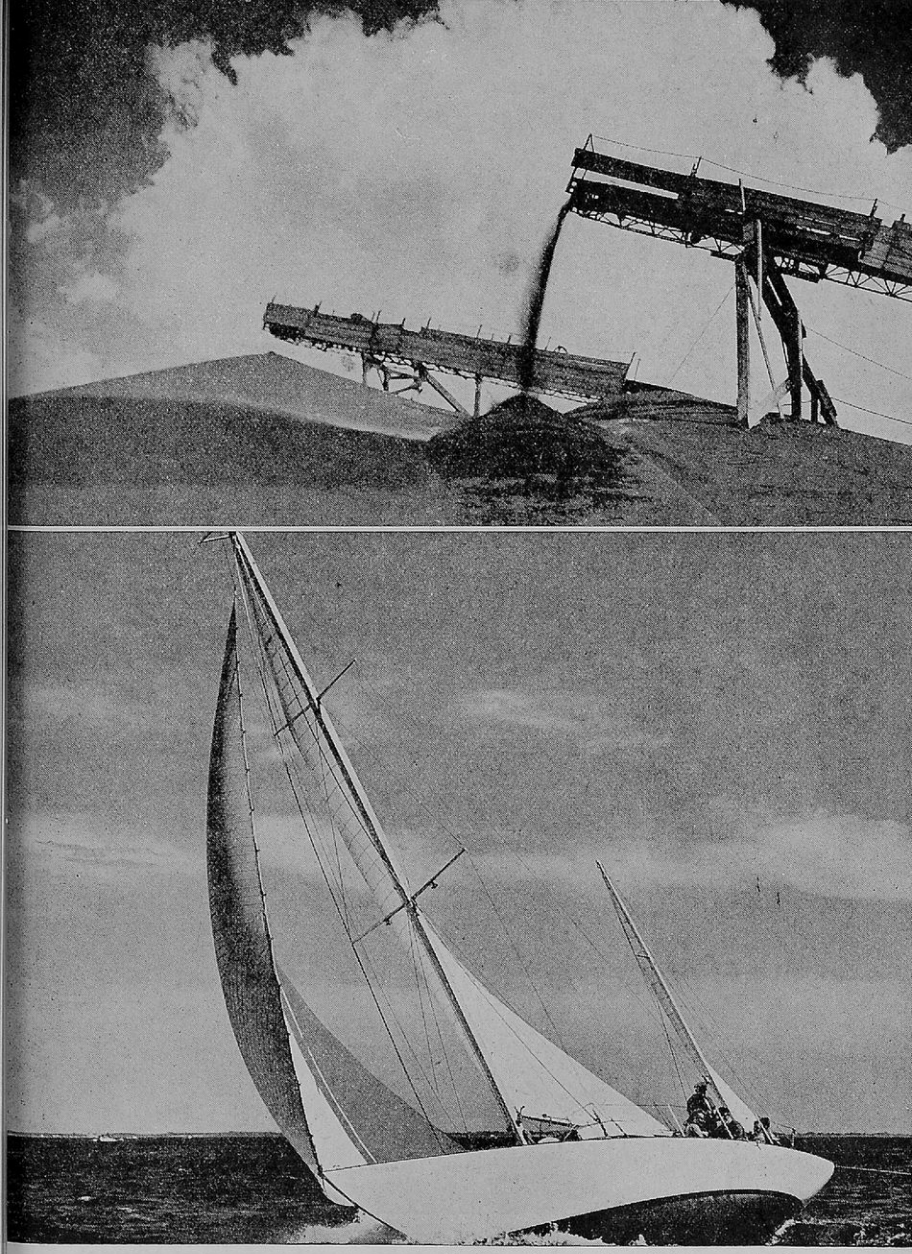

Courtesy, E. I. du Pont de Nemours & Co.

TITANIUM PAINT. The immense pile of black sand is ilmenite, which will be used to prepare titanium dioxide for the manufacture of titanium paint. The yacht has been painted with titanium dioxide paint.

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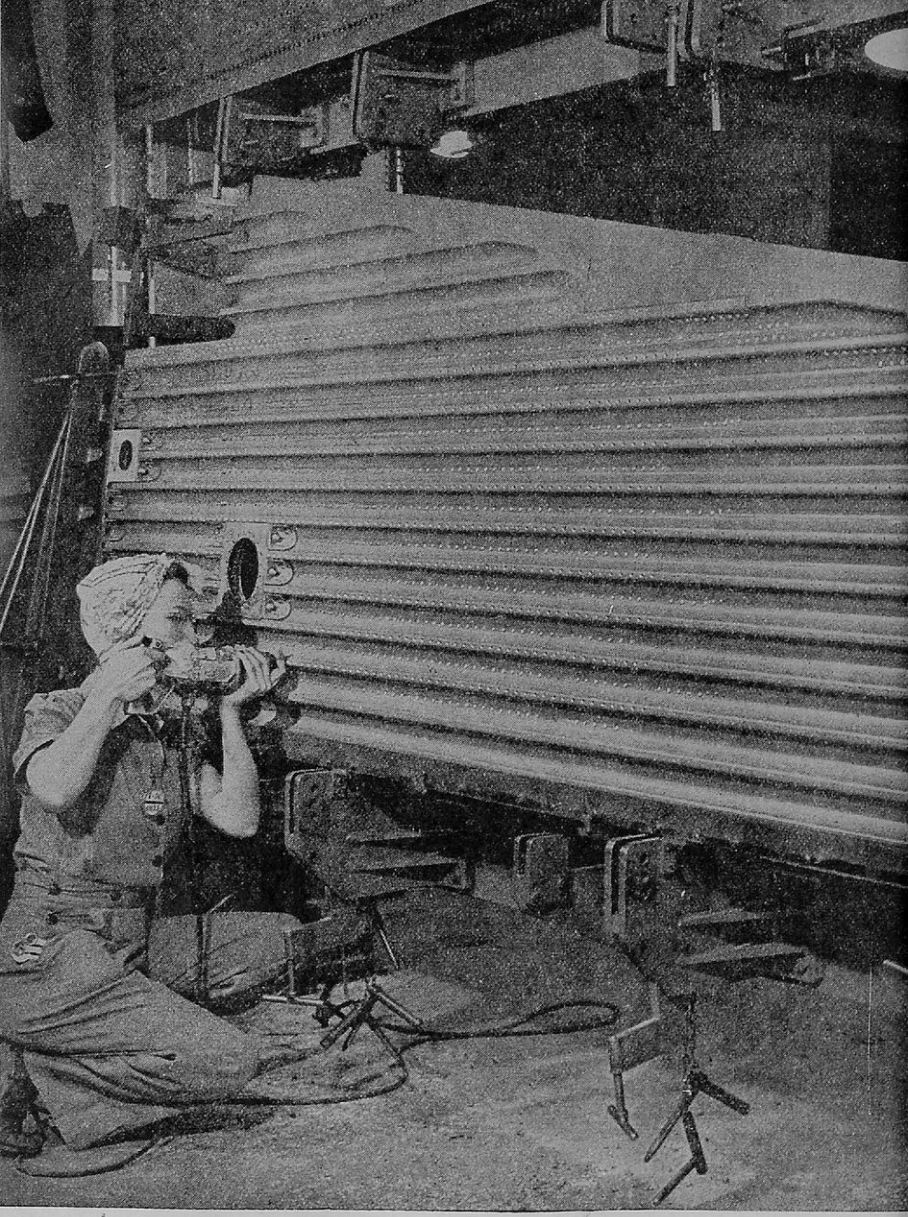

Courtesy, Lockheed Aircraft Corp.

ALUMINUM ALLOYS ARE USED IN AIRCRAFT. Aluminum and aluminum alloys need no paint. Aluminum can be powdered and made into a paint to protect other metal surfaces.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

to the wood and prevent the paint from spreading. Fewer coats are thus needed.

What gives the color to a paint? *Color pigments* are of two types. They are mineral colors and lakes. Mineral colors are metallic salts or oxides, or mixtures of them. Lakes are dyes precipitated on a more or less colorless base such as aluminum hydroxide or clay. The only color pigment that is an element is carbon black or lampblack, which is pure condensed soot.

A list of a few pigments follows.

Pigment	*Composition*
Lampblack	Carbon
Red lead	Lead oxide (Pb_3O_4)
Aluminum	Powdered aluminum
Venetian red	Ferric oxide and gypsum
Indian red	Ferric oxide
Vermilion	Amorphous mercuric sulfide
Burnt sienna	Ferric oxide and clay
Burnt umber	Ferric oxide and manganese dioxide
Ochre	Clay and ferrous hydroxide
Chrome yellow	Lead chromate
Cadmium yellow	Cadmium sulfide
Prussian blue	Ferric ferrocyanide
Paris green	Basic copper arsenite

This brief list gives a general idea of the nature of the color pigments. Many of them have been developed from natural earths, or minerals which have bright colors. The brighter colors are lakes. A typical lake can be prepared in the laboratory by precipitating aluminum hydroxide in a solution of alizarin red. If the precipitate is dried after filtration, a bright red substance of high coloring value is left. Lakes give bright clear colors, but some of them fade in bright light. Black is produced by using lampblack. Cobalt blue is an aluminate of cobalt. Ultramarine is pulverized lapis lazuli, a rare mineral. Artificial ultramarine is a compound formed by combining aluminum and sodium silicates with sodium sulfide.

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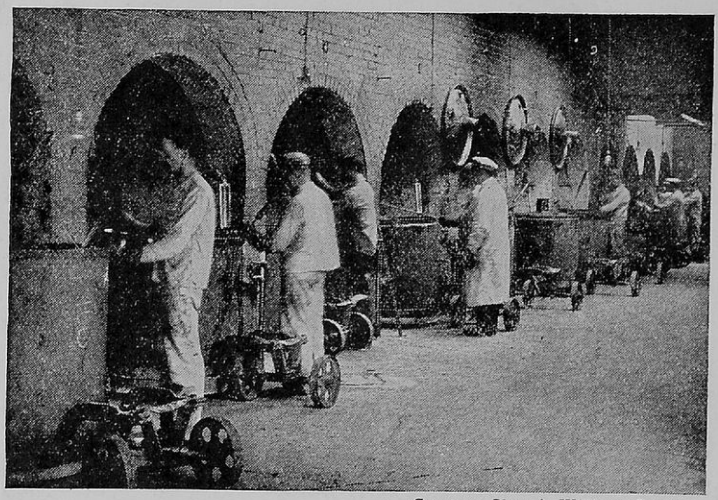

Courtesy, Sherwin-Williams Company

247. MAKING VARNISH. In these kettles, fossil and synthetic resins are heated with linseed oil until solution takes place. Careful attention must be given to the process.

How do oils, varnishes, and lacquers protect surfaces? Paints completely hide the surface to which they are applied. Sometimes you may wish to have the grain of wood visible, but still have it protected by a transparent film.

Rubbed oil finish enables you to see the beautiful grain of wood. The simplest film of this kind can be obtained by covering the surface with linseed oil which oxidizes to form a thin film of linoxyn. Antique furniture and gunstocks are often finished in this way. A more serviceable finish is obtained from varnish.

Varnish consists of fossil resins dissolved in linseed oil, with a drier added. These fossil resins are found in Australia, Africa, the Philippine Islands, and India. They are lumps of resin which exuded from coniferous trees of previous geological periods. In preparing varnish the linseed oil is

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heated in large open kettles and the gums added and stirred in until complete solution takes place. The drier is then added to this mixture.

Fossil resins are scarce and expensive. For cheaper varnish ordinary rosin is used. This is first treated with glycerol to produce glyceryl esters with the free acids present in the rosin. These ester gums and bakelite (page 585) are now used quite extensively in the preparation of varnish.

Varnishes made with linseed oil turn white when exposed to water. To prepare a varnish which will not turn white, tung oil is used in place of linseed oil. Spar varnishes used on boats and for exterior work are of this type.

Enamels are varnishes that contain a pigment. Enamels are usually made from ester gums instead of natural resins because the free organic acids (in the natural resins) act on pigments of a basic nature and produce solid compounds which make the enamel unfit for use. Quick-drying enamels and varnishes dry to a hard finish in a few hours when they are applied in thin layers. The drying of enamel and varnish is due to the formation of linoxyn by the oxidation of the unsaturated acid radicals in the linseed oil or the tung oil. In this respect, enamels and varnishes resemble paints.

Pyroxylin lacquer is one of the newest types of finish. Lacquer consists of varnish gums and nitrocellulose dissolved in a series of solvents and "plasticizers." Some of these solvents were chemical curiosities only a few years ago. They are esters such as amyl acetate, butyl propionate, ethyl lactate, diethyl carbonate, and ethyl acetate. Among the plasticizers are such compounds as tricresyl phosphate, diethyl phthalate, and butyl tartrate.

A concentrated solution of nitrocellulose in such solvents and plasticizers (mixed with solutions of resins and with color pigments added) forms a finish which dries rapidly to a fine smooth surface.

The drying of lacquer is not due to oxidation as in the case of paint and varnish; it is due to the evaporation of the solvent. The solvents are quite volatile and quickly give a firm surface.

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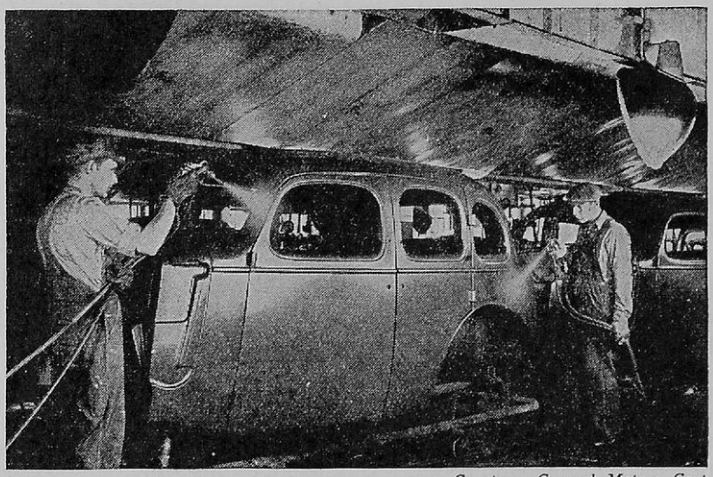

Courtesy, General Motors Corp.

248. APPLYING DUCO WITH A SPRAY GUN. Many protective coatings are now applied with an airbrush. This sprays the finish on the article more evenly than it can be applied with a brush. Nitrocellulose lacquers such as Duco are usually applied in this way.

The plasticizers evaporate more slowly and, due to this slower evaporation, prevent the residual lacquer from checking and turning color.

Lacquers are usually applied with an air spray and, since they dry so rapidly, have become the common finish applied to automobiles and furniture. They are quite resistant to weather and retain their gloss and beauty a long time.

These various protective coatings do more than protect the substance to which they are applied from the action of the elements. They add color and beauty. They make surfaces easier to keep clean, so they are a direct aid in sanitation. They provide a lustrous surface which no amount of polishing could put on a bare wood surface. They provide the medium by which the artist brings to us his dreams of beauty.

A freshly painted house helps the appearance of the whole neighborhood and makes it a better place to live in.

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Readings for Pleasure and Profit

HOWE, H. E. *Chemistry in Industry.* Vol. II, Chap. XIV, pp. 232-260, "Paints, Varnishes, and Colors."

ROGERS, ALLEN. *Manual of Industrial Chemistry.* Vol. I, Chap. XVII, pp. 489-500, "Pigments and Paint Oils"; Vol. 1, Chap. XVIII, pp. 501-511, "Manufacture and Use of Prepared Paint Products"; Vol. II, Chap. XXXVIII, pp. 1100-1107, "Shellac"; Vol. II, Chap. XL, pp. 1130-1141, "Varnish and Lacquers"; Vol. II, Chap. XLI, pp. 1143-1172, "Solvents and Nitrocellulose Lacquers."

Applying in Life What You Have Learned in Chemistry

Your little sister accidentally swallows a sweet-tasting solution of lead acetate. Your older brother gives her Epsom salt solution as an antidote. Explain its action, remembering that insoluble substances are not absorbed into the system.

Ask your father how the permanence of the older type of finish on cars compares with that of the lacquer finish.

Putting Chemistry to Work

A

(1) Why is a bucket of ordinary paint so heavy? (2) From your observations and use of peanut butter, would you class peanut oil as a drying or nondrying oil? (3) What advantages has varnish over paint as a finish for a mahogany table? (4) Old walnut furniture was often finished by rubbing it with linseed oil. How does this protect the surface? (5) Think out the results of these uses of oils: (a) linseed oil as a lubricant in machinery; (b) peanut oil (nondrying) in a paint; (c) mineral oil in a salad dressing. (6) What advantages do lacquers have over varnishes or enamels in our modern method of making automobiles? (7) What advantage does a varnish finish have over a rubbed-oil finish?

B

(8) How are varnishes like paints? How do they differ? How are lacquers like varnishes? How do they differ? (9) Why have nitrocellulose lacquers only recently come into use? (10) How do paints and varnishes aid in sanitation? (11) What function do paints and varnishes serve other than that of protecting the surface? (12) What reason would you suggest for the fact that such oils as lard oil and olive oil are not suited for use in paints? (13) What is

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the difference between the drying of paint and the drying of calcimine? (Calcimine is a suspension in water.) (14) What pigment should be used for painting the walls of chemical laboratories? Why? (15) Many people are now living in decorative homes because they are able to do the work themselves. Suggest advances in chemistry that have made this possible. (16) Why would you expect a mixture of red lead oxide and linseed oil to harden even under water? (17) It is said that an old Italian painter dissolved amber beads in linseed oil to make a varnish to complete one of his pictures. How does this compare with our modern method of making varnish?

Research and Activities That You Will Enjoy

A reported interview: If possible, talk with a paint chemist to learn his ideas of the difference between cheap paints and high-grade paints; the advantages or disadvantages of factory-mixed paints over hand-mixed ones. Report to the class the valuable information you gain.

A report: Ask a physician about lead poisoning. Ask a painter how he avoids lead poisoning. Tell the class what you learn.

Looking Back into Unit 16

Be sure you know the purpose of this unit. Read again the material on page 652, "Looking Ahead into Unit 16." Then study the following Summary Test.

Summary Test

1. *How are metals freed from their ores?*
   - (a) What are metals?
   - (b) How are metals found in nature?
     - *(1)* What metals are found uncombined?
     - *(2)* What common ores contain combined metals?
   - (c) Why are the processes of metallurgy important to you?
   - (d) How are metals obtained by reduction?
2. *How is iron produced and used?*
   - (a) How is iron found in nature?
   - (b) How is iron freed from its ores in a blast furnace?
     - *(1)* What chemical action occurs in a blast furnace?
     - *(2)* What type of iron is produced in a blast furnace?
   - (c) What is wrought iron? How is it made and used?

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(d) What is steel? How is steel made—
  (1) By the Bessemer process?
  (2) By the open-hearth process?
  (3) By the electric furnace process?
(e) What alloy steels are made and used? How are they used?

3. *How is copper produced and used?*
(a) How is copper found in nature?
(b) How is copper extracted from its sulfide ores?
  (1) How is the impure copper obtained?
  (2) How is the impure copper refined by electrolysis?
(c) What are the property-uses of copper?
(d) What copper alloys are used? How are they used?

4. *How has aluminum become an industrial and household servant?*
(a) What is the ore of aluminum?
(b) How is aluminum won from its ore?
(c) What are the property-uses of aluminum?

5. *Why are alloys more common than pure metals?*
(a) What are alloys? How are they prepared?
(b) What common properties of alloys differ from the pure metals? How do they differ?
(c) What alloys do you use most frequently? How do you use them?

6. *How is it possible to save metal surfaces?*
(a) How do some metals protect themselves against corrosion?
(b) How may metals that are not self-protecting be protected against corrosion—
  (1) By painting their surfaces?
  (2) By galvanizing or "tinning"?
  (3) By electroplating?
  (4) By metal-cladding?
  (5) By enameling?

7. *What is in a paint to give it protective qualities?*
(a) What makes up a paint?
  (1) What oils are the vehicles in paints?
    A. How do oils in paints protect surfaces?
    B. Why are some oils not used in paints?
  (2) What pigments are used in paints?
    A. What properties should a good pigment have?
    B. How are colors put into paints?

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(b) How is white lead made—
  (1) By the Dutch process?
  (2) By the Carter process?
(c) What pigments are used in interior paints? How are they made?
(d) How do varnishes and lacquers protect surfaces?
  (1) What is a varnish?
  (2) What is an enamel?
  (3) What are pyroxylin lacquers? What are their advantages?

Study now any weak point that the Summary Test may have revealed to you. Keep in mind that the facts you have learned should be *related,* the principles should be understood and *applied.*

Closing the Unit

As far as you go back in history, man has been trying to get more and better metals. In recent years methods have been developed for going deep into our "good earth" and for going to out-of-the-way places on the earth for raw metallic ores for your needs. Sulfide and oxide ores are the most common. The sulfide ores generally are roasted (oxidized) to the metallic oxide. Coke is usually used to reduce the oxide ores. The metallurgy of many metals, especially iron and copper, is spectacular and involves interesting chemical processes. The active metals are all prepared by the electrolysis of their ores (usually salts).

The "Big Three" among the metals in modern America are iron (steel), copper, and aluminum. It would seem, however, that the present period of industrial activity might well be called the *Age of Alloys.* Pure copper for electrical work and pure aluminum for some uses are essential. Iron, however, because of its relative softness and ease of corrosion, depends upon the presence of carbon and other nonmetals and metals to give it the properties necessary for its varied uses.

Industry is drawing on Nature's reserves at a tremendous rate. As the years go on and the supply of the richest ores eventually nears depletion, chemists must find ways of releasing metals from poorer sources or from compounds for which new metallurgical techniques must be worked out. Of course, chemistry will rise to the occasion, but since it is difficult to visualize a civilization in which iron and copper are not a part, it is well to consider seriously a wise conservation of the present industrial metals.

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One of the wisest steps in the conservation of metal resources is the proper surface protection of the metals which are now in use. This is gained in a number of ways—by using paints and enamels to prevent corrosion and to give improved appearance, by galvanizing with zinc to give durability and protection from corrosion, by tinning to permit the use of inexpensive iron as a base for "tin cans," and by coating with metals (and even rubber) by electrolysis. Several metals, such as aluminum and chromium, form thin films of protective oxides on their surfaces and these oxides act as a paint on an otherwise active metal. You, no doubt, can expect the chemist to evolve new methods for surface protection as need for further conservation arises.

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Looking Ahead into

Unit Seventeen

At last you have reached the final unit of *Chemistry and You*. Early in your study you learned that scientists believe that the number of natural elements is 92. You have studied a few of these, some rather extensively, others less thoroughly. In this unit you complete your present study by a survey of the remaining elements, some of which are commercially important, some too new to be very useful, some so rare that they can only find a limited usefulness; but all of these are interesting from the standpoint of future uses.

In this final unit you note why there are such wide variations in the costs of useful metals. You should also be interested in knowing about the metal which has served the civilized world through the centuries as a basis for exchange values; the metal which is vitally important in photography and the movies; the metals which are most effective in resisting the rusting influence of our atmosphere; the materials which permit a machine to "see" by means of an electric eye; materials which are poisons; materials which are very hard; materials which make possible our modern lighting systems, our modern machines, our numerous and useful alloys, and many other appliances which are in daily use.

You should also be interested in looking to the future to see whether the present generation has reached the peak of human accomplishment or whether still greater developments may be expected. Has mankind reached the end of the road called progress? Are there still more "worlds to conquer"?

Problem 75. *Why Are Gold and Platinum Expensive?*

Problem 76. *How Do the Properties of Silver Serve Photography?*

Problem 77. *How Do Other Elements Serve Man?*

Problem 78. *What of the Future?*

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Precious Metals: Precious Metals and the Less Common Elements

Problem 75

WHY ARE GOLD AND PLATINUM EXPENSIVE?

If you compare the cost of one metal with others, you may be impressed with the enormous differences in their market values. Iron sells normally at less than one cent per pound; while lead costs six cents; tin, about 65 cents. Silver costs nearly $10.00 per pound, while gold and platinum are sold for many times their weight in silver, and radium is worth about one hundred thousand times its weight in gold. It is evident that this wide variation in market prices is caused in part by the relative abundance of the metals. Iron is very abundant and so it is the cheapest metal which we know, while radium, being extremely rare, is the most precious substance known.

The total quantity in the earth's crust is not the only factor which determines the market price of a metal. Aluminum is more abundant than iron, but it sells for more than twenty times as much. Iron is both abundant and easily obtained from its ores, while the extraction of aluminum is difficult and expensive. As a result of such conditions, both the supply of a metal and the ease with which it may be made available help to determine the market value.

Another important factor in determining the cost of a metal is its usefulness. Calcium is perhaps 100,000 times as abundant as tin or mercury, and its separation from the ore presents no particular difficulties. However, because there is very little use for the metal calcium, its production is limited and its price is comparatively high.

Since the price of gold and platinum makes these metals among the most precious of our articles of commerce, you know

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that they must be very scarce, very difficult to purify, or very useful. You shall see that the metallurgy of these metals is simple. Hence you can conclude that gold and platinum must have distinctive properties that make them extremely useful. How do these expensive metals serve our modern world?

How long have gold and platinum been used? Some people believe that gold was the first metal used by primitive man, because it is found almost entirely in the uncombined state and because it is so easily worked into useful forms. Certainly its use was fairly common before the first written records of human history. It has continued through all the centuries to play an important part in influencing the conduct of both individuals and nations. It has been said that gold has influenced the behavior of mankind more than have all the other metals combined. So it is evident that gold is an important substance, even though it makes up only a few ten-millionths of one per cent of the earth's crust.

Platinum also has been used for many centuries although it has always been less conspicuous than gold. The Egyptians are known to have used alloys of platinum as early as the seventh century B.C. but its distinctive properties were not valued as at present. For a time the only use of platinum was to adulterate gold, and for this reason platinum was looked upon as a metal of bad reputation. Under normal conditions now its price is approximately three times that of gold.

How is gold found in nature? Gold is usually found in the uncombined state, rarely in compounds. It is found in the form of tiny flakes, which may be too small to be seen without the aid of a microscope. These are frequently scattered through veins of quartz so a ton of ore may yield only a fraction of an ounce of gold. Sometimes these veins are very rich, as for example the famous Comstock lode at Virginia City, Nevada, where the miners are reported to have removed $11,000,000 in five days. Rarely is gold found in large nuggets such as the one that was found in Australia in 1869; it weighed 190 pounds. Much gold is now recovered in the refining of such metals as silver, copper, and lead.

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How is gold separated from sand and rock? When gold-bearing rock weathers, the fragments are frequently carried away by running water. As a result gold mixed with sand is sometimes found along streams or on ocean beaches. From this source the gold may be separated from the sand by taking advantage of its greater weight and washing the lighter sand away. The method of "panning" uses a large shallow pan which is operated by hand. "Sluicing" employs an inclined trough which contains depressions in which the heavy gold collects while running water washes away the sand. These methods are not expensive to operate, but they do not extract all the gold. They have been used in essentially their present form for many centuries.

Modern methods of winning gold from its ores may be illustrated by (1) the chlorination process, (2) the amalgamation process, and (3) the cyanide process. In all of these the first step consists in thoroughly pulverizing the ore.

The chlorination process depends upon the ability of chlorine to attack gold and form the soluble chloride $AuCl_3$. The source of chlorine is either liquid chlorine or bleaching powder and sulfuric acid. The solution of gold chloride is removed, and the gold is precipitated by H_2S. The gold sulfide is dried and ignited, resulting in the liberation of the metal. This method is effective but it is not very widely used because of the cost of the chemicals and the difficulty of supplying them.

The amalgamation process depends upon the fact that gold unites readily with mercury forming an amalgam. The finely crushed ore is fed in a thin layer over copper plates which have been coated with mercury. The particles of gold are picked up by the mercury and at intervals the amalgam is removed. By heating the amalgam in an iron retort, mercury is distilled away and used over again. The gold remains behind in the retort. This method is easily operated and is efficient in dealing with certain types of ores. It removes the larger grains of gold and as a result it is now used in connection with the cyanide process which is especially successful in the winning of fine grains of the precious metal.

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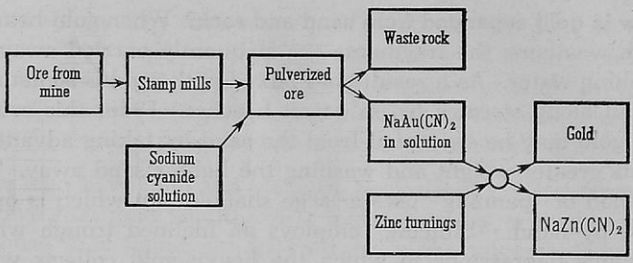

249. THE CYANIDE PROCESS OF EXTRACTING GOLD. Ore from the mine is crushed and treated with a dilute solution of sodium cyanide. The gold dissolves forming a double cyanide [$NaAu(CN)_2$] from which the gold is precipitated by displacement with zinc.

The cyanide process depends upon the ability of a dilute solution of sodium cyanide to dissolve gold. In this process a soluble double cyanide is formed:

$$4\,Au + 8\,NaCN + 2\,H_2O + O_2 \rightarrow 4\,NaAu(CN)_2 + 4\,NaOH$$

The gold is recovered by allowing the resulting solution to trickle over zinc turnings, and the gold is displaced by the more active metal zinc. This method is especially successful in working ores that contain sulfides. It is so efficient in removing gold that it has been successfully applied to the tailings from other methods.

How is gold purified? Gold produced by any of these methods contains other metals as impurities, especially copper, lead, zinc, or silver. The refining of gold is sometimes called "parting." It may be accomplished electrolytically or by the use of acids which dissolve everything except the gold.

In the chemical parting process either sulfuric acid or nitric acid is used. If the impure metal contains less than 70 per cent of silver the separation is difficult. In such cases some silver is actually added in order to make the separation easy. Here we have a peculiar case in which we actually add an impurity in order to aid in the removal of the same impurity.

Electrolytic refining of gold is now generally used in the United States. A bar of the impure metal forms the anode,

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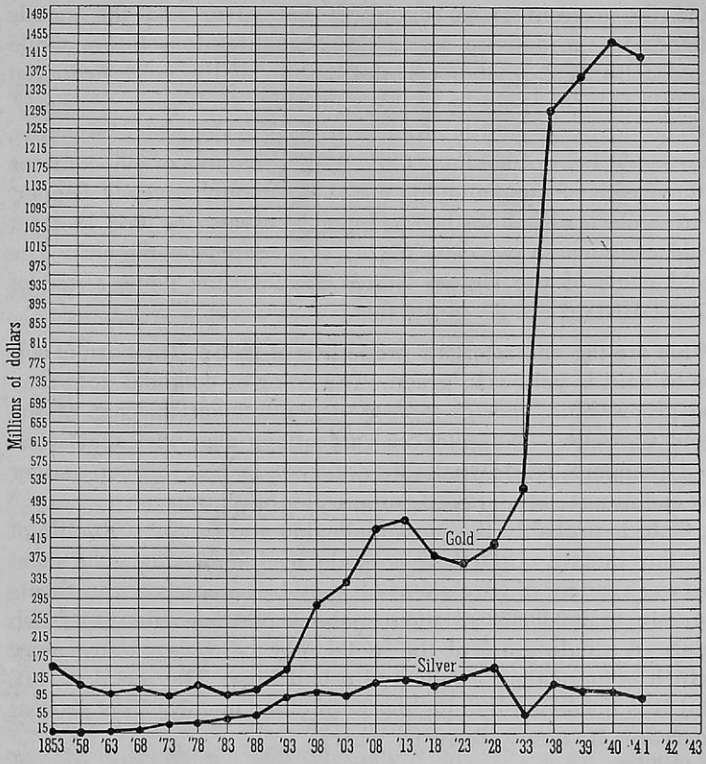

250. WORLD'S PRODUCTION OF GOLD AND SILVER. The cyanide process of extracting gold was developed in 1887-89. The gold fields of South Africa and Alaska were discovered in the 90's. During the World War there was a drop in the production of gold. The world's production in 1935 was nearly 30 million ounces, valued at more than 646 million dollars. Of this amount Africa produced 43%, Europe 18%, the United States 12%, and Canada 11%. Read about the United States Gold Depository at Fort Knox, Kentucky. Can you see any connection between higher prices and the increased production of gold? Most of the silver produced in America is produced as a by-product in the refining of other metals. During the depression years of 1929-33 the output of silver declined due to lack of demand for other metals. Can you see why it was that there was no corresponding decline in the production of gold during the depression years of 1929-33?

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and the current is so regulated that silver and the metals higher in the activity series are brought into solution while gold collects as a sludge in the bottom of the cell. Prepared in this manner, gold has a high purity.

The purity of gold is often expressed in degrees of fineness, pure gold being 1000 fine. Gold with a fineness of 900 contains 10 per cent of some alloying metal, commonly silver or copper. Pure gold is also described as being 24 carats fine, and 18 carat gold contains 25 per cent (6/24) of some cheaper metal. The gold coins of the United States are 900 fine while those of Great Britain are 22 carats fine.

What are the characteristic properties of gold? The normal color of gold is yellowish green. The color of colloidal gold may be green, blue, red, or yellow, depending on the size of the gold particles. The color of gold alloys also varies between red (copper), white (palladium, nickel, or zinc), green (silver or cadmium), blue (iron), or purple (aluminum).

Gold is probably the most malleable and the most ductile of all our metals. Gold leaf is made by hammering gold sheet between layers of parchment. It may be hammered into sheets so thin that 300,000 of them make a pile less than one inch high. A single gram of the metal may be drawn into a wire which is more than a mile and a half long. The metal is soft, but it is hardened by alloying with other metals. This process increases its ability to resist wear.

Gold is the least active of the common metals. It successfully resists the corroding action of alkalies, of all simple acids, of oxygen, and of the weathering process. Its best solvents are aqua regia, chlorine, and dilute solutions of cyanides.

How is gold used? Gold is almost universally used as a coin metal. Most nations have used it as a standard of exchange values. It has also been used for many centuries in making jewelry and ornamental vessels. Gold leaf is highly prized for architectural decorations. In chemical factories and laboratories its ability to resist corrosion makes it very useful for a variety of purposes. Its uses would be extended largely if it were obtainable at a lower cost.

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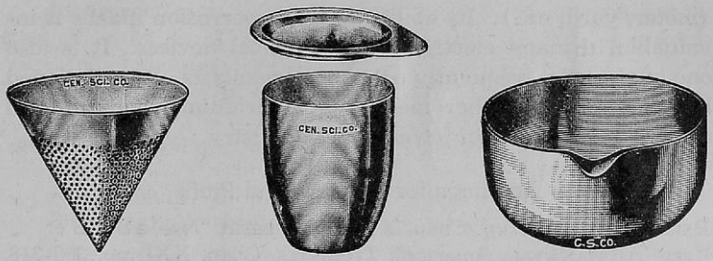

251. PLATINUM LABORATORY WARE. Platinum is almost invaluable for certain laboratory procedures. Here are a few pieces of platinum ware used in quantitative analysis.

Where does platinum come from? Platinum, like gold, is generally found mixed with sand along streams where it has been concentrated by running water. A few large nuggets have been found, the largest weighing over 21 pounds. It was found in Russia in 1843. Formerly Russia produced nearly all the world's supply of platinum, and it is still one of the leading producers. Colombia, South Africa, Canada, Japan, Australia, and the United States (Alaska and California) now contribute to the total production.

What properties are characteristic of platinum? The color of platinum is white. It is a little harder than gold, and it is also extremely malleable and ductile. When heated or chilled, it expands and contracts less than any other pure metal.

Platinum is like gold in resisting corrosion effectively. No single acid dissolves the pure metal, but aqua regia dissolves it readily. Chlorine, fused nitrates, hydroxides, and peroxides attack it. It will alloy with some easily reducible metals. When heated in contact with burning charcoal or coke, it becomes brittle. Then crucibles may be easily broken.

How is platinum used? Platinum finds extensive use for many scientific purposes. Its low coefficient of expansion makes it useful for sealing in glass. Its coefficient of expansion is so low that its alloy with iridium is used as the standard unit of length

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(meter, yard, etc.). Its ability to resist corrosion makes it invaluable in many electrical and chemical devices. It is also one of the most frequently used metal catalysts. It is hardened by alloying with other metals (gold, iridium, rhodium, and others) and is used in jewelry and dentistry.

Readings for Pleasure and Profit

BEERY, PAULINE. *Stuff.* Chap. XVI, pp. 298-320, "Noble Stuff."
REED, A. MAXWELL. *America's Treasures.* Chap. XXI, pp. 308-318, "Hoarding Gold and Silver."

Putting Chemistry to Work

A

(1) Why is it possible to separate gold or copper from sand with running water? (2) How many commercial materials can you name that "are worth their weight in gold"? (3) Which should be more expensive, 18-carat gold or 22-carat gold? Ask a jeweler which should wear longer in a ring. (4) Could you lift a gold bar which is 10 cm long, 4 cm wide, and 2 cm thick? Explain. (Specific weight of gold is 19.3.) How many pounds would such a gold bar weigh? (5) Comment on the statement: "The 'chemically-patriotic' person will be satisfied with platinum jewelry substitutes. There may be other reasons!" (6) Mercury "dissolves" gold. Suppose you got mercury on a gold ring. Suggest the result and remedy.

B

(7) List some of the uses of platinum. Why is it used in jewelry? (8) In some ways platinum resembles silver, tin, and aluminum. How could you distinguish it from each of these metals? (9) How are gold and silver reclaimed as by-products in the electrolytic refining of copper? (10) The mineral iron pyrite (FeS_2) is frequently called "fool's gold" because it looks like gold. How could you tell it from gold?

Research and Activities That You Will Enjoy

An interview: Ask a jeweler what metals are used to harden platinum so it will be suitable for use in jewelry. Also ask him how he tests the purity of gold. If he does not mention it, ask him about the touchstone method.

A forum: By means of a small discussion group, develop the theme, "Chemistry is international."

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Advanced topics: (a) Look up the prices of platinum for the past 25 years; see whether you can tell why the Russian government found platinum unsuitable as a coin metal. (b) Make a list of the current prices of some of the important commercial metals. Compare prices with their uses. (c) How do the prices of magnesium and aluminum compare by the pound? by the cubic meter?

Problem 76

HOW DO THE PROPERTIES OF SILVER SERVE PHOTOGRAPHY?

Silver was used in very early times because it occurs in the uncombined state, and its brilliant color, permanence, and workability made it attractive. It has always been a favorite metal for coins, utensils, and ornaments.

What properties distinguish silver? Silver is a brilliantly white metal which retains its color well in both dry and moist air. Its bright surface is the best reflector of light which we have, but unfortunately the metal tarnishes quickly in an atmosphere containing a trace of H_2S. It is a little harder than gold, and it stands next to gold in malleability and ductility. It is the best conductor of heat and electricity among the metals. Silver is a relatively inactive metal, but it is more active than either gold or platinum. It resists the action of oxygen well, but it is particularly sensitive to the effect of sulfur and sulfur compounds. The formation of black silver sulfide (Ag_2S) gives a film which quickly dulls the brilliant luster of the pure metal. Acids, in general, attack silver slightly, but nitric acid dissolves silver quite rapidly, forming silver nitrate which is readily soluble.

Where do we get our silver? Native silver is found in veins mixed with rock. It also is found in the compound silver sulfide (Ag_2S) which is usually associated with the sulfides of copper, lead, nickel, arsenic, and antimony. Most of our silver in the United States is obtained as a by-product

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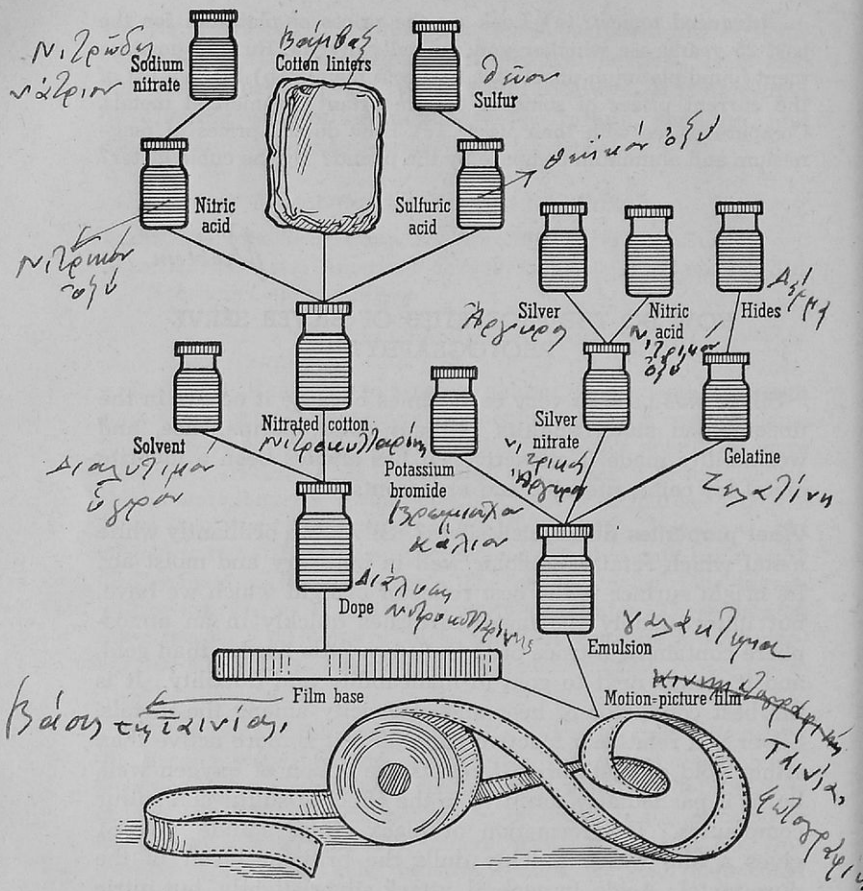

252. WHAT GOES INTO A PHOTOGRAPHIC FILM

in the refining of other metals, particularly copper, lead, and gold. The cyanide process is used successfully with some ores, especially those which contain AgCl or fine particles of metallic silver. The metal dissolves in NaCN forming $NaAg(CN)_2$, from which silver is precipitated by zinc. Mexico is the leading producer of silver, with the United States standing second.

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How is silver used? Silver is familiar in coins, ornaments, tableware, mirrors, and jewelry. In order to improve the wearing qualities of the soft metal, it is alloyed with some other metal such as copper. Sterling silver contains 7.5 per cent copper. A considerable portion of the silver now produced goes into some form of the photographic industry. It is reported that the manufacture of the moving pictures in the United States consumes over 150 tons of silver annually.

How is silver essential in photography? The first step in making a picture consists in dissolving silver ingots in nitric acid. If a solution of silver nitrate is mixed with a soluble halide (such as NaCl, NaBr, or NaI), there is precipitated an insoluble silver halide (AgCl, AgBr, or AgI). These compounds are quickly blackened by light, the amount of the discoloration being proportional to the strength of the light which falls upon them.

A light-sensitive plate is made by spreading over a glass or celluloid support a thin film of an emulsion which contains gelatin and the silver halides. When such a plate is placed in a camera, it is exposed by opening the shutter for a moment. Light from the object in front of the camera is brought to a focus upon the plate, and the silver halide records the intensity of the light reflected from various parts of the object. The plate is now taken to a dark room and put into a developer. This consists of a mild reducing agent (pyrogallol or hydroquinone) which has the ability of reducing to metallic silver those portions of the plate upon which the light fell during the exposure. Other parts of the plate are not changed by the developer.

The next step consists in removing from the plate those unchanged silver halides which were not affected by the light during the exposure. This is the step known as "fixing." A solution of hypo (sodium thiosulfate) is the fixing bath, which removes the unchanged silver halides and makes it safe to bring the plate into the light. After the plate is washed (to remove all traces of hypo) and dried, it is called a negative because the lights and shades of the object are reversed in

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the image as it appears on the plate at this stage of the process. Any object which is white, appears black in the negative because such objects reflect the most light and consequently cause the greatest change in the silver salts. Black objects which reflect very little light cause very little change in the silver halides and make few, if any, dark areas on the plate.

A picture or positive is obtained by covering a piece of paper with an emulsion which also contains some light-sensitive silver halides. This is placed under the negative and exposed to light that shines through the negative. An image appears on the paper, but its colors are again reversed so it looks like the original object which was in front of the camera when the shutter opened. The positive is treated in much the same manner as the plate, and so finally becomes a finished photograph. Motion-picture films are made in much the same manner from the original "master" or negative film.

How do blueprints differ from photographs? Silver salts are not the only compounds which are changed by exposure to light. Consequently, there are other methods of taking pictures or making reproductions. A common and important process is that which produces blueprints.

The sensitive paper used in making blueprints is coated with a freshly prepared mixture of ferric ammonium citrate and potassium ferricyanide. This mixture produces a compound known as ferric ferricyanide, which has a bronze-green color and is readily soluble in water. On exposure to light, some of the ferric iron is reduced to the ferrous condition; and an intensely blue compound, which is insoluble in water, is formed.

To copy a tracing or to print a picture, the tracing or the negative is placed over the sensitive paper and exposed to light. The reduction to the blue ferrous compound is accomplished wherever light falls upon the paper, but those portions which are shielded from the light are still covered with the water-soluble ferric compound. After exposure the paper is washed in water. In this water the soluble ferric salt is removed, and the white paper beneath is exposed. As a result

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the black lines of the tracing are reproduced as white lines on a blue background. Similarly the negative is reproduced in a blue and white positive.

The blue iron compound, which is produced by the reducing effect of the sunlight, is similar in composition to the substance known as Prussian blue $[Fe_4(FeC_6N_6)_3]$ which is used in the laundry as bluing.

Readings for Pleasure and Profit

NEBLETTE, BREHM, PRIEST. *Elementary Photography.*
(Eastman's) *Elementary Photographic Chemistry.*

Putting Chemistry to Work

A

(1) What two reasons can you give for using copper in silver coins? (2) A photographer uses a gold solution for toning. Explain from your knowledge of the activity series what happens during the toning process. Why is toning desirable? Is the "spent" toning solution worthless? What would you do to find out? (3) What is the anode in a silver electroplating bath? Why is not some cheaper metal used?

B

(4) Why are photographic films and prints placed in a hypo solution before being brought into the light? (5) How is silver chloride prepared from silver? Write equations. (6) A silver dollar weighs about 26.5 grams. What weight of silver nitrate and what weight of copper nitrate could be prepared from it?

Research and Activities That You Will Enjoy

A project: Prepare some blueprint paper and use it to make blueprints. Display your success to the class. Investigate before you begin.

Interesting topics: (a) How mirrors are silvered (b) How United States mints make silver coins (c) Coinage system of different countries (d) Color photography (e) Dangers of the unreliability of photographic records (f) Photography in advertising and in industry (g) Daguerreotypes.

A real problem (for the amateur photographer): See if you can recover silver from a "spent" hypo solution.

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Problem 77

HOW DO OTHER ELEMENTS SERVE MAN?

You have studied some of the most important of the chemical elements and their uses in human service. Our study has been directed by the double desire of gaining a general knowledge of the way in which chemistry serves our world and of learning the principles which are employed in chemical industries of various sorts. The elements which you have already studied have been selected as samples of chemical behavior and usefulness. There are many others that have similar behaviors and uses. In the remaining time at your disposal you can do little beyond a brief enumeration of the larger points of interest concerning the remaining elements. Such a tabulation will be confusing unless you keep in mind the family relationships which are so helpful in grouping together important facts concerning similar elements. Therefore you should review the study of the Periodic Table (Fig. 113, page 338) and be ready to use the principles noted there in your study of the remaining chemical elements.

In this problem you will study a few of the remaining nonmetallic elements. Then you will find many curious and stimulating facts concerning that interesting group of elements which behave sometimes as nonmetals and sometimes as metals. Finally, you will survey briefly some of the characteristics of some of the remaining metals.

Selenium is used in the "electric eye." Selenium and tellurium are two elements which closely resemble sulfur, but differ from it in being more closely related to the metals. Selenium is found associated with sulfur and the sulfides. It has several allotropic modifications, one of which has the curious behavior of serving as an electrical insulator in the dark, but becoming a fairly good conductor in the light. Consequently it is one of the substances used in making the photoelectric cell, the device commonly called the electric eye. Most of the selenium is used in glassmaking where in small

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quantities it helps in correcting the green color of ferrous compounds and in larger amounts it produces the red glass used for danger signals.

Tellurium is quite like selenium, but it looks a little more like a metal. Curiously enough the only gold compounds we find in nature are telluride ores. There is no important use for tellurium.

The nitrogen family includes nitrogen, phosphorus, arsenic, antimony, and bismuth. The first two members are acid-forming elements almost exclusively, the last two are chiefly metallic in nature while arsenic is an *amphoteric* element; that is, its oxides under some conditions are acidic and under other conditions are basic.

This amphoteric property is well illustrated by arsenic trioxide. It reacts with hydrochloric acid to form arsenic chloride and water:

$$As_2O_3 + 6\ HCl \rightarrow 2\ AsCl_3 + 3\ H_2O$$

Here the products are a salt and water; the hydrochloric acid has been neutralized. In this case arsenic trioxide acts as a basic oxide.

Arsenic trioxide also reacts with sodium hydroxide to produce sodium arsenite and water:

$$As_2O_3 + 6\ NaOH \rightarrow 2\ Na_3AsO_3 + 3\ H_2O$$

Here the sodium hydroxide has been neutralized. In this case the arsenic trioxide acts as an acidic oxide.

The nitrogen family well illustrates two facts of general importance: (1) the basic properties of a family increase as the atomic weights increase; and (2) if an amphoteric element like arsenic has more than one valence, it is always more acidic in the higher state of valence.

Phosphorus compounds are valuable components of artificial fertilizers. Phosphorus resembles nitrogen in many ways but differs from it sharply in its behavior toward oxygen. Phosphorus takes fire spontaneously in the air so it is used in starting fires. Red phosphorus and P_4S_3 are the common

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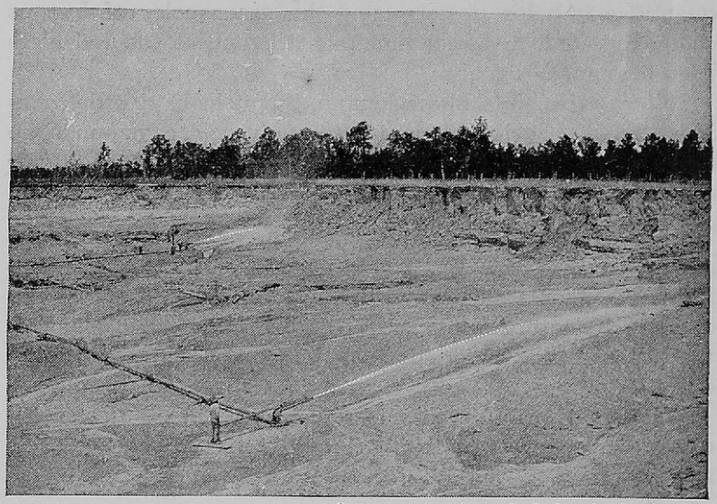

Courtesy, American Agricultural Chemical Co.

253. MINING PHOSPHATE ROCK. All phosphorus compounds are produced from phosphate rock which is calcium phosphate. Here is shown the mining of the rock in Florida.

combustible components in matches. The native source of phosphorus is the rock phosphate whose formula is $Ca_3(PO_4)_2$; it is found extensively in Florida and Tennessee. This same compound is found in the bones of animals. Phosphorus is commonly known in two allotropic modifications: (1) red phosphorus, a hygroscopic powder which does not take fire at room temperature, and (2) yellow (or white) phosphorus, a waxy solid which is poisonous and easily ignited at room temperature. The most characteristic reaction of phosphorus is its combustion in oxygen forming either P_2O_3 or P_2O_5. The latter has remarkable affinity for moisture, and as a result it is one of our best reagents for drying gases. When it reacts with water, it forms a series of phosphoric acids of which H_3PO_4 is by far the most important. Phosphorus compounds are essential for plant growth, and as a result they are components of artificial fertilizers. The native ore $Ca_3(PO_4)_2$ is insoluble so it is changed to more soluble salts such as $CaHPO_4$ or $Ca(H_2PO_4)_2$.

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Arsenic compounds are used to kill plant pests. In nature arsenic is associated with the metals, especially those which are found as sulfides. In roasting such ores, the arsenic is burned to As_2O_3. Arsenic is almost entirely a by-product which is obtained in the metal industries. The element has a metallic appearance, but its uses as a metal are limited. It is used in the production of certain alloys such as arsenic bronze and speculum metal. It also is used as a hardening agent for lead in the manufacture of shot. The most abundantly used compound of arsenic is "white arsenic" (As_2O_3), the compound usually sold at the drugstores as "arsenic." It is used in medicine, in glassmaking, in preserving hides and museum specimens, in tanning leather, and in making other arsenic compounds. It is an active poison, although its action is slow. Some arsenic compounds are highly colored, so arsenic pigments are sometimes used; however the poisonous nature of arsenic limits their use. Compounds such as sodium arsenite (Na_2HAsO_3), calcium arsenate [$Ca_3(AsO_4)_2$], lead arsenate [$Pb_3(AsO_4)_2$], and Paris green [$Cu(C_2H_3O_2)_2 \cdot Cu_3(AsO_3)_2$] are widely used as cattle dips, as weed killers, or to destroy insects (such as the boll weevil, cabbage worm, or potato bug) which feed upon useful crops.

Antimony was used in the type that was set for this book. Antimony is found in sulfide ores, especially stibnite, a black ore, Sb_2S_3. The element is prepared by heating stibnite with iron, or by reduction of the oxide with carbon. Antimony has a bright metallic luster. The main uses of the element are in the production of alloys such as hard lead, type metal, bearing metal, and battery plates. Some of the compounds of antimony are used in medicine, such as butter of antimony ($SbCl_3$) and tartar emetic, which is potassium antimonyl tartrate ($K \cdot SbO \cdot C_4H_4O_6$).

Bismuth is used in electric fuses. Bismuth is almost wholly metallic in behavior. Most of the supply of bismuth is recovered as a by-product in the electrolytic refining of lead. The metal has a brilliant luster with a slightly reddish tinge. It has a low melting point (269°). The main use of

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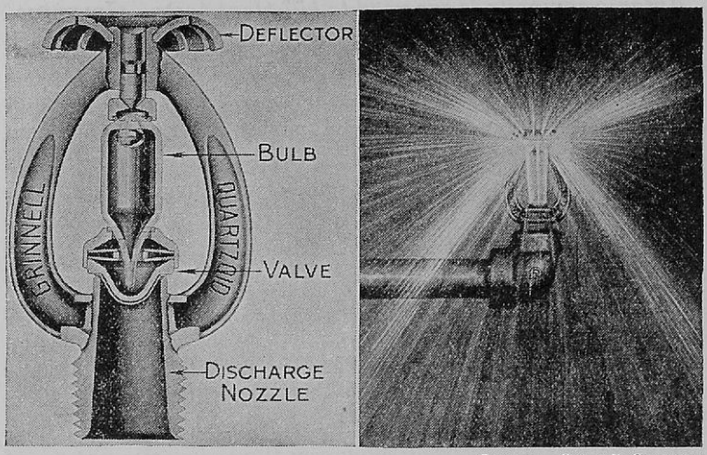

Courtesy, Grinnell Company

254. SPRINKLER HEADS FOR AUTOMATIC SPRINKLERS. Warehouses, department stores, and factories are protected against fire losses by automatic sprinkler systems. The sprinkler heads contain a strip of low-melting bismuth alloy which melts, if the temperature gets too high, and releases the water.

the metal is in making low-melting alloys for electric fuses, automatic fire alarms, and automatic sprinkler systems. Some compounds of bismuth are used in ceramics and paints, but the most important uses are in medicines and cosmetics. The subnitrate of bismuth, a mixture of salts of somewhat uncertain composition, is used to correct digestive disturbances and in treating eczema and ulcers, as well as in making face powder. For many centuries bismuth compounds have been used in the manufacture of face powders.

How are the amphoteric elements used? Closely related to the nitrogen family are the other members of Group V, *vanadium, columbium,* and *tantalum.* These three elements are mainly useful as metals. *Vanadium* is used chiefly in the steel industry both to remove impurities and to form a valuable alloy called ferrovanadium. Vanadium steel stands strain, vibration, and shock; hence it is useful in the manufacture of automobiles.

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Columbium improves stainless steel. Columbium is a rare metal, which only recently has found a valuable use in improving stainless steel.

Tantalum is used in making laboratory utensils and surgical instruments. Tantalum is another rare metal, but its uses are somewhat more varied. The Balkite rectifier, which changes an alternating electric current into a direct current, contains a strip of tantalum as its most essential part since it allows the electric current to pass in only one direction. The metal is very resistant to corrosion, and as a result it is useful in making laboratory utensils, electrodes, X-ray targets, dental and surgical instruments, and standard weights. Tantalum carbide (ramet) is extremely hard and finds valuable uses in making tools for cutting other metals.

Chromium, molybdenum, and tungsten form another group of interesting elements which are both metallic and nonmetallic. They all find uses in both capacities, although as usual the metallic nature increases as the atomic weight increases.

Chromium is used in making an extremely hard and strong steel. Chromium has been used for more than a century and a half as the chromates and dichromates, but it is only within the past decade or so that industry has learned to produce the metal and use it in various ways. The main ore is called chrome iron ore [$Fe(CrO_2)_2$] from which the valuable alloy called ferrochrome is produced by reduction in an electric furnace. The process of plating chromium by the electrolysis of its solutions has recently been made possible. The coating of chromium produced in this way has found extended use for decorative purposes as well as for increasing the hardness (and resistance to wear) of dies, cutting tools, bearings, metals, and many machine parts. Chrome steel is characterized by extreme hardness and strength, so it is used for cutting tools, safes, bank vaults, and heavy machinery. Stainless steel contains chromium as well as nickel. The alloys stellite (Cr, W, Co) and illium (Cr, Ni, Cu, Mo, W, Mn, Al, Fe) are extremely resistant to corrosive influences.

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Chromium compounds are also useful. Chrome iron ore is used in making a refractory which is used in lining high-temperature furnaces. The oxide Cr_2O_3 (chromic oxide) has a deep green color, and it is used as a pigment in paints and in ceramic products. Extensive use is made of chrome alum $[K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot (H_2O)_{24}]$ in tanning leather, in printing calico, and in waterproofing fabrics. The oxide (CrO_3) called "chromic acid" or chromium trioxide is a powerful oxidizing agent. It is used in the laboratory as a "cleaning solution." It also is useful in medicine, photography, dyeing, tanning, bleaching, etching metals, and in purifying oils. It reacts with basic materials forming two important classes of salts: (1) the chromates, like K_2CrO_4 which is useful in dyeing and in manufacturing ink, and lead chromate ($PbCrO_4$) a brilliant yellow pigment (chrome yellow); (2) the dichromates like $K_2Cr_2O_7$ which is a powerful oxidizing agent extensively used in the laboratory and in many industries, and $[(NH_4)_2Cr_2O_7]$, a compound whose molecule contains both an oxidizing end and a fuel end. When a pile of this substance is ignited with a fuse paper it burns itself, forming a miniature volcano.

Molybdenum is used in high-speed steels and corrosion resisting alloys. Molybdenum has long been used in its salts, the molybdates, such as sodium molybdate (Na_2MoO_4) and ammonium phosphomolybdate $[(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot (H_2O)_x]$. The latter is used commonly in the detection and determination of phosphates. Other molybdates are used in dyeing silk, wool, and leather and in producing colored glazes. As a metal, molybdenum is used in high-speed steels, many corrosion resisting alloys, as a support for the filaments of incandescent lamps, for the heating element in electric heating devices, and for various purposes in the radio industry.

Tungsten is used in the filaments of electric lamps. Tungsten is similar to molybdenum, but its uses emphasize its metallic nature. Pure or "ductile" tungsten is extremely ductile, approaching gold in this respect. Its fine wires are used in the filaments of household electric lamps. Tungsten is one

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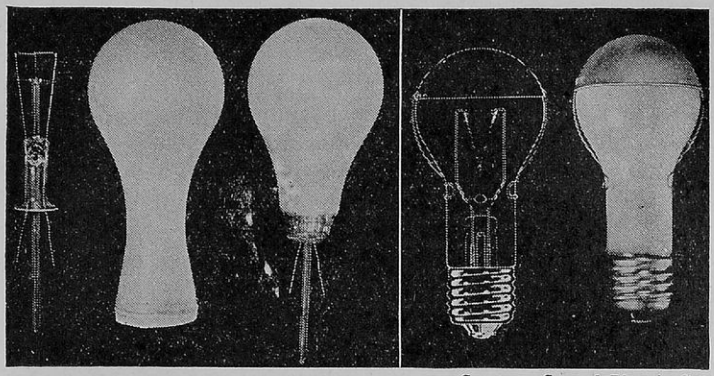

Courtesy, General Electric Co.

255. A MAZDA LAMP. The modern incandescent lamp contains a filament of tungsten as its source of light. The passage of an electric current through the tungsten produces a brilliant white light.

256. DIAGRAM OF A SUN LAMP. The sun lamp contains a drop of mercury. When the filament in the lamp is heated, the mercury vaporizes. The light radiated is similar to the light of the sun.

of the heaviest and hardest metals and it has the highest melting point of all the metals. It resists corrosion both by acids and by alkaline solutions, but dissolves in a mixture of nitric and hydrofluoric acids and in fused alkali. It is used as contact points in spark plugs and telegraph keys, in X-ray tubes, in electric furnaces, and in radio tubes. Ferrotungsten is used in steel making, and tungsten alloy steel (high-speed steel or self-hardening steel) has greatly increased the output of machine shops. Tungsten carbide (carboloy) is one of the hardest substances known; it is used in cutting steel.

Manganese is important in the production of steel. Manganese resembles chromium in many respects, though it appears in the Periodic Table in a different family. The principal ore is pyrolusite (MnO_2) which may be reduced in a furnace by carbon. It alloys with iron, producing ferromanganese and spiegeleisen which are important in the production of steel. The addition of these substances to steel aids in removing sulfur and oxygen. Manganese alloy steel is distinguished by its

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ability to resist wear. The most important nonferrous alloys of manganese include a bronze, which is used in making the propeller blades of steamships because it does not corrode in salt water, and a brass called manganin which is used in making standard electric resistance boxes.

MnO_2 is used in chemical laboratories as a catalyst (page 48) and as an oxidizing agent (page 312). It also is employed in glassmaking both to correct the green color of ferrous compounds and to make the popular black glass. It is used also in dry cells and in paints.

The manganates are oxidizing agents. K_2MnO_4 is a typical example of such a compound; when diluted its solution shows various color changes, hence it is known as a "chameleon solution."

The permanganates, like $KMnO_4$, are extremely efficient and useful oxidizing agents. Potassium permanganate has a persistent pink or reddish purple color which is useful because its appearance in a solution indicates that all oxidizable material has been acted upon. Consequently, it finds extensive applications in analytical procedures. It is also employed as a disinfectant, deodorant, and germicide.

What other metals are commercially important? There are other commercially important metals which may be remembered by association with some of the typical elements which already have been studied in more detail.

Closely related to sodium are the alkali metals lithium, potassium, rubidium, and cesium. As usual, the metallic properties increase as the atomic weight increases.

Potassium is an essential element for plant growth. Potassium resembles sodium closely, but it is less abundant in nature. It is an essential element for plant growth. It is obtained from brines and from deposits which remain after brines or sea water have evaporated. The main supply comes from the Stassfurt deposits in Europe and the Searles Lake area in southern California. Great deposits of potassium salts are also being mined in New Mexico. The metal is prepared in about the same way as sodium is prepared. These two metals

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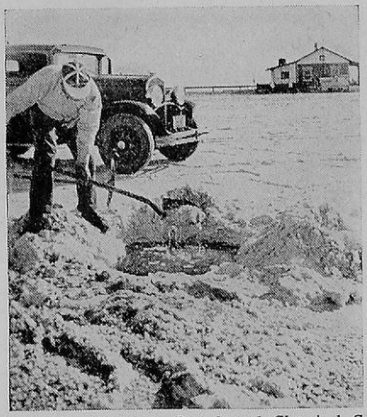

This hole is in the crust of crystals that cover Searles Lake which is a concentrated solution of sodium chloride, potassium bromide, borax, and other salts. The total depth is not known, but soundings have been made to a depth of 600 ft. The house covers the intake of a pipe line that supplies brine from which valuable mineral salts are separated.

Courtesy, American Potash and Chemical Co.

257. Six Hundred Feet to the Bottom!

are much alike both in physical and chemical properties. Potassium compounds such as KOH, KCl, K_2SO_4, $KHCO_3$ are similar to the corresponding sodium compounds.

Lithium has a limited use in electric storage cells and in other commercial products. Lithium is also like sodium but is lighter in weight and less active chemically. Its compounds find a limited use in making artificial mineral waters, in medicine, in storage cells, in glass, and in red fire.

Rubidium and cesium make efficient radio tubes. Rubidium and cesium are very rare alkali metals which are highly prized because they make efficient radio tubes. Cesium is very soft (m.p. 26.5°). It is the most active metal known, and its hydroxide CsOH is the most powerful base known.

The detection of the alkali metals, lithium, sodium, potassium, rubidium, and cesium is commonly accomplished by means of the spectroscope. This is an instrument which records the wave length of the light emitted by a glowing metal, or metallic salt. Light from a flame passes through a slit and strikes a prism, which analyzes the light, giving various wave lengths. The observer sees a series of bright lines whose color and position are determined by the wave length of the

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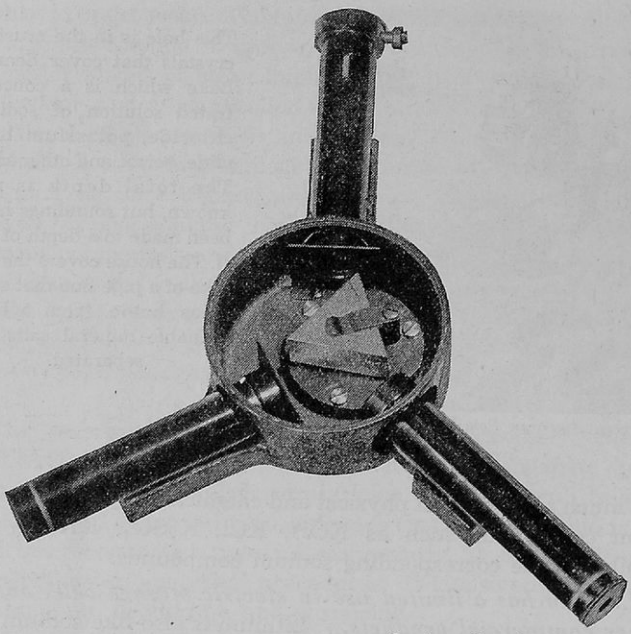

Courtesy, Bausch and Lomb

258. A SPECTROSCOPE. This instrument can be used to detect the presence of various elements from the color of light which they emit. Light from the substance to be tested passes through the prism where it is sorted out into its various wave lengths. The number and position of the various colored lines so produced tell what elements are present.

light emitted. Lithium gives two prominent lines, one yellow and one bright red; sodium gives two bright yellow lines which are very close together; potassium gives a violet flame and a brilliant red spectrum line; rubidium gives three red lines and two blue-green ones; cesium has a line in the red-yellow region and two beautiful blue lines.

World War II increased the importance and availability of magnesium. Magnesium may be prepared by the electrolysis of melted magnesium chloride, which is obtained from sea water or from brines taken from deep wells, the best known and most productive of which are in the central part of

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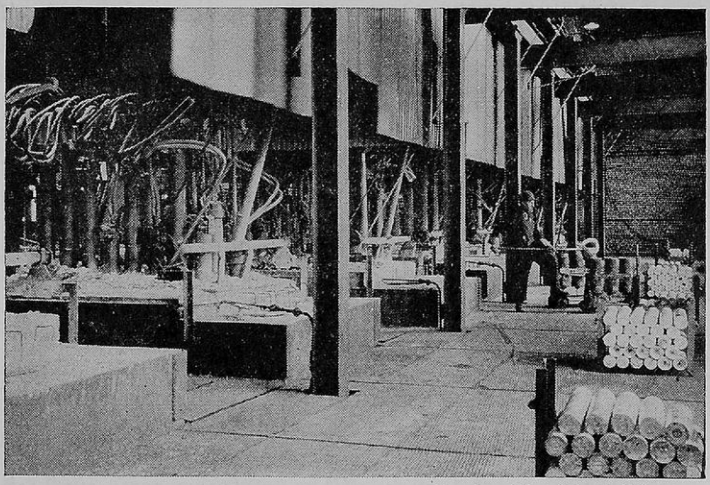

Courtesy, Dow Chemical Company

259. FURNACES FOR PRODUCING METALLIC MAGNESIUM. On the left is a row of low boxlike furnaces holding fused magnesium chloride from which an electric current produces chlorine and metallic magnesium.

Michigan. Reduction of magnesium oxide with carbon or ferrosilicon is also being developed.

Magnesium is light and ductile, easily acted upon by acids, and easily burned. Its ease of burning and its brilliance while burning explain its use in signal flares and flash bulbs.

Magnesium alloys are very useful since they combine lightness, hardness, strength, and machining qualities to a remarkable extent. Airplanes need light-weight engines, pistons, and frames, now successfully made from magnesium alloys. The most important magnesium alloys are those with aluminum (magnalium, duralumin, Dowmetal). It has been estimated that the United States in 1942 was capable of producing 50 times the amount of magnesium consumed here in 1935.

Mercury is used in thermometers and barometers; it has many other uses. Mercury may be extracted from its sulfide ores by heat alone, and it may be purified by distillation. It

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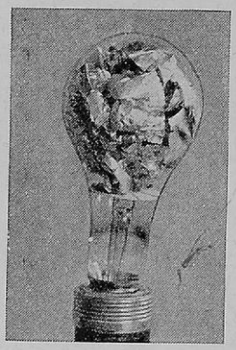
is a brilliant metal, liquid at ordinary temperatures, a good conductor of heat and electricity, and relatively inert chemically. It is extensively used in thermometers, barometers, vacuum pumps, electric lamps, and even in engines where it replaces steam. Mercuric chloride (bichloride, $HgCl_2$) is known as corrosive sublimate, a violent poison used in dilute solutions for sterilizing surgical instruments and preserving anatomical specimens. Mercurous chloride (HgCl), for many years used in medicine, is called calomel. Mercuric sulfide (HgS) is a brilliant red pigment known as vermilion. Mercury forms alloys with many other metals. These are known as *amalgams*, some of which are used in dentistry.



260. FLASHLIGHT BULB. This bulb contains a sheet of aluminum foil.

Tin is used in making tin plate. Tin is found as the oxide SnO_2. Formerly it was supplied from the historic mines of Cornwall, but now is supplied mainly by the Malay States, Dutch East Indies, and Bolivia. The metal is prepared by reduction of the ore with carbon. It is a white metal which retains its color unusually well. The main use is in making tin plate, which is made by dipping thin sheets of iron into molten tin. The coating of tin should be continuous because "pinholes" expose iron which rusts quickly. A thicker layer of tin is deposited electrolytically in the preparation of parts for radios and electric refrigerators. Artificially prepared stannic oxide is used in making opaque glass, porcelain-lined sinks, and bathroom fixtures. Stannic chloride ($SnCl_4$) is used in dyeing and weighting silk; stannous chloride ($SnCl_2$) is a useful reducing agent in the laboratory.

Lead is used in the "plates" of your car battery; lead has many important special uses. Lead is an important metal which has been used since early historic periods. Its main ore is galena (PbS) which forms shining cubes. The winning of the metal from the ore is a long and rather complicated

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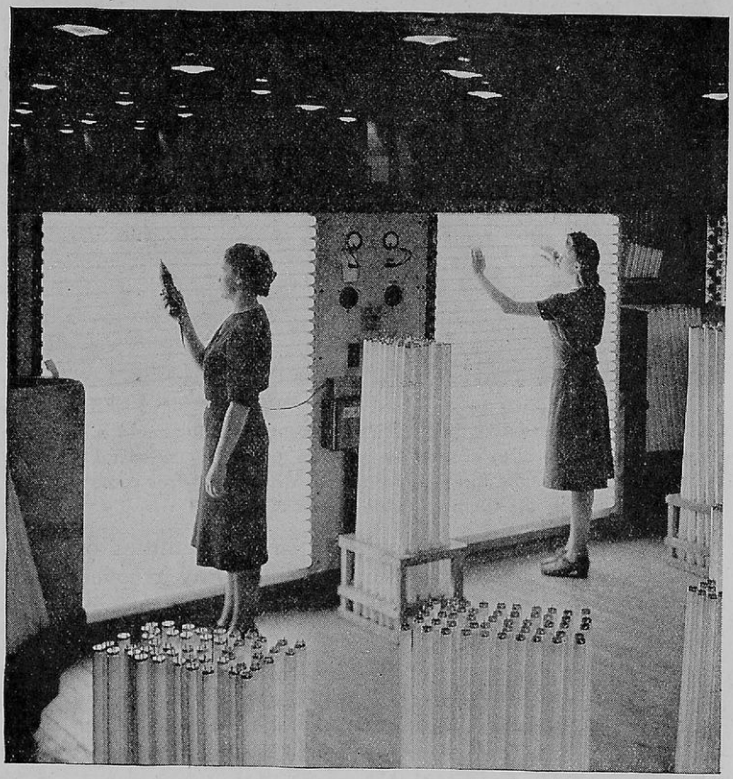

Courtesy, General Electric Co.

TESTING TUBES FOR FLUORESCENT LAMPS. In the tube of each lamp is a trace of mercury, a small amount of argon, and a coating of fluorescent powder. The mercury vapor produces ultraviolet light which strikes the fluorescent coating and is re-radiated as visible light. A much higher proportion of the electrical energy is converted to light than in the ordinary filament lamp. Various colors can be produced by varying the composition of the fluorescent compounds which line the inner surface of each tube. The proper combinations of these fluorescent materials produce a white light which has a close resemblance to ordinary sunlight.

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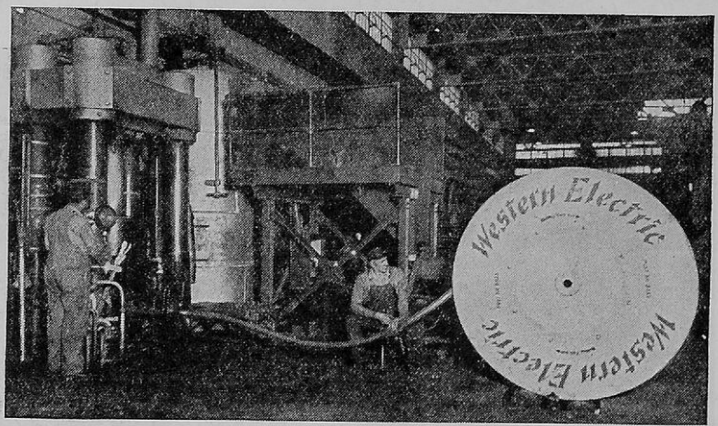

Courtesy, Western Electric Company

262. COVERING TELEPHONE CABLES. These great machines mold a covering of a lead antimony alloy around the wires in the cable. The metal is forced through a die to make the pipelike sheath while the wires come through an opening in the center of the die.

process. In the purifying of lead, small quantities of gold, antimony, bismuth, and silver are frequently recovered, so lead of high purity is little, if any, more expensive than the metal as it comes from the furnace. Lead is a soft, easily melted (327°) metal which has a brilliant luster, although its surface tarnishes quickly. It has very little strength, but it is quite plastic at 300° C., so it may be shaped readily and used in "wiping" joints. Mercury and lead are the heaviest of the common metals. Lead is the cheapest of the inert metals, consequently it finds extensive uses where corrosion is liable to take place, such as linings for vats, sinks, "lead chambers," and for waste pipes, cable coverings, battery plates, and a great variety of special uses. Lead forms many useful alloys, among them solder, bearing metals, type metal, pewter, and terne plate. Most of the compounds of lead are poisonous so they are used in insecticides. Lead poisoning was formerly one of the most prevalent occupational diseases, but is now effectively controlled by the use of aspirators and by thorough cleanliness. Lead monoxide (litharge, PbO) is used in the rubber, ceramic,

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and paint industries. Lead dioxide (PbO_2) is an efficient oxidizing agent used in making safety matches. Red lead (minium, Pb_3O_4) finds many uses, such as in the manufacture of ointments, glass, glazes, varnishes, and storage battery plates. Lead chromate ($PbCrO_4$) is a brilliant yellow pigment (chrome yellow); and basic lead carbonate is the paint material known as white lead, for centuries the standard paint base. (See page 708.)

Cobalt is used in making alloys which resist corrosion effectively. Cobalt resembles iron rather closely. It is white, magnetic, very hard, and quite malleable and ductile. The metal is used especially in making alloys such as cochrome (Co, Cr) and stellite which resist corrosion effectively. Cobalt steels are especially valuable in making steel magnets. The compounds of cobalt are extensively used blue pigments for the paint and ceramic industries.

Nickel is used in making alloys for the heating units in electric irons; it has a wide variety of uses. Nickel resembles cobalt and iron. It is familiar as a coin metal, and it has long been used as a metal coating (nickel plate) to improve the appearance of iron and to protect it from rusting. Nichrome and chromel are nickel-chromium alloys, widely used in heating units for electrical household devices. Nickel steel is tough and strong. Monel metal (Ni, Cu) is popular in kitchens and machinery for processing foods because it is very resistant to corrosion. The alloy known as invar (Ni, Fe) has a very low coefficient of expansion; it is valuable for making surveyors' tapes and pendulums for clocks.

Readings for Pleasure and Profit

SLOSSON, EDWIN E. *Creative Chemistry.* Chap. XIV, pp. 285-296, "Metals (Old and New)."

STOKLEY, JAMES. *Science Remakes Our World.* Chap. X, pp. 111-128, "New Metals."

WEEKS, MARY ELVIRA. *The Discovery of the Elements.* Chap. III, pp. 20-27, "Zinc, Cobalt, Nickel, Manganese"; Chap. V, pp. 50-63, "Tungsten, Molybdenum, Chromium"; Chap. VII, pp. 77-96, "Columbium, Tantalum, Vanadium."

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Putting Chemistry to Work

A

(1) Why is it so important for a painter to wash his hands thoroughly before eating lunch? (2) How can you start a fire without using phosphorus or its compounds? (3) How is chemistry applied in the manufacture of automatic sprinklers and fire-alarm systems? (4) Why are photographic flash bulbs superior to the old flashlight powders? (5) What property of mercury makes it suitable for use in thermometers? (6) Formerly an arsenic pigment was used for printing green wallpaper. Why is this now forbidden? (7) A tiny crystal of blue vitriol was allowed to rise to the top of the mercury in a barometer. The mercury fell to a lower level. Explain.

B

(8) What substances are used to extinguish fires? Tell the reason each is used. (9) Review the types of fire extinguishers and the chemistry involved in their use. (10) Make a brief review chart of baking powders. (11) Cesium is the most active metal known. What would you expect to happen when it is dropped on water? when it is exposed to air? (12) Why does the statement that hydrogen can be prepared by the action of a metal on hydrochloric acid need to be qualified? (13) How many allotropic forms do you know for phosphorus, carbon, sulfur, oxygen? Do metals display allotropy? Be able to prove your answer.

Research and Activities That You Will Enjoy

Chemical magic — "pharaoh's serpents": When solutions of sodium thiocyanate and mercuric chloride are mixed, a precipitate of mercuric thiocyanate [$Hg(CNS)_2$] is formed. When dried and made into cones, it ignites readily with a flame, and burns to a curious snake-like ash.

A report: (a) Extraction of gold from sea water (b) Chemistry of inks (c) Beryllium, a metal with possibilities.

Interviews: (a) Ask an engineer to tell you about mercury vapor engines and their probable future. (b) Ask a photographer to tell you how a flashlight bulb is made and why these particular materials are selected. What would you expect to find in a used flash bulb? Try it. (c) Ask an automobile salesman to explain to you the advantages of molybdenum steel. (d) Ask a machinist about high-speed steel and the effect it has had on machine shop practice. (e) Ask an electrical engineer about the use of the "elec-

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tric eye." What materials other than selenium are used in the "electric eye"? (f) Ask an illuminating engineer to explain the use of neon in signs and aviation beacons.

Problem 78

WHAT OF THE FUTURE?

You have studied some of the basic principles of chemistry and observed some of the applications of science to modern ways of living. What of the future? Can you expect additional discoveries which may contribute to the comfort, safety, health, or happiness of mankind?

It is natural for a beginner to feel that all the important discoveries have been made and that it is impossible for the new generation to add to the sum of human knowledge. It is true that you have at your command the accumulated wisdom of the ages. Each generation has been able to make its contributions. This process has continued through the centuries with increasing effectiveness. It is probable that no decade in human history has made greater strides in its scientific advancement than the present generation is making. It is not at all likely that this progress will come to a sudden stop. It is much more probable that the future will make available new developments which will be factors as important and as useful in human society as any of the basic discoveries of the previous generations.

So you must not regard chemistry as a finished science to which the coming generation is unable to contribute. It is much wiser to regard chemistry as a growing science, one whose history and achievements are worthy of respect; but above all one whose progress is rapid because of the wide variety of fields which are teeming with opportunities.

Does youth have a chance? It is natural for young people to feel that they have little chance to make worth-while contributions because there are so many persons with wide experience and broad viewpoints. However, the enthusiasm and

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determination of youth sometimes succeed where more mature judgment fails. Note the following example.

There are few things more inspiring to younger students of science than the history of the aluminum industry. Just recall that aluminum is the most abundant metal of the earth's crust. There is more aluminum within the reach of man than any other metal. Yet the amount of aluminum used today is insignificant compared with the amount of iron that is used. For many years aluminum was not available, and at present it is available only at a price that is considerably higher than the price of iron. Why was aluminum so long in arriving? Because it is never found in the uncombined form and is generally found in compounds which are *very stable*. It has been very hard to get it out of these compounds. Some of the most skillful scientists of Europe and America had worked long and faithfully at this task, but their results were not satisfactory. It remained for an American boy, Charles Hall, just graduating from Oberlin College, to find the secret which made possible the aluminum industry. After diligent search, he found that the aluminum ore, bauxite, dissolved readily in molten cryolite and that upon electrolysis this solution gave the metal aluminum. All of this metal which is used today is prepared by relatively simple modifications of the Hall process.

Two tables will show how the aluminum industry has grown. The table on page 753 shows how the price of this metal has fallen as the methods of production were improved, while the table following shows the rapid increase in the use of this interesting metal. Note that in the early days, aluminum was a precious metal, although its compounds were "as common as dirt" and "every clay bank along the road side is a potential mine of aluminum." In those early days it was a curiosity available only in very small quantities. It was produced by the use of sodium, itself an expensive metal. The drop in price in 1856-57 was due to an improved method of producing sodium. The fact that the price of aluminum did not change to any great extent from 1862 to 1886, indicates that for a quarter of a century no progress had been made in the solution of this problem. Hall's discovery in 1886 brought a great increase

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in production and a corresponding decrease in cost. The industry stands as a monument to the work of an American youth and as an inspiration to young scientific workers everywhere. Today aluminum is used as a component of the light aluminum alloys that have attracted wide attention in airplane construction, in industry, and in the defense of our country.

But, you may object, this work has been done; there is nothing left for us to do. Even in the aluminum industry there remain many problems worthy of your best efforts.

There are many problems yet to be solved in regard to welding, soldering, patching, machining, plating, and finishing aluminum. These processes have been difficult to carry out and special skill is required in their operation. The wide range of usefulness of aluminum powder and aluminum foil suggest that other applications are to be expected. It is safe to say that we have scarcely begun to know aluminum and that the immediate future will see great strides in the utilization of this interesting metal.

PRICE OF ALUMINUM PER POUND

1855	in England	$275.00	1910		$0.228
1855	in U. S.	90.00	1913	(Nov.)	0.19–0.19½
1856		27.00	1917	(Jan.)	0.63–0.65
1857		22.50	1921	(Jan.)	0.27
1862		12.00	1929	(April)	0.24–0.26
1886		12.00	1937	(Jan.)	0.229
1895		0.55	1940		0.20
1898		0.325	1941		0.17
1900		0.32	1942		0.15
1905		0.32	1943		0.15

PRODUCTION OF ALUMINUM IN AMERICA

1883	83 lbs.	1918	(War Period)	225,000,000 lbs.
1885	283 lbs.	1926		304,000,000 lbs.
1895	920,000 lbs.	1930		224,000,000 lbs.
1900	7,150,000 lbs.	1935		110,000,000 lbs.
1905	11,347,000 lbs.	1940		420,000,000 lbs.
1910	47,754,000 lbs.	1941		626,000,000 lbs.
1915	99,000,000 lbs.	1944	(Estimated capacity)	2,400,000,000 lbs.

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Fourteen of the most abundant elements are almost unknown as useful elements; here is an opportunity for youth. You have learned that there are ninety-two elements in the Periodic Table and that it is possible these have all been discovered. If you select the twenty-four elements which are most abundant in the earth's crust, you may be surprised to find that fourteen of them are almost unknown as useful elements or at least are such recent additions that their uses are very limited. Certainly there is much for the future to learn about such elements.

Knowledge concerning some of the best-known elements is by no means complete. Few materials enter into modern life in a greater variety of ways than iron, yet new information concerning iron is increasing daily especially in such forms as special alloy steels. There is much to learn also about sodium, copper, lead, zinc, and other useful metals.

The second most abundant element is silicon. Its compounds have been known and used since the very earliest times, but the element itself is still largely unknown so far as general usefulness is concerned. Calcium, potassium, magnesium, titanium, manganese, fluorine, barium, strontium, zirconium, and lithium are all elements that are found in abundance in the earth's crust, yet as useful elements they are mostly unknown. Many of these elements are known to have interesting properties, which might find important applications if more were known about them. Certainly here are abundant opportunities for study in preparing such materials for a useful setting in this modern world.

If you turn your attention to the less common elements you find that here also are numerous opportunities for enlarging mental horizons. Beryllium, the lightest rigid metal, is almost unknown commercially, but it has interesting possibilities. Compounds of titanium and zirconium find some uses, but the elements themselves are still chemical curiosities. The metals ruthenium, rhodium, palladium, osmium, and iridium are similar to platinum but the specific uses for any of these interesting metals are extremely limited. Some use has been made of helium in airships, of neon in advertising signs, and

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of argon in electric lamps; but these gases and the other inert gases (xenon and krypton) should have much wider uses. The rare earths make up a curious group with remarkably similar properties. Some members of the group are used to a limited extent, but the group as a whole is almost unknown and unused. The very complexity of the problem is a definite challenge to the courage of youth.

Even such a hasty enumeration as this must convince you that knowledge is after all very limited and that there is still much work for future generations to do before chemistry can be regarded as a completed science. Especially is this so if the compounds of the known elements are considered. Then the possibilities of new and useful developments really have no limit.

There is opportunity for youth in the chemistry of medicine. Chemistry has always been closely associated with medicine and the struggle against disease. In the early days the main function of the chemist was to provide remedies with which to cure human ills. While the scope of chemistry has broadened to include many other fields, it still is interested in providing suitable materials for the medical profession.

There have been great advances made in providing suitable antiseptics and disinfectants, but there is much yet to be accomplished in this direction. We need materials which are efficient in sterilizing wounds and controlling parasitic forms of life, while at the same time these materials must not be hostile to the higher forms of life. We need specific remedies for many diseases which now baffle the skill of medical science.

To illustrate how chemistry is able to assist in the war on disease let us use our imagination. Suppose there is a disease for which there is no effective remedy, but some relief is gained by the use of a certain treatment. How can the chemist help? First he can study the material used in the treatment and by modifying the conditions or the structure of the molecules, he can learn what there is about the treatment that contributes toward its partial success. Then he can search the possibilities of chemical modifications, prepare other similar

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materials, and learn how to increase the potency of the remedy. This was exactly the method used by German scientists in their efforts to combat such diseases as African sleeping sickness and syphilis. (See page 555.) After many preparations were tried, their efforts were successful and the valuable drug called salvarsan was produced. The success which has been accomplished with this drug has led to the discovery of several others of similar nature. This group of drugs has been of priceless importance in combating diseases which have taken a heavy toll in human life. Similar success is greatly needed in dealing with many other disease conditions.

There is opportunity for youth in chemical engineering. Chemistry finds many applications in the various branches of engineering. Many times the difficulties that an engineer encounters resolve themselves into questions of the composition of the materials which he is compelled to use. Here a knowledge of chemistry is a very direct help. In providing suitable feed water for a boiler, durable materials for a house, efficient metals for a machine, or strong and permanent parts for a bridge, the chemist must be ready to supply materials of proper composition. By varying the composition of steel he can produce a product which is brittle or tough, hard or soft, magnetic or nonmagnetic, one which expands much or little. Much still remains to be done in adapting different materials to present-day needs.

There is a need of better information regarding engineering materials. As an example, engineers have failed to eliminate the corrosion of iron and steel in many steel products. It has been stated that one-sixth of the iron products manufactured now are required to replace metal which is unfit for further use because of the effect of corrosion. This represents an annual loss of over two hundred million dollars. Here certainly is a field which offers a promising outlook for a successful solution of an urgent problem.

There is opportunity for youth in the chemistry of agriculture. The agricultural chemist must know what substances are required by growing food crops; he must know where these sub-

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stances can be obtained and how they may be prepared for the use of food crops. He must study the methods of shipping foods and learn how they may be brought to the consumer in prime condition. He must know the best ways of preserving foods and the materials which prevent deterioration without interfering with food values. He must apply the science of nutrition to the raising of stock and learn to use the most approved sanitary methods in dealing with dairy products.

Chemistry during National Emergency. In times of national emergency scientific advancement is stimulated. Developments come with amazing rapidity and must be adjusted and applied to peacetime conditions after the period of emergency is over. This is a problem which requires the services of trained scientific minds.

In conclusion, success is not to be found in luck but in patient, diligent, and untiring effort; you cannot dream yourself into success. In your study of chemistry you have learned some of the most fundamental principles upon which the science is based. You also have tried to see how the facts of chemistry are applied in making living conditions better, safer, and more comfortable. Much has been accomplished; knowledge is increasing every day. But only a beginning has been made. Much detail has of necessity been omitted from this book. If certain phases of chemistry have especially interested you, it may be to your advantage to continue your study further.

One precaution is needed in this outlook. You must not expect to find in chemistry the open sesame for success unless you are willing to work long and hard in the face of discouragements. Success in science is not to be found in luck but in patient, diligent, and untiring effort. You cannot dream yourself into success in any field. Work and a desire to serve your fellow human beings are essential.

Readings for Pleasure and Profit

Coith, Herbert. *So You Want to Be a Chemist?* McGraw-Hill (1943).

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Summary Test

1. *Why are gold and platinum expensive?*
   (a) What factors determine the cost of metals? How do they?
   (b) How long have gold and platinum been used?
   (c) How is gold obtained and purified—
      (1) By the chlorination process?
      (2) By the amalgamation process?
      (3) By the cyanide process?
   (d) What are the property-uses of gold?
   (e) What are the property-uses of platinum?
2. *How does silver serve photography?*
   (a) What properties distinguish silver?
      (1) Where do we get our silver?
      (2) What are the uses of silver?
   (b) How is silver essential in photography?
   (c) How are blueprints made and used?
3. *How do other elements serve man?*
   (a) What are some other useful nonmetallic elements?
   (b) What uses of the elements and their compounds do you associate—
      (1) With boron, selenium?
      (2) With the nitrogen family: phosphorus, arsenic, antimony, bismuth?
   (c) What little-known metallic elements are useful?
   (d) What uses of the elements and their compounds do you associate—
      (1) With columbium, tantalum, chromium, molybdenum, tungsten, manganese?
      (2) With potassium, lithium, rubidium and cesium, magnesium?
      (3) With zinc, mercury, tin, lead, cobalt, nickel?
4. *What of the future?*
   (a) Why can we feel certain that the peak of chemical achievement has not been reached?
   (b) What valuable traits of young scientists aid in their advancement?
   (c) What opportunities for advancement are found—
      (1) In the application of property-uses of little-known elements? *(2)* In medicine?
      (3) In chemical engineering? *(4)* In agriculture?

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Underwood & Underwood

PANNING FOR GOLD.

(d) How is the following quotation from Sir Michael Foster a good motto for a young scientist?

"Nature is ever making signs to us, she is ever whispering to us the beginnings of her secrets; the scientific man must be ever on the watch, ready at once to lay hold of nature's hint, however small, to listen to her whisper, however low."

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The Appendix:

Some Valuable Information for Reference Study and Laboratory Work

I. THE METRIC SYSTEM

The metric system is a decimal system. In all scientific measurements the metric system is used. Since it is based on decimals (that is, developed on the basis of *tens*), the metric system is an easy system for making calculations. This system of measurement was developed by the French in 1795. At present it is used in everyday affairs in all the major civilized countries of the world except the United States and Great Britain.

What are the units in the metric system? The metric unit of length is the meter (abbreviated m), or the centimeter (cm), which is one one-hundredth of a meter. Originally the meter was designed as one ten-millionth of the earth's quadrant, the distance from the north pole to the equator. Due to the inaccurate methods of measurement employed at the time, the calculation of the meter was slightly incorrect. It is now defined as the distance between two hair lines on a platinum-iridium bar at 0° centigrade. The original bar is kept at the Bureau of International Weights and Measures near Paris, France, but we have a duplicate of it in the United States Bureau of Standards at Washington.

The metric unit of volume, or capacity, is the liter (l), which is defined as the capacity of a cubical box with dimensions of ten centimeters on each edge. A liter, therefore, contains one thousand cubic centimeters (cc). More accurately, one one-thousandth of a liter should be called a milliliter (ml).

The metric unit of weight, or mass, is the kilogram (kg) which is the weight of a liter of pure water at 4° centigrade. A kilogram contains one thousand grams.

You are familiar with the decimal system used in United States coins. A similar relation is found among the units and subunits in the metric system as shown in the table on the next page.

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THE UNITS AND SUBUNITS IN THE METRIC SYSTEM

Mill .001 Thousandth	*Cent* .01 Hundredth	*Dime* .1 Tenth	*Dollar* 1 One	1000 1000 Times
prefix: *milli-*	*centi-*	*deci-*		*kilo-*
millimeter	*centimeter*	decimeter	*meter*	*kilometer*
milliliter	centiliter	deciliter	*liter*	kiloliter
milligram	centigram	decigram	*gram*	*kilogram*

The units in italic type are used frequently. You should carefully and thoroughly think through their relation to larger and to smaller units. It will also be well for you to learn the meanings of the most-used prefixes: *milli* for thousandth, *centi* for hundredth, and *kilo* for thousand times as great.

The metric units are related. The metric units of length, volume, and weight are related. You will remember that the liter is the capacity of a cubical box ten centimeters on an edge. Likewise, the kilogram is the weight of a liter of pure water at 4° centigrade. There is no such convenient relation among the English units of length, volume, and weight.

II. METRIC UNITS

UNITS OF LENGTH, VOLUME, AND WEIGHT

The standard unit of the metric system is the *meter.* It is a unit of *length.* Its multiples and sub-multiples are obtained decimally.

1 meter (m) = 10 decimeters (dm)
1 dm = 10 centimeters (cm)
1 cm = 10 millimeters (mm)
1 mm = 1000 microns (μ)
1000 m = 1 kilometer (km)

The metric unit of *volume* is the *liter.* It is a cubic decimeter.

1 liter (l) = 1000 milliliters (ml)

The metric unit of *weight* (mass) is the *kilogram.* It is the weight of 1 liter of water at 4° C.

1 kilogram (kg) = 1000 grams (g)
1 g = 1000 milligrams (mg)

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METRIC-ENGLISH CONVERSION FACTORS

To change a measurement in	*To a measurement in*	*Multiply by*
Meters	Inches	39.37
Inches	Centimeters	2.54
Quarts (liquid)	Liters	.946
Liters	Quarts (liquid)	1.057
Kilograms	Pounds	2.205
Pounds	Grams	453.6
Ounces (fluid)	Milliliters	29.57
Ounces (avoir.)	Grams	28.35
Grams	Grains	15.432
Tons (short)	Kilograms	907.185
Cubic yards	Cubic meters	.765
Cubic inches	Milliliters	16.387

CONVENIENT RELATIONS

1 ml of water at 4° C. weighs 1 g.
A 5¢ piece weighs about 5 g.
A dime weighs about 2.5 g.
A dime is about 1 mm thick.
A quart is about 1 liter
An ordinary test tube holds about 25 ml.

20 drops =about 1 ml
1 teaspoon = 5 ml
1 tablespoon= 15 ml
1 cup =237 ml

III. REDUCTION OF GAS VOLUMES TO STANDARD CONDITIONS—ABSOLUTE SCALE OF TEMPERATURE

You are familiar with the fact that the volume of a given quantity of any gas varies with the pressure to which it is subjected. If the pressure upon it is doubled, the volume is reduced one-half. The relationship between the volume of a gas and its pressure was studied by Robert Boyle. In 1660 he stated the results of these studies in *Boyle's law:*

> The volume of a gas varies inversely with its pressure.

Since pressure has such an effect on the volume of a gas, it is necessary to use some standard pressure when you compare various gases. Also since the atmospheric pressure varies from day to day, the volume of any given weight of gas also varies. For purposes of comparison an atmospheric pressure of 760 mm is used as standard pressure.

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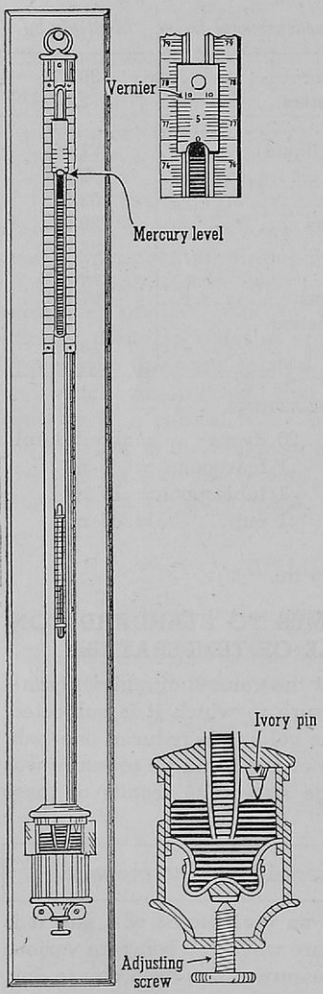

A MERCURY BAROMETER

Air pressure is measured by a barometer. In its simplest form a barometer consists of a tube about a meter long which has been filled with mercury and inverted with the open end in a dish of mercury. The mercury falls in the tube until the weight of the part left in the tube is balanced by the pressure of the air. Since the length of the mercury in the tube is proportional to its weight or downward pressure, it is possible to measure air pressure by measuring the *length* of the mercury column.

How to compute volume changes due to changes in pressure. Suppose that yesterday you collected 200 ml of air at a pressure of 750 mm, and today the barometer is 742 mm. What will the volume of the gas be today? By noting the two pressures, you see that the pressure is less today than it was yesterday. A decrease in pressure means an *increase in volume.* Arrange the two pressures in a fraction whose numerator is *greater* than the denominator and multiply the gas volume by this fraction:

$$200 \times \frac{750}{742} = 202.42 \text{ ml}$$

Suppose that you collect 85 ml of hydrogen at 745 mm pressure and you wish to know what volume it will occupy at standard pressure (760 mm). By noting the two pressures you see that the new pressure is greater than the pressure under which the gas was

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collected. This means a *decrease* in volume. Arrange the two pressures in a fraction that will have the numerator *less* than the denominator. Multiply the given volume by this fraction.

$$85 \times \frac{745}{760} = 83.32 \text{ ml}$$

To solve a problem involving a change of gas volume under pressure, decide first from the pressure change whether the volume will be increased or decreased. Then arrange the pressures in a fraction which will express this result and multiply the observed volume by this fraction.

How a new temperature scale was developed. You know, of course, that when solids, liquids, or gases are heated, there is an increase in volume. The ordinary mercury thermometer tells the changes in temperature because the volume of mercury varies with changes in temperature. While all solids and liquids show different rates of expansion for the same change in temperature, all gases show the same rate of expansion. For each degree rise in temperature the *volume* of all gases increases $\frac{1}{273}$ of the volume which it occupies at 0° C. This statement applies only to gases that are *free to expand* as the temperature rises.

Suppose that you have a volume of gas at 0° C. and that its temperature rises one degree. *If the gas cannot expand,* its *pressure* increases $\frac{1}{273}$. Gas pressure is caused by the impact of molecules striking the walls of the containing vessel. The number of molecules has not increased, and since the pressure has increased, the velocity with which these molecules strike the walls of the containing vessel must have increased. If the temperature is lowered from 0° C. to −10° C., the pressure becomes $\frac{263}{273}$ of what it was at 0° C. This means that the rate of molecular motion must have decreased at the same rate. If this same rate of decrease of molecular motion continues, at −273° C. all molecular motion ceases. This is the point of absolute zero.

A temperature scale has been developed starting with this point (absolute zero) as 0 and using the same size degrees that are used on the centigrade scale. This scale is known as the *absolute* temperature scale. Its zero point is —273° C. The freezing point of water is 273° A. and the boiling point is 373° A. The absolute scale is very useful in determining volume changes of gases due to

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changes in temperature for *the volume of a gas varies with its absolute temperature.* This is known as *Charles' law.*

How to compute volume changes due to changes in temperature. Suppose that you have 200 ml of hydrogen at 20° C. and the temperature changes to 5° C. What will its volume be under these changed conditions?

First change the centigrade temperatures to absolute temperatures. This is done by adding 273 to each. The 20° C. becomes 293° A. and 5° C. becomes 278° A. The temperature is lowered so the volume of the gas must *decrease.*

Arrange these absolute temperatures in a fraction, so the numerator is *less* than the denominator, and multiply the gas volume by this fraction:

$$200 \times \frac{278}{293} = 189.76 \text{ ml}$$

Suppose that you have 80 ml of oxygen at 0° C. and you wish to know what volume it will occupy at 100° C.

First change centigrade temperatures to absolute temperatures. The 0° C. becomes 273° A. and 100° C. becomes 373° A. The temperature rises so the volume *increases.* Arrange the absolute temperatures in a fraction to express this change and multiply the gas volume by this fraction:

$$80 \times \frac{373}{273} = 109.3 \text{ ml}$$

How to correct gas volume for temperature. (1) Change centigrade temperatures to absolute temperatures. (2) Decide from the temperature changes whether the volume will increase or decrease. (3) Arrange the absolute temperatures in a fraction which will express this effect. (4) Multiply the given gas volume by this fraction.

How to correct a gas volume for both temperature and pressure. It is often necessary to correct gas volumes for both temperature and pressure changes. This can be done in a single operation by combining the two equations.

Suppose that you have 300 ml of nitrogen measured at 754 mm pressure and 21° C. What volume will it occupy at 760 mm pressure and 0° C.?

First change the centigrade readings to absolute temperatures. The 21° C. becomes 294° A. and 0° C. becomes 273° A. Inspection shows that the volume of the gas will be lowered by the temperature

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change and also by the pressure change. The fractions then become $\frac{273}{294}$ and $\frac{754}{760}$. Multiplying the gas volume by these two fractions you have: $300 \times \frac{273}{294} \times \frac{754}{760} = 276.36$ ml

Suppose that you have 400 ml of hydrogen measured at 10° C. and 740 mm pressure. What volume will it occupy at 20° C. and 760 mm pressure?

First convert the centigrade temperature readings to absolute readings. The 10° C. becomes 283° A. and 20° C. becomes 293° A.

Inspection shows that the effect of the temperature change is to increase the volume of the gas while the pressure changes cause a decrease in the volume. Pressures and temperatures should be arranged in fractions to show these results independently of each other. The gas volume should then be multiplied by these fractions:

$$400 \times \frac{293}{283} \times \frac{740}{760} = 404.1 \text{ ml}$$

How to make corrections for gases measured over water. Gases are often measured over water. When this is done, the gas contains some water vapor mixed with it. This water vapor exerts pressure, so the barometric pressure is not the true pressure of the gas. To get the true gas pressure, it is necessary to subtract (from the atmospheric pressure) the pressure exerted by the water vapor. For each temperature, water vapor exerts a definite pressure. This pressure is listed on page 773.

Ninety ml of nitrogen is measured over water at 745 mm pressure and 20° C. What is its volume at standard conditions of temperature and pressure (0° C. and 760 mm)?

First change the centigrade readings to absolute temperatures. The 20° C. becomes 293° A. and 0° C. becomes 273° A. By inspection you can see that due to both temperature and pressure changes the volume will be decreased. The statement of the problem then becomes:

$$90 \times \frac{273}{293} \times \frac{745}{760} = ?$$

745 mm does not represent the true pressure of the gas. Part of this is due to the presence of water vapor. To get the true pressure of the gas, this pressure due to water vapor must be subtracted from 745 mm. Reference to the table shows that at 20° C. water

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vapor exerts a pressure of 17.4 mm. Subtracting this from the observed atmospheric pressure the problem now becomes:

$$90 \times \frac{273}{293} \times \frac{745 - 17.4}{760} = 80.28 \text{ ml}$$

To be sure you understand these operations try a few exercises based on volume changes due to changes in temperature and pressure.

(1) 78 ml of air measured at 758 mm pressure will have what volume at 730 mm pressure?

(2) 100 ml of hydrogen measured at 27° C. is cooled to 10° C. What volume does it now occupy?

(3) 50 ml of oxygen measured at 17° C. and 750 mm pressure has what volume at 20° C. and 740 mm pressure?

(4) 120 ml of nitrogen is measured over water at 745 mm pressure and 18° C. What volume will the dry gas occupy at 760 mm and 0° C.?

IV. TEMPERATURE SCALES

When the barometer stands at 760 mm, the temperatures at which pure water freezes and boils are taken as fixed points on common thermometer scales.

Water freezes at 0° centigrade (C.) or 32° Fahrenheit (F.)

Water boils at 100° C. or 212° F.

Room temperature is about 20° C. or 68° F.

To convert a temperature expressed on the Fahrenheit scale to one on the centigrade scale, subtract 32 and multiply by 5/9. Thus,

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

To change centigrade degrees to Fahrenheit degrees, multiply by 9/5 and add 32. Thus,

$$^\circ \text{F.} = 9/5\ ^\circ \text{C} + 32$$

The absolute temperature (° A. or T.) is found by adding 273 to the centigrade reading (t), or

$$T = 273 + t$$

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V. IMPORTANT TEMPERATURES

(Given at standard pressure)

Degrees Centigrade		*Degrees Centigrade*	
−273.13	Absolute zero	444.6	Sulfur boils
−268.9	Helium boils	550	First visible red heat
−252.7	Hydrogen boils	650	Dull red heat
−195.8	Nitrogen boils	660	Aluminum melts
−183	Oxygen boils	800	Red heat
−112	Grain alcohol freezes	804	Table salt melts
−78.5	Carbon dioxide sublimes	1000	Bright red heat
−38.8	Mercury freezes	1063	Gold melts
−33.4	Ammonia boils	1083	Copper melts
−10	Sulfur dioxide boils	1200	Yellow heat
0	Ice melts (water freezes)	1350	White heat
20	Room temperature (average)	1375	Temp. of glass furnace
37	Temp. of body (normal)	1452	Nickel melts
60	Wood's metal melts	1535	Iron melts
78.4	Grain alcohol boils	1600 ±	Sand melts
100	Water boils	2500 ±	Temp. oxy-hydrogen flame
112.8	Sulfur (rhombic) melts	2700 ±	Temp. oxy-acetylene flame
170	Sugar melts	3370	Tungsten melts
231.8	Tin melts	4000 ±	Temp. electric arc
327.5	Lead melts	6000 ±	Temp. sun's surface
419.4	Zinc melts		

VI. TESTS FOR GASES

COMBUSTIBLE GASES

H_2	Odorless; begins burning with a "pop," flame almost invisible, moisture forms on cold glass inverted over flame.
CO	Burns with pale blue flame, forming only carbon dioxide (see test below).
CH_4	Burns with a luminous flame, forming carbon dioxide and water; does not decolorize bromine water.
C_2H_4	Odor; burns with smoky flame; decolorizes bromine water.
C_2H_2	Burns with very sooty flame.
H_2S	Odor of "ripe" eggs; burns with bluish flame, forming sulfur dioxide; darkens paper wet with a lead salt solution.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

VI. TESTS FOR GASES
(Continued)

NONCOMBUSTIBLE GASES—TURN MOIST LITMUS PAPER RED

HCl	Very strong pungent odor; fumes in moist air; with ammonia forms "smoke."
SO_2	Characteristic odor of burning sulfur; decolorizes potassium permanganate solution.
Cl_2	Greenish-yellow color; bleaches moist litmus.
CO_2	No color or odor; forms precipitate with limewater.
NO_2	Brown color; characteristic "sickening" odor; very soluble.
HF	Etches glass; congeals and turns a drop of water white.

NONCOMBUSTIBLE GASES

N_2	Acts negative to all common tests; reacts with hot magnesium to form nitride which acts with hot water to yield ammonia (see test below).
NH_3	Characteristic odor; turns litmus paper blue; with hydrogen chloride forms "smoke."
O_2	Odorless; glowing splint blazes; reacts with nitric oxide to form brown nitrogen dioxide.
N_2O	Sweetish odor; glowing splint blazes; does not react with nitric oxide.
NO	Exposed to air forms brown nitrogen dioxide.
Br_2	Red vapor or easily volatile liquid; bleaches litmus.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

VII. PHYSICAL PROPERTIES OF GASES

SLIGHTLY SOLUBLE

Name	Formula	Color	Odor	Density (g per l) (STP)	Sp. wt. Air = 1 (STP)	Solubility, 760 mm (Vols. in 1 vol. H_2O) 0° C.	20° C.
Hydrogen	H_2	No	No	.0898	.069	.021	.018
Nitrogen	N_2	No	No	1.251	.967	.024	.015
Carbon monoxide	CO	No	No	1.251	.967	.035	.023
Oxygen	O_2	No	No	1.429	1.105	.049	.031
Methane	CH_4	No	No	.717	.554	.055	.033
Nitric oxide	NO	No	?	1.34	.837	.074	.047
Ethylene	C_2H_4	No	Yes	1.26	.975	.226	.122

MODERATELY SOLUBLE

Carbon dioxide	CO_2	No	No	1.977	1.529	1.713	.878
Nitrous oxide	N_2O	No	Yes	1.978	1.53	1.305	1.670
Acetylene	C_2H_2	No	No(?)	1.173	.907	1.73	1.03
Hydrogen sulfide	H_2S	No	Yes	1.539	1.19	4.67	2.58
Chlorine	Cl_2	Green	Yes	3.21	2.486	4.61	2.26

VERY SOLUBLE

Bromine	Br_2	Red	Yes	7.14	5.54	60.5	21.3
Sulfur dioxide	SO_2	No	Yes	2.927	2.64	79.8	39.4
Hydrogen chloride	HCl	No	Yes	1.639	1.268	525.	445.
Ammonia	NH_3	No	Yes	.771	.596	1176.	702.
Hydrogen fluoride	HF	No	Yes	1.786[1]	1.381[1]	Very soluble	
Nitrogen dioxide	NO_2	Brown	Yes	2.05[1]	1.59[1]	reacts	

[1] Estimated at standard conditions.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

VIII. SYMBOLS, ATOMIC NUMBERS, AND ATOMIC WEIGHTS OF THE NATURAL ELEMENTS

(1947)

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	(227)[1]
Alabamine[2]	Ab	85	(221)
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.944
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	79.916
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	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium	Cb	41	92.91
Copper	Cu	29	63.54
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	163.5
Hydrogen	H	1	1.0081
Illinium[2]	Il	61	(146)
Indium	In	49	114.76
Iodine	I	53	126.92
Iridium	Ir	77	193.1
Iron	Fe	26	55.84
Krypton	Kr	36	83.7
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutecium	Lu	71	175.0
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Masurium[2]	Ma	43	.....
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	31.02
Platinum	Pt	78	195.23
Polonium	Po	84	(210)
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protoactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.88

[1] Weights shown in parentheses are approximate.

[2] Existence reported but not finally verified.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Element	Symbol	Atomic Number	Atomic Weight
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Virginium[2]	Vi	87	(224)
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

[1] Weights shown in parentheses are approximate. [2] Existence reported but not finally verified.

Synthetic Elements (1947)

Americium	Am	95	241, 242	Plutonium	Pu	94	238, 239
Astatine	At	85	211	Technetium	Tc	43	99
Curium	Cm	96	240, 242	———	——	61	147
Neptunium	Np	93	237, 239				

IX. VAPOR PRESSURE OF WATER

(in mm of mercury)

$$\text{Relative humidity} = \frac{\text{Vapor pressure at dew point}}{\text{Vapor pressure at room temperature}}$$

Corrected pressure of gas collected over water = barometer reading − vapor pressure at temperature of H_2O

Temp. °C.	Vapor Pressure in mm Hg	Temp. °C.	Vapor Pressure in mm Hg	Temp. °C.	Vapor Pressure in mm Hg
0	4.6	12	10.4	24	22.2
1	4.9	13	11.1	25	23.5
2	5.3	14	11.9	26	25.0
3	5.6	15	12.7	27	26.5
4	6.1	16	13.5	28	28.1
5	6.5	17	14.4	29	29.7
6	7.0	18	15.3	30	31.5
7	7.5	19	16.3	35	41.8
8	8.0	20	17.4	40	54.9
9	8.5	21	18.5	50	92.0
10	9.1	22	19.6	60	149.4
11	9.7	23	20.9	100	760.0

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

X. PHYSICAL CONSTANTS OF THE COMMON ELEMENTS

Element	*Symbol*	*Density*[1]	*Melting Point, °C.*	*Boiling Point, °C.*	*Year Discovered*
Aluminum	Al	2.7	660	1800	1828
Antimony	Sb	6.68	630.5	1380	1450
Arsenic	As	5.7	...	sub. 615	1694
Barium	Ba	3.5	850	1140	1808
Bismuth	Bi	9.8	271	1450	1450
Bromine	Br	3.12(l)	−7.2	58.8	1828
Calcium	Ca	1.55	810	1170	1808
Carbon	C	2.26−3.51	3500	4200	....
Chlorine	Cl	3.214(g)	−101.6	−34.6	1774
Chromium	Cr	7.1	1615	2200	1797
Copper	Cu	8.92	1083	2300	....
Gold	Au	19.3	1063	2600	....
Helium	He	.18(g)	−272	−268.9	1895
Hydrogen	H	.0899(g)	−259.2	−252.7	1766
Iodine	I	4.93	113.5	184.35	1811
Iron	Fe	7.86	1535	3000	....
Lead	Pb	11.34	327.5	1620	....
Magnesium	Mg	1.74	651	1110	1829
Manganese	Mn	7.2	1260	1900	1774
Mercury	Hg	13.55(l)	−38.9	356.9	....
Nickel	Ni	8.9	1452	2900	1751
Nitrogen	N	1.251(g)	−209.9	−195.8	1772
Oxygen	O	1.429(g)	−218.4	−183	1774
Phosphorus	P	1.82−2.2	44.1	280	1669
Platinum	Pt	21.45	1755	4300	1741
Potassium	K	.86	62.3	760	1807
Silicon	Si	2.4	1420	2600	1823
Silver	Ag	10.5	960.5	1950	....
Sodium	Na	.97	97.5	880	1807
Sulfur	S	1.96−2.07	112.8	444.6	....
Tin	Sn	7.3	231.85	2260	....
Tungsten	W	19.3	3370	5900	1781
Zinc	Zn	7.1	419.3	907	1520

[1] In this table gases are indicated by (g) and liquids by (l). Density for solids and liquids is expressed as g per ml, gases as g per l.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XI. GASES (AND VOLATILE COMPOUNDS) THAT MAY RESULT FROM DOUBLE-DECOMPOSITION REACTIONS

The following are gases at ordinary temperatures:

HCl, H_2S, HBr, HF

The following are unstable compounds which yield gases:

$H_2CO_3 \rightleftarrows H_2O + CO_2$ $NH_4OH \rightleftarrows H_2O + NH_3$ $H_2SO_3 \rightleftarrows H_2O + SO_2$

The following have boiling points below that of sulfuric acid (338°):

	Boiling point, ° C.		Boiling point, ° C.
H_2O	100°	HNO_3	86°
HCl	110°	HNO_3 (in water)	120°
HBr	126°	$HC_2H_3O_2$	118°

XII. CHEMICAL REACTIONS FOR IDENTIFYING TEXTILE FIBERS

Test	*Animal Fibers*		*Vegetable Fibers*		
Reagent	Wool	Silk	Cotton	Linen	Rayon
Flame	Burns slowly, odor of burning hair		Burns when removed from flame, odor not disagreeable		
10% NaOH	Dissolves completely		Does not dissolve		
HNO_3	Turns yellow as in the test for protein		No apparent action		
Conc. HCl	Unaffected	Dissolves	Unaffected		Dissolves slowly
Elsner's Reagent[1]	Unaffected	Dissolves	Unaffected		

[1] 500 g $ZnCl_2$, 20 g ZnO, 425 ml, H_2O.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XIII. SOME TESTS FOR THE METALS

FLAME TESTS

When compounds of the metals indicated below are held in the flame on a platinum wire, the flame shows the following colors:

Metal	*Color*	*Metal*	*Color*
Barium	Yellowish green	Sodium	Yellow
Calcium	Orange red	Strontium	Red (crimson)
Copper	Emerald green	Potassium	Violet
Lithium	Red (carmine)		

BORAX BEAD TESTS

Clear glassy borax beads are made by fusing borax in a small loop on a platinum wire. The hot bead is touched to a speck of the compound to be tested and reheated either in the oxidizing (outer) flame or in the reducing (inner) flame.

Metal	*Oxidizing flame*	*Reducing flame*	*Metal*	*Oxidizing flame*	*Reducing flame*
Chromium	Green	Green	Manganese	Violet	Colorless
Cobalt	Blue	Blue	Nickel	Brown	Colorless or turbid
Iron	Yellow	Green			

COBALT NITRATE TESTS

The substance is intensely heated on a charcoal block before and after being moistened with a dilute solution of cobalt nitrate.

Metal	*Color*
Aluminum	Blue (when Al compound is infusible)
Magnesium	Pale pink (not very satisfactory)
Zinc	Green

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XIV. SOME SUBSTANCES WITH COMMON NAMES

Common Name	*Chemical name*	*Formula*
Alum	Potassium aluminum sulfate	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot (H_2O)_{24}$
Ammonia water	Ammonium hydroxide	NH_4OH
Aqua fortis	Nitric acid	HNO_3
Aqua regia	Hydrochloric and nitric acids	$3\,HCl + HNO_3$
Asbestos	Magnesium silicate	$Mg_3Si_2O_7 \cdot (H_2O)_2$
Baking soda	Sodium hydrogen carbonate	$NaHCO_3$
Bleaching powder	Calcium oxychloride	$CaOCl_2$
Blue vitriol	Copper sulfate	$CuSO_4 \cdot (H_2O)_5$
Borax	Sodium tetraborate	$Na_2B_4O_7 \cdot (H_2O)_{10}$
Brimstone	Sulfur	S
Brine	Table salt solution	NaCl
Calcite	Calcium carbonate	$CaCO_3$
Calomel	Mercurous chloride	HgCl
Carbolic acid	Phenol	C_6H_5OH
Carbonic acid gas	Carbon dioxide	CO_2
Carborundum	Silicon carbide	SiC
Caustic potash	Potassium hydroxide	KOH
Caustic soda	Sodium hydroxide	NaOH
Chalk (ppt.)	Calcium carbonate	$CaCO_3$
Charcoal	Carbon (impure)	C+
Chile saltpeter	Sodium nitrate	$NaNO_3$
Cinnabar	Mercuric sulfide	HgS
Coke	Carbon (impure)	C+
Copperas	Ferrous sulfate	$FeSO_4$
Corrosive sublimate	Mercuric chloride	$HgCl_2$
Cream of tartar	Potassium hydrogen tartrate	$KHC_4H_4O_6$
Diamond	Carbon	C
Dry ice	Carbon dioxide (solid)	CO_2
Epsom salt	Magnesium sulfate	$MgSO_4 \cdot (H_2O)_7$
Fire damp	Methane	CH_4
Fluor spar	Calcium fluoride	CaF_2
Galena	Lead sulfide	PbS
Glucose	Dextrose	$C_6H_{12}O_6$
Grain alcohol	Ethyl alcohol (ethanol)	C_2H_5OH
Graphite	Carbon	C
Green vitriol	Ferrous sulfate	$FeSO_4$
Gypsum	Calcium sulfate	$CaSO_4 \cdot (H_2O)_2$
Household ammonia	Ammonium hydroxide	NH_4OH
Hypo	Sodium thiosulfate	$Na_2S_2O_3 \cdot (H_2O)_5$

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XIV. SOME SUBSTANCES WITH COMMON NAMES (Continued)

Common Name	*Chemical Name*	*Formula*
Iron pyrites	Iron disulfide	FeS_2
Kaolin (clay)	Hydrogen aluminum silicate	$H_2Al_2(SiO_4)_2 \cdot H_2O$
Lampblack	Carbon	C
Laughing gas	Nitrous oxide	N_2O
Lime, quick	Calcium oxide	CaO
Lime, slaked	Calcium hydroxide	$Ca(OH)_2$
Limestone	Calcium carbonate	$CaCO_3$
Limewater	Calcium hydroxide solution	$Ca(OH)_2$
Litharge	Lead monoxide	PbO
Lunar caustic	Silver nitrate	$AgNO_3$
Magnesia	Magnesium oxide	MgO
Marble	Calcium carbonate	$CaCO_3$
Marsh gas	Methane	CH_4
Moth balls	Naphthalene	$C_{10}H_8$
Muriate of potash	Potassium chloride	KCl
Muriatic acid	Hydrochloric acid	HCl
Niter (saltpeter)	Potassium nitrate	KNO_3
Oil of vitriol	Sulfuric acid	H_2SO_4
Pearl	Calcium carbonate	$CaCO_3$
Peroxide	Hydrogen peroxide	H_2O_2
Plaster of Paris	Calcium sulfate	$(CaSO_4)_2 \cdot H_2O$
Potash	Potassium carbonate	K_2CO_3
Pyrolusite	Manganese dioxide	MnO_2
Quartz	Silicon dioxide	SiO_2
Quicklime	Calcium oxide	CaO
Quicksilver	Mercury	Hg
Rochelle salt	Sodium potassium tartrate	$NaKC_4H_4O_6$
Sal ammoniac	Ammonium chloride	NH_4Cl
Sal soda	Sodium carbonate	$Na_2CO_3 \cdot (H_2O)_{10}$
Saltpeter	Potassium nitrate	KNO_3
Sand	Silicon dioxide (impure)	SiO_2
Slaked lime	Calcium hydroxide	$Ca(OH)_2$
Soda, baking	Sodium hydrogen carbonate	$NaHCO_3$
Soda ash	Sodium carbonate	Na_2CO_3
Soap	Sodium stearate (mainly)	$C_{17}H_{35}COONa$
Spirits of hartshorn	Ammonium hydroxide	NH_4OH
Sugar	Sucrose	$C_{12}H_{22}O_{11}$
Sugar of lead	Lead acetate	$Pb(C_2H_3O_2)_2$

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XIV. SOME SUBSTANCES WITH COMMON NAMES (Continued)

Common Name	*Chemical Name*	*Formula*
Table salt	Sodium chloride	$NaCl$
Vinegar	Acetic acid, dil. sol.	$HC_2H_3O_2$
Water glass	Sodium silicate	Na_2SiO_3
White lead	Lead carbonate, basic	$Pb(OH)_2 \cdot 2PbCO_3$
White vitriol	Zinc sulfate	$ZnSO_4$
Wood alcohol	Methyl alcohol (methanol)	CH_3OH
Zinc white	Zinc oxide	ZnO

XV. TESTS FOR COMMON ACID RADICALS

To test for ↓	*Add* ↓	*Result* ↓
Chloride	$AgNO_3$	White ppt. insoluble in HNO_3
Sulfate	$BaCl_2$	White ppt. insoluble in HCl or HNO_3
Carbonate	HCl	Gas CO_2 which turns limewater cloudy
Nitrate	$FeSO_4$ + conc. H_2SO_4	Brown ring forms
Sulfide	HCl	Gas H_2S which turns lead acetate paper black
Bromide	Cl_2 water + CS_2	CS_2 is colored red
Iodide	Cl_2 water + CS_2	CS_2 is colored violet
Sulfite	HCl	Gas SO_2 which decolorizes $KMnO_4$ solution
Phosphate	Ammonium molybdate solution and warm	Yellow ppt. insoluble in HNO_3

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XVI. APPROXIMATE HEATS OF FORMATION

The *heat of formation* of a compound is the number of calories which is liberated (or absorbed in the case of negative numbers) when one gram-molecular weight of the compound is formed from its elements. (Table is from Lange's *Handbook of Chemistry*, 1937.)

Compound	*Heat of formation in calories*	*Compound*	*Heat of formation in calories*	*Compound*	*Heat of formation in calories*
C_2H_2	−54,300	H_2O	68,380	KNO_3	119,000
$AlCl_3$	161,800	H_2O_2	45,300	K_2SO_4	338,620
Al_2O_3	399,000	H_2S	5,260	CH_4	20,340
NH_3	10,940	$FeCl_3$	96,040	C_8H_{18}	67,760
$BaSO_4$	340,200	Fe_2O_3	192,200	$AgCl$	30,590
C_6H_6	−195,500	$FeSO_4$	231,950	Ag_2O	6,950
CaC_2	13,160	PbO	52,470	$AgNO_3$	30,110
$CaCl_2$	190,200	PbS	22,200	Ag_2S	5,020
CaO	151,900	$MgCl_2$	153,200	$NaCl$	98,360
CO_2	94,380	MgO	143,900	$NaOH$	102,700
CO	26,430	$HgCl_2$	53,300	$NaNO_3$	112,450
CS_2	−19,000	HgO	21,700	H_2SO_4	189,750
CCl_4	33,190	HNO_3	42,400	SO_2	69,260
$CuCl_2$	62,500	NO	−2,160	SO_3	103,200
CuO	34,900	NO_2	−2,650	$C_{12}H_{22}O_{11}$	535,600
$CuSO_4$	178,700	P_2O_5	365,200	$SnCl_4$	127,400
HBr	8,600	KBr	94,030	SnO_2	138,100
HCl	22,000	$KClO_3$	89,870	$ZnCl_2$	99,555
HF	64,000	KCl	104,800	ZnO	85,000
HI	−6,400	KI	71,920	ZnS	45,880

XVII. GENERAL RULES OF SOLUBILITY

All nitrates, acetates, and chlorates are soluble.

All common compounds of sodium, potassium, and ammonium are soluble.

All chlorides are soluble except those of silver, mercurous, and lead. (Lead chloride is noticeably soluble in hot water.)

All sulfates are soluble except those of lead, barium, strontium, and calcium. (Calcium sulfate is slightly soluble.)

The normal carbonates, phosphates, silicates, and sulfides are insoluble except those of sodium, potassium, and ammonium.

All hydroxides are insoluble except those of sodium, potassium, ammonium, calcium, barium, and strontium.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

XVIII. SOLUBILITY CHART

S—soluble in water I—insoluble P—partially or slightly soluble D—decomposed or acted on by water	Acetate	Bromide	Carbonate	Chlorate	Chloride	Hydroxide	Iodide	Nitrate	Oxide	Phosphate	Silicate	Sulfate	Sulfide
Aluminum	S	S	D	S	S	I	S	S	I	I	I	S	S
Ammonium	S	S	S	S	S	S	S	S	–	S	–	S	S
Barium	S	S	I	S	S	S	S	S	P	I	I	I	D
Bismuth	–	P	I	–	D	I	I	D	I	I	–	D	I
Cadmium	S	S	I	S	S	I	S	S	I	–	–	S	I
Calcium	S	S	I	S	S	P	S	S	P	I	I	P	D
Copper	S	S	I	S	S	I	S	S	I	I	I	S	I
Ferrous	S	S	I	S	S	I	S	S	I	I	I	S	I
Ferric	S	S	D	S	S	I	S	S	I	I	I	S	I
Lead	S	P	I	S	P	I	P	S	I	I	I	I	I
Magnesium	S	S	I	S	S	P	S	S	P	I	I	S	D
Manganese	S	S	I	S	S	I	S	S	I	I	I	S	I
Mercurous	P	I	I	S	I	–	I	S	I	I	–	I	I
Mercuric	S	I	I	S	S	I	I	S	I	I	–	I	I
Nickel	S	S	I	–	S	I	S	S	I	I	–	S	I
Potassium	S	S	S	S	S	S	S	S	S	S	S	S	S
Silver	P	I	I	S	I	–	I	S	I	I	–	P	I
Sodium	S	S	S	S	S	S	S	S	S	S	S	S	S
Zinc	S	S	I	S	S	I	S	S	I	I	I	S	I

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XIX. BRÖNSTED THEORY OF ACIDS AND BASES

The Arrhenius theory regarding acids and bases (page 203) is a satisfactory theory so long as water solutions are made. The chemical processes of today in the making of plastics, artificial rubber, artificial silk—are using increasing quantities of solutions that are nonaqueous; that is, the substances are not dissolved in water but in other types of solvents such as ether.

When acids and bases are studied in nonaqueous solvents, it is necessary to expand somewhat our ideas concerning the behavior of acids and bases in solutions. The Brönsted theory attempts to present an explanation of the chemical action of acids and bases in *any* type of solution.

What is the new view of acids? An acid has been described as a substance which yields hydrogen ions (H^+). The ionization of hydrochloric acid, a typical acid, has long been represented in this way: $HCl \rightleftarrows H^+ + Cl^-$. You are familiar with the idea that hydrochloric acid is an acid because it yields hydrogen ions. But since the hydrogen ion (H^+) is a single proton (review page 159), we may say that an acid is a substance which *gives up a proton,* and a new definition is: *An acid is a proton donor* ("giver"). Under this new definition many substances can be classed as acids which according to the Arrhenius theory would not be regarded as acids at all.

What is the expanded view of bases? In considering the ionization of hydrochloric acid ($HCl \rightleftarrows H^+ + Cl^-$), two additional facts should be noted carefully: (1) When HCl acts as an acid (proton donor), it produces a second product, a chloride ion (Cl^-); and (2) this Cl^- unites with the proton to produce HCl by a reversal of the previous reaction. Hence we may say that Cl^- is the opposite of an acid since it *accepts a proton.* Since bases are the opposites of acids, we may expand our notion of a base which according to the Brönsted theory is now defined as a *proton acceptor.* Under this definition NO_3^-, SO_4^{--}, PO_4^{---}, CO_3^{--}, S^{--}, Br^-, and I^- are all bases since they accept one or more protons. These ions behave like the hydroxyl ion (OH^-) which we have formerly

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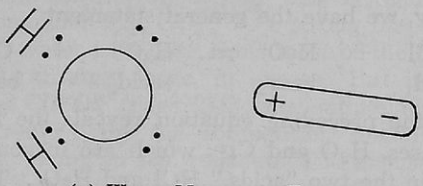
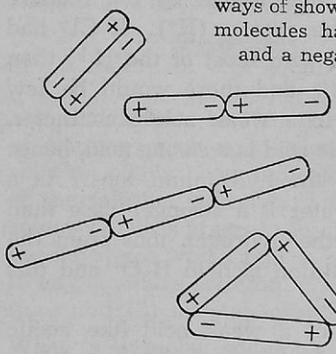
considered as the cause of basic properties. Each of these bases (SO_4^{--}, OH^-, etc.) reacts with a proton with a different degree of activity. Consequently some of these ions are strong bases and others are weak bases. The strongest base that we know in water solution is OH^-.

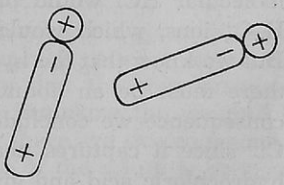
The bases compete with each other for the proton. When hydrogen chloride gas dissolves in water, there is considerable heat liberated, and we know the liberation of energy indicates that a chemical reaction has taken place. It is believed that the solvent, water, has taken part in this reaction. In order to understand what has happened, we need to



(A) WATER MOLECULES. Two ways of showing that water molecules have a positive and a negative region.



(B) WATER MOLECULES. Water molecules tend to cling together and form groups.



(C) HYDRONIUM IONS. Diagrams showing the formation of hydronium ions, by the association of water molecules and hydrogen ions.

remember that in a water molecule the positive and negative charges are not uniformly distributed throughout its mass. In other words each molecule of water can be thought of as having a positive "end," (H^+), and a negative "end," (OH^-).

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When such molecules approach strongly charged ions, like H^+, it is believed that combination takes place forming a hydrated hydrogen ion, $H^+ \cdot H_2O$, which is usually written H_3O^+ and called the *hydronium ion.* This according to the Brönsted theory is the ion which gives the characteristic behavior of an acid. The more complete reaction which takes place when hydrogen chloride gas dissolves in water may be written:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$

It is obvious from this expression that water has accepted a proton, so water is a base; also that the hydronium ion, H_3O^+, may give up a proton (hydrogen ion) and so it is an acid. Consequently, we have the general statement

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{H_2O} \rightleftarrows \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{Cl^-}$$

A study of the preceding equation reveals the fact that we have two bases, H_2O and Cl^-, which are in competition for the protons in the two "acids," HCl and H_3O^+. The behavior of the resulting solution will be determined by the relative affinity of these two bases for the proton (H^+). If Cl^- had the greater affinity and combined with most of the H^+, then molecular HCl would predominate and there would be few H_3O^+ ions, which would result in a weak acidic character. But we know that the hydrochloric acid is a strong acid, hence there must be an abundance of the hydronium ions. As a consequence we conclude that water is a stronger base than Cl^- since it captures nearly all the hydrogen ions from the hydrochloric acid and gives a solution rich in H_3O^+ and this produces a strong acidic character.

If we consider the ionization of a weak acid like acetic acid we have the equation:

$$\underset{\text{acid}_1}{HC_2H_3O_2} + \underset{\text{base}_2}{H_2O} \rightleftarrows \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{C_2H_3O_2^-}$$

In this case $C_2H_3O_2^-$ is a *stronger base* than H_2O and so combines with nearly all the protons giving molecular $HC_2H_3O_2$. As a consequence there are few hydronium ions formed, which condition is characteristic of a weak acid.

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In general, then, a weak acid (like $HC_2H_3O_2$, H_2CO_3, or HCN) yields a base (such as $C_2H_3O_2^-$, CO_3^{--}, S^{--}, CN^-) which has a strong affinity for H^+. As a consequence their solutions contain few hydronium ions and give only feeble acidic behavior. On the other hand strong acids (like HCl, HNO_3, H_2SO_4, HBr, or HI) yield bases which have weak affinity for the hydrogen ion (proton) and as a result there is an abundance of H_3O^+ with consequent strong acidic properties.

How the Brönsted theory explains hydrolysis. The Brönsted system of nomenclature is efficient in explaining the behavior of salts in water solutions. For example, the basic reaction of sodium carbonate solution, page 212, is readily explained when we remember that CO_3^{--} is a strong base and, in competition with water as a base, wins most of the protons (H^+), leaving OH^-, strongly basic, in excess. But in the case of a solution of $CuSO_4$ (page 212), the sulfate ion is a feeble base since water wins the competition forming many hydronium ions, giving an acid reaction. The Brönsted viewpoint is equally effective in explaining many other chemical phenomena, including solutions in nonaqueous solvents.

XX. EXPRESSING THE CONCENTRATION OF SOLUTIONS

If it is known how much solute is held in a given volume of solution, such a solution is commonly called a *standard solution.* This term indicates merely that the concentration of the solution is known, but it does not show the weight of solute which is present. In chemistry there are two commonly used systems which tell us how much of the solute is present in any standard solution. These are known as (1) *molar solutions* and (2) *normal solutions.*

What is a molar solution? Sodium sulfate, Na_2SO_4, has a molecular weight of 142 (that is 46 + 32 + 64). Expressed in grams, 142 grams = the *gram-molecular weight* of sodium sulfate. 142 grams represent one *mole* of sodium sulfate. A *molar solution* of sodium sulfate or any soluble substance contains a mole of the sodium sulfate or soluble substance in one liter of *solution.* Thus a molar solution of sodium sulfate is prepared by first dissolving 142 grams of sodium sulfate in

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water and then adding enough water to make 1000 ml of the solution. By proper arithmetical determination, varying volumes, for example 500 ml, of molar solutions may be prepared or solutions of varying molarities, for example, 0.1 (1/10) M, 3 M, etc., may be prepared by weighing out the proper amount of solute, dissolving it in water, and making up to the required volume. *It should be noted that equal volumes of molar solutions contain the same number of molecules of the solute.*

Can you? Show by proper steps how you will determine that 82 grams of sodium phosphate (Na_3PO_4) must be weighed out to prepare 250 ml of a 2 M solution of sodium phosphate; that 3.42 grams of barium hydroxide will be required to prepare 100 ml of a 0.2 M (or M/5) solution of $Ba(OH)_2$.

What is a normal solution? A solution of an acid which contains one gram (more accurately 1.008 g) of hydrogen per liter is known as a *normal solution.* It is obvious that a normal solution of HCl would contain one mole (36.5 g) per liter of the solute. But a liter of a normal solution of H_2SO_4 would contain a half-mole $\frac{(98\text{ g})}{2}$ of acid, and a liter of H_3PO_4 would contain $\frac{98}{3}$ g of solute.

The term normal solution is not limited to acids but is also used with respect to bases and salts, when their solutions contain the *equivalent* of one gram of hydrogen per liter. Thus one liter of normal $Ca(OH)_2$ would contain $\frac{74}{2} =$ 37 g of solute; and a liter of normal $CaCl_2$ would contain $\frac{111}{2} = 55.5$ g of the solute.

Can you? Prove that a half-liter of normal $AlCl_3$ contains 66.67 g and that 0.5466 of Na_3PO_4 will be required to make 100 ml of 0.1 N solution.

Note that:

(1) A liter of any normal solution contains one gram of hydrogen or its equivalent.

(2) Equal volumes of all normal solutions contain the same amount of hydrogen or its equivalent.

(3) Any volume of any normal acid will exactly neutralize an equal volume of any normal base.

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How may the concentration of hydrogen ion be expressed? It is sometimes convenient to express numerically the concentration of hydrogen ions, H^+. The most widely used method is commonly called the pH (power of hydrogen concentration) system. The pH of a solution is obtained by taking the reciprocal of the logarithm of the hydrogen ion concentration expressed in grams per liter ($pH = \log\frac{1}{H^+}$).

To make this clearer, suppose we dilute a normal acid solution with nine parts of pure water. It will then be one-tenth normal (N/10) and will contain 0.1 gram of hydrogen per liter. Expressed with a negative exponent, the concentration is 10^{-1}. Then the pH is 1. In like manner, if a quantity of *this* solution is diluted with nine parts of water, we obtain a solution which is .01 N or has pH of 2.

By such continued dilution, we have the data shown in the table, p. 788.

Pure water conducts electricity very, very slightly which means that some of its molecules are dissociated into ions but not enough to be detected by indicators. Careful measurements of this conductivity show the hydrogen ion content to be 0.000,000,1 gram per liter, or a pH of 7. Since there is an equal quantity of hydroxyl ions, this pH value of 7 is the neutral point. Acids have a pH value less than 7 while bases have a pH value greater than 7.

This is a convenient method of expressing small differences in the acidity or alkalinity of solutions, especially those which are near the neutral point. Frequently these small differences are of great importance in biological, electrolytic, and fermenting processes, and in farming, baking, and in the manufacture of soap, washing powder, tooth paste, shaving cream, and many other products.

In the table are listed the pH values of several common substances such as foods, products of the animal body, materials found in nature. Notice also that column 4 shows that at a pH of 4 there are 1000 times as many H^+ as there are in the same volume of pure water. Likewise, for a pH of 10, there are 1000 times as many OH^- as there are in an equal volume of pure water. The pH of 10 also indicates that there are 1/1,000 as many H^+ as there are in an equal volume of pure water.

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The pH System of Indicating Degree of Acidity and Alkalinity

Normal strength of acid and base	*Concentration of H+ in grams per liter*	*Exponent*	*Number of times acidity or alkalinity exceeds that of water*	*pH*	*pH of some 0.1N acids and bases*		*Average pH of some familiar substances*
Normal acid	1.	10^{0}	10,000,000 ↑	0			
0.1N	0.1	10^{-1}	1,000,000	1	HCl	(1.0)	
					H_2SO_4	(1.2)	
0.01N	0.01	10^{-2}	100,000	2			lemons (2.3)
0.001N	0.001	10^{-3}	10,000 ACIDIC	3	$HC_2H_3O_2$	(2.9)	apples (3.0) sauerkraut (3.5) stomach contents (3-4)
0.0001N	0.0001	10^{-4}	1,000	4			tomatoes (4.2)
0.00001N	0.00001	10^{-5}	100	5	H_2BO_3	(5.2)	bile (5.4-8.5) asparagus (5.5) saliva (5.75-7.05)
0.000001N	0.000001	10^{-6}	10	6			cow's milk (6.6) blood serum (7.4)
0.0000001N	**0.0000001**	10^{-7}	**Neutral**	7	H_2O	(7.00)	human urine (7.35-7.43) pancreatic juice (7.5-8.0)
0.000001N	0.00000001	10^{-8}	10	8			sea water (8.2) $NaHCO_3$ (8.4)
0.00001N	0.000000001	10^{-9}	100	9			$Na_2B_4O_7$ (9.2)
0.0001N	0.0000000001	10^{-10}	1,000	10	milk of magnesia	(10.5)	
0.001N	0.00000000001	10^{-11}	10,000 BASIC	11	NH_4OH	(11.1)	
0.01N	0.000000000001	10^{-12}	100,000	12	limewater	(12.3)	sodium silicate (12.2)
0.1N	0.0000000000001	10^{-13}	1,000,000	13	NaOH	(13.0)	
Normal base	0.00000000000001	10^{-14}	10,000,000 ↓	14			

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XXIII. SOME LEADING TYPES OF ARTIFICIAL RUBBER (CONTINUED)

Compared with Natural Rubber

Strength	*Stretch*	*Resistance to—* *Weather*	*Abrasion*	*Chemicals*	*Characteristics*
84%	100%	good	excellent	poor; not oil resistant	Vulcanizes well; best for tires; most widely used in U.S. and Germany
100%	92%	good	somewhat inferior	generally good; resistant to oil	Vulcanizes with S,C + accelerators; "the synthetic rubber of a hundred uses"
72%	92%	good	fair	excellent	Resists diffusion of gases (U.S. product)
17%	92%	good weakened by heat	poor (20%)	excellent especially to oil	Does not swell in oils and fats. (U.S. product)
20%-114%	unvulcanized 0.3%-75%	excellent; but softened by heat	good at normal temperature	excellent; good for waterproofing	Does not vulcanize. Inert to oxygen, acids, bases, oil. (U.S. product)
82%	117%	excellent, especially to light and air	excellent; (90%-125%)	excellent to heat and many solvents	Vulcanizes without S or C; first produced in U.S. in 1931.

Special reagents include butadiene, $CH_2:CH\cdot CH:CH_2$; styrene, $C_6H_5\cdot CH:CH_2$; acrylonitrile, $CH_2:CH\cdot CN$; isobutylene, $CH_2:C<^{CH_3}_{CH_3}$; isoprene, $CH_2:CH\cdot C<^{CH_2}_{CH_3}$; ethylene dichloride, $CH_2Cl\cdot CH_2Cl$; vinyl chloride, $CH_2:CHCl$; vinyl acetylene, $CH:C\cdot CH:CH_2$; which reacts with HCl giving chloroprene which is chlorobutadiene, $CH_2:CCl\cdot CH:CH_2$.

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XXIV. COMMON FOODS AS SOURCES OF VITAMINS

	A	B	C*	D	G
 LIVER	++ to +++	++	+	− to +	+++
 GLANDULAR MEATS AND HEART	+ to ++	++	+?		++ to +++
 BEEF	+	++	− to +		++
 VEAL	− to +	+?			++
 PORK	− to +	+ to ++	?		++
 LAMB	− to +	+	− to +		++
 OYSTERS	++	++	+	++	++
 COD LIVER OIL	++++	−	−	++++	−
 EGGS	+++	+ to ++	−?	++	+++
 MILK	+++	++	− to +	− to +	+++
 BUTTER	+++	−	−	+	−
 OLEO MARGARINE (animal fat only)	+++	−	−	− to +	−
 WHOLE WHEAT BREAD	++	++			++
 APPLES, BANANAS	+ to ++	+ to ++	++		++
 ORANGES, GRAPE FRUIT, LEMONS	+ to ++	++	+++		++
 STRINGBEANS, PEAS	++	++	++ to +++		− to +
 POTATOES	+	++	++		++
 CARROTS	+++	++	++		++
 LETTUCE	+ to ++	++	+++		++
 SPINACH	+++	++	+++	− to +	++
 TOMATOES, CABBAGE	++	++	+++		++

* Vitamin C greatly reduced or destroyed by most methods of cookery.

Note
+ contains vitamin ++ good source
+++ excellent source ++++ extraordinary source
− no appreciable amount ? doubtful

Courtesy, National Live Stock and Meat Board, Chicago.

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XXV. RELEASING ATOMIC ENERGY

The liberation of the energy that is stored up in the atom has been a dream of scientists for many years. This potential energy has been recognized as an immense storehouse of power. Its use might revolutionize existing methods of transportation and industry. The partial realization of this dream in our day represents one of the most important scientific developments of all time. While these first manifestations of immense power have been extremely spectacular, their scientific significance has been a secondary consideration in the minds of most persons. But it is safe to predict that these initial demonstrations will open the way to vast new fields of investigation, the ultimate achievements of which are beyond the grasp of the imagination. It is important, then, that we try to understand something of this new source of energy.

Atomic energy comes from nuclear reactions. What are nuclear reactions? Ordinary chemical reactions and the formation of compounds can be explained in terms of planetary *electrons* (page 163)—the nuclei of atoms remaining unchanged. In marked contrast the transmutations of elements described on page 356 occur when the *nuclei* of the atoms are changed. Particles having considerable energy are hurled out of the nucleus, causing a rearrangement of the remaining particles in the nucleus. New elements are thus formed.

In the case of a radioactive element, such as radium or uranium, disintegration occurs spontaneously with the evolution of considerable heat. The energy coming from the nucleus of an atom is referred to as "atomic energy," although it should more properly be called "nuclear energy."

Why neutrons are efficient "bullets" to shoot at the nucleus. Various projectiles have been used in bombarding the nucleus of an atom. These include electrons, alpha particles (helium nuclei), protons (hydrogen nuclei), deuterons (heavy hydrogen nuclei), and neutrons. The neutron is commonly used to produce a nuclear reaction because it is the only one of

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these particles which does not carry an electric charge. Since it is electrically neutral, a neutron is not repelled as it approaches the positively charged nucleus, but readily enters it. The effect produced by the bombarding neutrons depends, at least in part, upon the speed with which they are traveling at the moment the hit occurs. Fast-moving projectiles have more energy and are more liable to break up the nucleus, while slow-moving neutrons cause less change or they may even be absorbed by the nucleus, thus increasing the mass of the bombarded atom.

What is the source of atomic energy? When the weights of the particles involved in a nuclear reaction are determined very accurately, it is frequently found that the sum of their masses is slightly greater *before* the nuclear reaction than after the reaction has occurred. Scientists believe that, in this case, some of the mass has changed into energy. From mathematical analysis Einstein concluded that if a bit of matter could be completely destroyed—annihilated—tremendous quantities of energy would be evolved. The formula that he derived looks very simple. It is:

$$\text{Energy} = \text{loss of mass} \times (\text{velocity of light})^2$$

or as he wrote it: $E = m c^2$. The velocity of light is 30,000,000,000 cm per sec. which means that light will go around the world at the equator more than seven times in one second. A little thought about the equation will show you why the energy is so tremendously large even though the loss of weight is exceedingly small.

The conversion of mass into energy is an idea that is very new to most of us who have believed in the Law of Conservation of Mass. We may wonder why this relation between mass and energy was not detected earlier in ordinary chemical changes. The obvious reason is, of course, that any changes in mass in chemical reactions are extremely small, and it is impossible by present methods to detect such very slight changes. It was not until the huge energy changes in nuclear reactions were discovered that changes in mass large enough to be detected were found.

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Uranium as a source of atomic energy. Uranium is the heaviest element in nature. It has an atomic number 92 and an atomic weight (mass number) approximately 238. An atom of uranium, then, has 92 electrons in the shells around its nucleus in which there are 92 protons and 146 neutrons. Its structure is represented in Figs. A and B. Compare Fig. A with the diagrams of the simpler atoms shown on page 160.

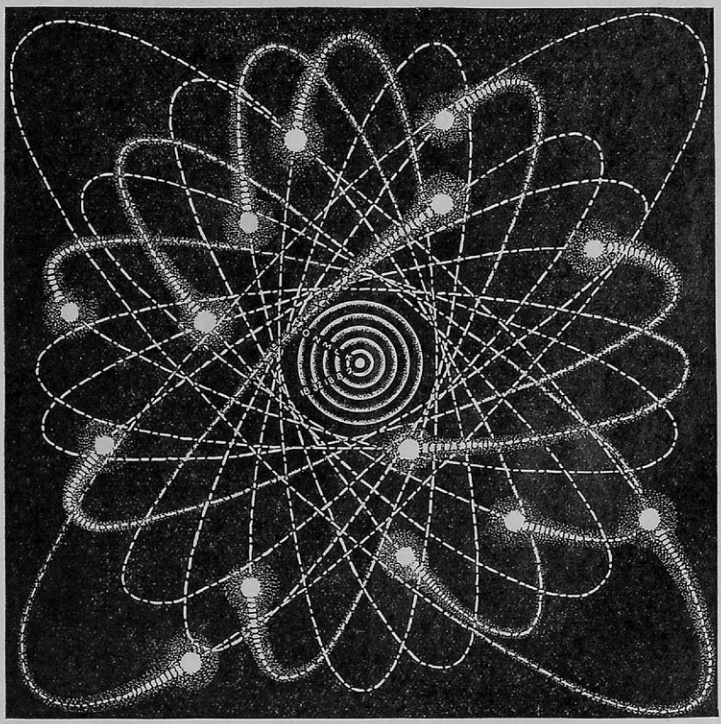

FIG. A. URANIUM ATOM. The nucleus is surrounded by seven shells of electrons, the first five of which (K, L, M, N, O) are shown in compact form. The electrons of the two outermost shells (P and Q) are represented as moving in their individual orbits about the nucleus. There are 92 protons and 146 neutrons in the nucleus; there are 92 planetary electrons in the seven shells.

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Thus it appears that if a heavy atom like uranium could be completely exploded, an unbelievably large amount of energy would be liberated. Only a small portion of this potential nuclear energy has as yet been set free by the most destructive of the atom bombs. It is believed that the energy which has been released represents only about one-tenth of one per cent of the total energy of the atom. Although this is only a very small fraction of the possible total energy, it has been calculated that a pound of uranium liberates almost instantly (0.000,001 sec.) more than a million times as much energy as can be obtained from the burning of a pound of high-grade coal. In the burning of the coal many minutes are usually required to liberate its energy.

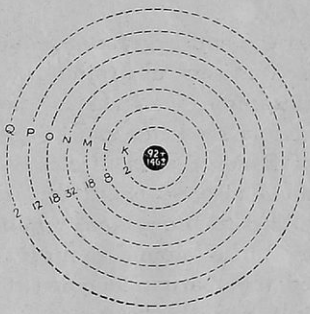

FIG. B. URANIUM (U^{238}) ATOM. The nucleus is shown in more detail at the right.

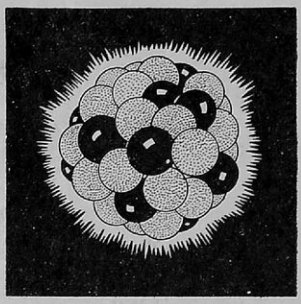

FIG. C. URANIUM U^{238} NUCLEUS. This nucleus contains 92 protons and 146 neutrons.

An isotope of uranium known as U^{235} is one source of atomic energy. Uranium has several isotopes (see page 345), the most abundant of which is U^{238}. This isotope makes up about 99.3 per cent of ordinary uranium. One of the less abundant isotopes is U^{235} which makes up about 0.7 per cent of the uranium of nature. Since U^{235} is unstable, it has been recognized for several years as a possible source of atomic energy.

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When U^{235} is bombarded with *slow* neutrons, its nucleus is split into two fragments. This process is known as *nuclear fission.* As a result of this splitting process lighter atoms are formed. For example, barium and krypton have been shown to come from the fission of U^{235}.

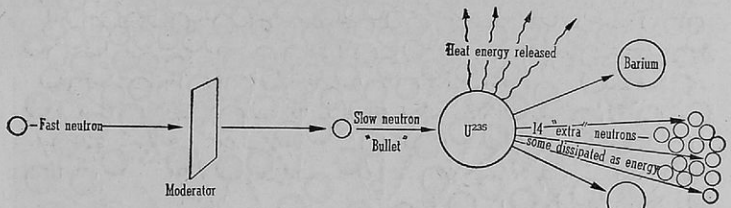

FIG. D. FISSION OF U^{235} ATOM.

By checking the structure of barium and krypton, products of this fission process, you discover that several uranium neutrons are not accounted for. For example, U^{235} has 143 neutrons; barium gets 81 of these uranium neutrons and krypton gets 48 of them. So this type of fission leaves 14 uranium neutrons unaccounted for. It should also be noted that the atomic number of barium (56) added to the atomic number of krypton (36) gives 92 which is the atomic number of uranium. It must not be assumed that barium and krypton are the only fragments which result from the fission of U^{235}. Many other fragments have now been identified, ranging from selenium (No. 34) to lanthanum (No. 57). These fragments are isotopes of elements in the middle of the periodic table; they are mostly radioactive elements containing very great amounts of kinetic energy.

The fission of a U^{235} atom furnishes neutron "bullets" which "trigger" the fission of other U^{235} atoms. Several of these 14 "extra" neutrons may be slowed down enough to produce fission of near-by atoms of U^{235}. So the fission reaction spreads rapidly to other near-by atoms. This continuing series of reactions which is self-sustaining is known as a *nuclear chain reaction.* (Study Fig. E.)

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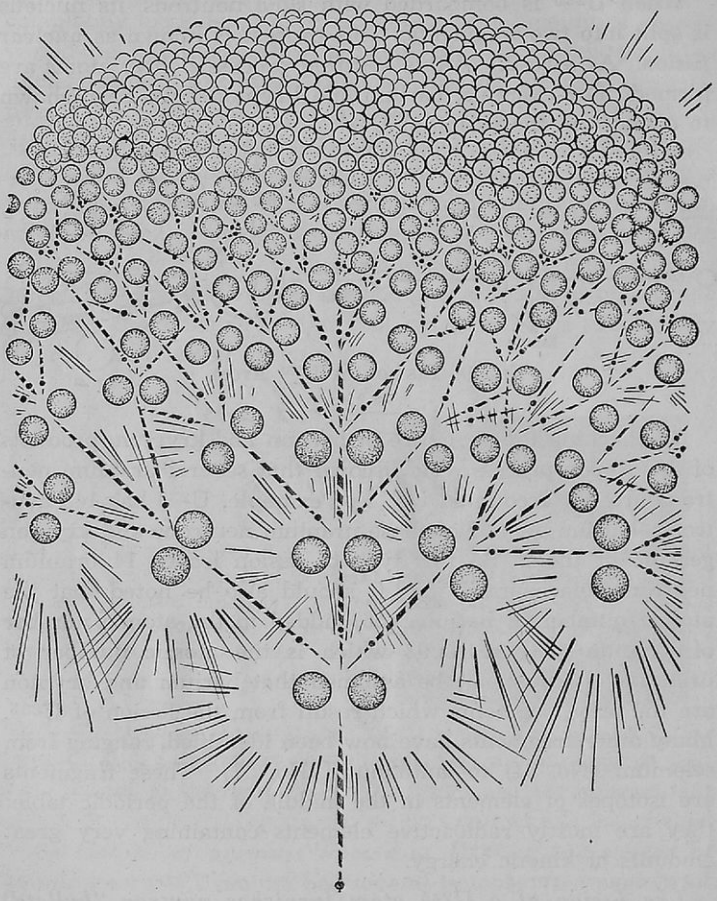

FIG. E. CHAIN REACTION. Fission of one atom of U^{235} produces fission in neighboring atoms.

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A chain reaction will not take place in a lump of U^{235} that is too small because there are not enough uranium atoms within the range of the expelled neutrons. But a larger piece of material, if it exceeds the "critical mass," will permit fission to spread from one atom to its numerous neighbors, thus greatly increasing the total amount of energy which is set free. You can see that a very rapid chain reaction is necessary for the explosion of an atom bomb.

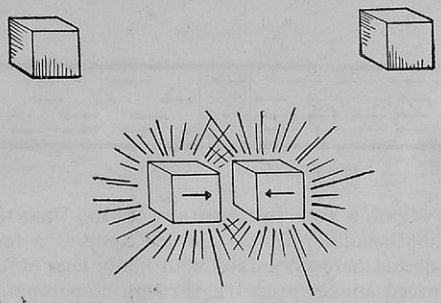

FIG. F. DIAGRAM OF TWO PIECES OF U^{235}. If two pieces of U^{235}, each less than the critical mass, are far enough apart so the neutrons of one do not bombard the other, no chain reaction results. (See top of this illustration.) But if these pieces are brought together rapidly and their combined masses exceed the critical mass, a violent chain reaction is started.

Several of the 14 "extra" neutrons from each of these fission reactions may be lost by absorption, but it is thought that some of them are transformed into energy including heat. This is possible as revealed by the Einstein mass-energy equation given in the middle of page 794. As a result of this transformation a tremendous amount of energy is liberated. When the nucleus of a U^{235} atom undergoes fission, it is estimated that the energy released is equivalent to 200 million electron volts.[1] It is further estimated that a single atom bomb has the same destructive effect as 20,000,000 pounds of TNT.

[1] An electron volt is defined as the energy acquired by an electron when it falls through a potential of one volt. It is equivalent to 1.59×10^{-12} erg or to 3.798×10^{-20} mean gram-calories.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

The isotopes of uranium are separated to obtain concentrated U^{235}. Since the proportion of U^{235} in the uranium of nature is small (0.7%), the energy that is released from uranium is greatly increased by segregating the U^{235} from a large quantity of natural uranium material. Also, impurities are apt to absorb too many of the "extra" neutrons, so a successful chain reaction requires not only a concentration of fissionable material, but also a high degree of purity of the material.

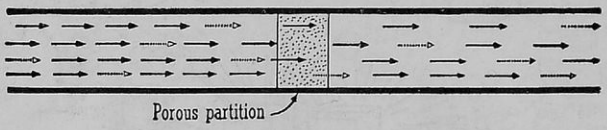

FIG. G. ONE METHOD FOR THE SEPARATION OF URANIUM ISOTOPES. Gaseous uranium hexafluoride, UF_6, which contains a few ions of the U^{235} isotope (dotted arrows) mixed with many ions of U^{238} (regular arrows), is forced under pressure through a porous partition. A heavy isotope passes through the partition more slowly than a lighter one; consequently, the *proportion* of U^{235} becomes somewhat greater, as indicated by the decreased number of solid arrows on the right-hand side of the diagram. By repeating this process the concentration of U^{235} becomes still greater, but the separation does not become complete.

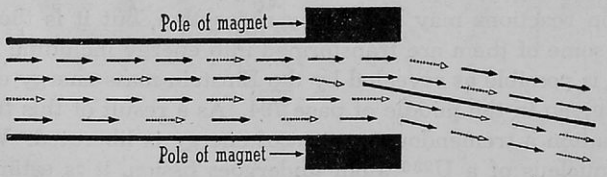

FIG. H. ANOTHER METHOD FOR THE SEPARATION OF URANIUM ISOTOPES. Gaseous uranium ions are passed between the poles of a powerful magnet. The ions are deflected by the magnet. The lighter isotope is deflected more than the heavier one. A screen may be so placed as to effect a partial separation of U^{235} from U^{238}. By repeating this process the concentration of U^{235} becomes greater.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

New synthetic elements are being produced by atomic energy research. Slow neutrons cause fission of U^{235} but not of U^{238}. They are absorbed by U^{238} forming the unstable isotope U^{239}. This new form of uranium promptly loses a beta particle and becomes a new element, neptunium (Np), with atomic number 93 and atomic weight 239. This new element (Np) is unstable and also gives up a beta particle forming another new element, plutonium (Pu), so this series of changes makes it possible to start a large number of chain reactions with uranium. Like U^{235}, plutonium has been used to produce an "atomic explosion."

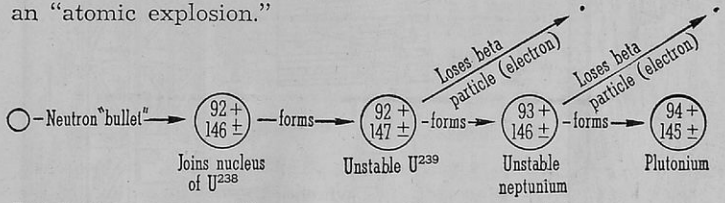

FIG. I. FORMATION OF NEPTUNIUM AND PLUTONIUM. When the nucleus of U^{238} absorbs an extra neutron it becomes the unstable atom U^{239}; this unstable atom loses an electron (negative charge) from a neutron, thus forming one more proton and one less neutron to make the new element neptunium. The nucleus of this atom also loses an electron, forming plutonium, which undergoes fission like U^{235}.

What problems confronted the Manhattan District Project? The behaviors of the radioactive elements described in the last few paragraphs were widely known and generally recognized by scientists by the year 1940. When the Manhattan District Project was organized for the development of the atom bomb, the main problems were concerned with the setting up of these reactions on a large scale, the control of the process to insure safe handling, and the sudden liberation of as much energy as possible at a designated moment. The successful detonation of five atom bombs has shown that these problems have been solved, at least in large measure. The much discussed "secrets" of the atom bomb have mostly to do with engineering problems of this sort, which are largely mechanical, and not with the fundamental reactions involved.

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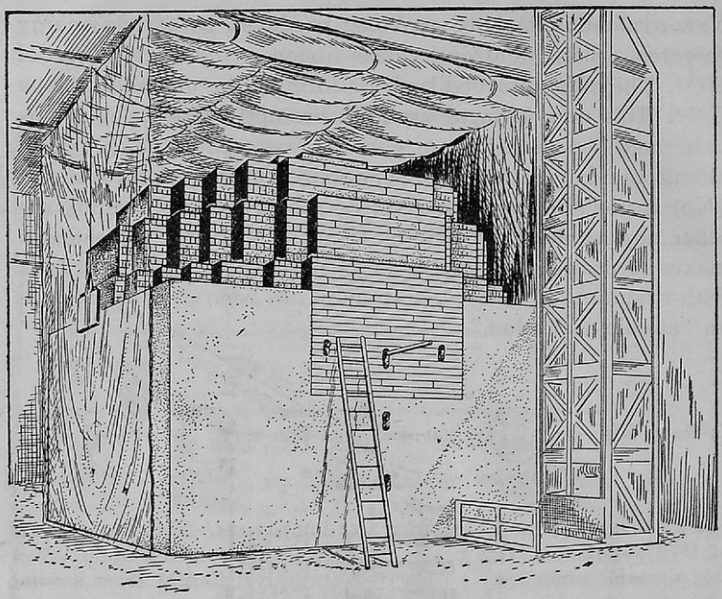

FIG. J. EXTERIOR VIEW OF THE FIRST URANIUM PILE. (From the official drawing.)

How the fast-moving neutrons are slowed down. A very essential part of the experimental work was in regard to the control of the high-energy neutrons. It has been recognized for some time that when these neutrons collide with an atom some of the energy is taken up by the atom which rebounds or recoils from the impact. This effect is more pronounced in the case of the light atoms because of their greater recoil from the collision. Carbon in the form of graphite was found to be the most available material for slowing down the neutrons. One of the difficulties in the development of the chain reaction came from the presence of impurities in the uranium metal and the graphite. These impurities caused the absorption of so many neutrons that a chain reaction would not take place. The task of preparing many tons of extremely pure uranium and graphite presented very difficult problems.

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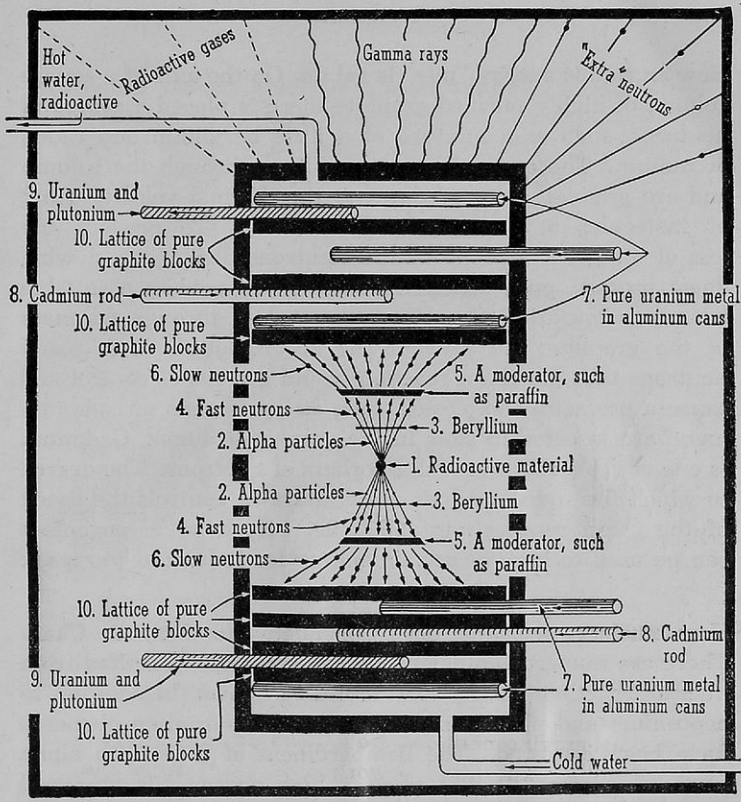

FIG. K. DIAGRAMMATIC CROSS SECTION SHOWING THE PRINCIPLES INVOLVED IN A CHAIN-REACTING PILE OF URANIUM-GRAPHITE. Radium or other radioactive material (1) gives off alpha particles (2), which pass through beryllium (3) and dislodge fast neutrons (4). When these fast neutrons pass through a "moderator" such as paraffin (5) their speed is decreased, causing the slow neutrons (6) which are capable of starting a chain reaction in pure uranium metal which is held in aluminum cans (7). The reaction is prevented from reaching explosive violence by rods of cadmium metal (8) which absorb many neutrons. The reaction increases in violence as these cadmium rods are gradually withdrawn. After a time the uranium and plutonium may be removed (9); it now contains about 0.1% plutonium. The apparatus is packed in a lattice of pure graphite blocks a few of which are shown (10), and the operators are protected from the harmful radiations and gases by an extensive shield of graphite blocks which build up the completed pile (Fig. J). The plutonium can be concentrated by chemical steps which are carried out by remote control in underground concrete cells.

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How an atomic energy "pile" is set up. On the axis of a square column of highly purified graphite there is placed a source of neutrons, such as a mixture of a little beryllium and radon or radium. The emitted neutrons diffuse through the column and are gradually slowed down to the thermal velocity (that of molecules at ordinary temperatures). To prevent the loss of too great a proportion of neutrons during the slowing down process, pure uranium metal is scattered in a suitable lattice configuration (see Fig. 76, page 204) through the mass of the graphite. To prevent the accumulation of so many neutrons that the chain reaction would get out of control and cause a premature explosion, long strips or rods of cadmium metal are inserted in slots in the graphite column. Cadmium is one of the most powerful absorbers of neutrons. The degree to which the cadmium rods are withdrawn controls the speed of the chain reactions in the "pile." Such an arrangement can be used to harness atomic energy for industrial purposes.

How nuclear reactions have extended the Periodic Chart. There are numerous other products which have resulted from nuclear reactions of the sort described above. In addition to neptunium and plutonium, two other trans-uranium elements have been prepared. The bombardment of U^{238} with alpha particles (helium nuclei) of very high energy has produced element 95^{241}, which has been given the name americium. Similar bombardment of Pu^{239} produces two different isotopes of a new element, which have been identified as 96^{240} and 96^{242}. This element has been named curium in honor of Pierre and Marie Curie, the discoverers of radium.

The new elements are radioactive and emit alpha particles. The presence of these elements after uranium in the Periodic Chart and their structures, which resemble those of the Rare Earth group, suggest the existence in this trans-uranium region of a group of elements analogous to the Rare Earth group. Other work completed some years ago revealed the possibility of such a group.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Atomic energy research is furnishing many "tracer" elements for biological studies. Bombardment by neutrons of other materials which have been placed in the uranium pile have revealed the formation of isotopes of hydrogen (H^3), carbon (C^{14}), phosphorus (P^{32}), sulfur (S^{35}), chlorine (Cl^{36}), and iodine (I^{131}). These isotopes have the same chemical properties as the stable forms of the same elements, but some of the isotopes are radioactive, and this fact makes it possible to detect their presence readily wherever they may be. As a consequence, it is possible to follow their transformations when they enter into chemical reactions. For example, the atoms of radioactive carbon, C^{14}, may replace a few of the ordinary carbon atoms in a food product like sugar, $C_{12}H_{22}O_{11}$. As the molecules containing these radioactive isotopes pass through different body processes, their progress may be followed by the use of a Geiger counter which reveals the presence of a radioactive substance. In this manner it is possible to follow the chemical changes in digestion and to observe the progress of medicines in the study of disease. These tracer elements are already being used experimentally and it is expected that they will be of great assistance in these and other fields.

Can the future of atomic energy be predicted? It is unfortunate that the first manifestations of power from the atom should have been used as an instrument of destruction. This enormous storehouse of energy can be directed toward peaceful means; it can promote the progress of civilization to an amazing degree. Atomic energy, liberated gradually, is a possible driving power for vast industrial enterprises. In fact it is safe to say that the atomic age is here, ready to take a greater and greater part in the industrial world.

The atomic engine diagrammed on page 806 has a tremendous weight. But experiments with the bombardment of other materials besides uranium, including gases, indicate that relatively light atomic engines are practicable. Such atomic engines can be used to propel railroad locomotives. Time may be

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needed to harness this source of energy to the task of moving objects as light as passenger automobiles. But that possibility, apparently, is not too remote.

It is to be profoundly hoped that mankind will learn to make full use of liberated atomic energy as a source of power to take care of peacetime needs. Let us also hope that its awesome possibilities will teach the nations of the world that war is senseless as a means of settling disputes.

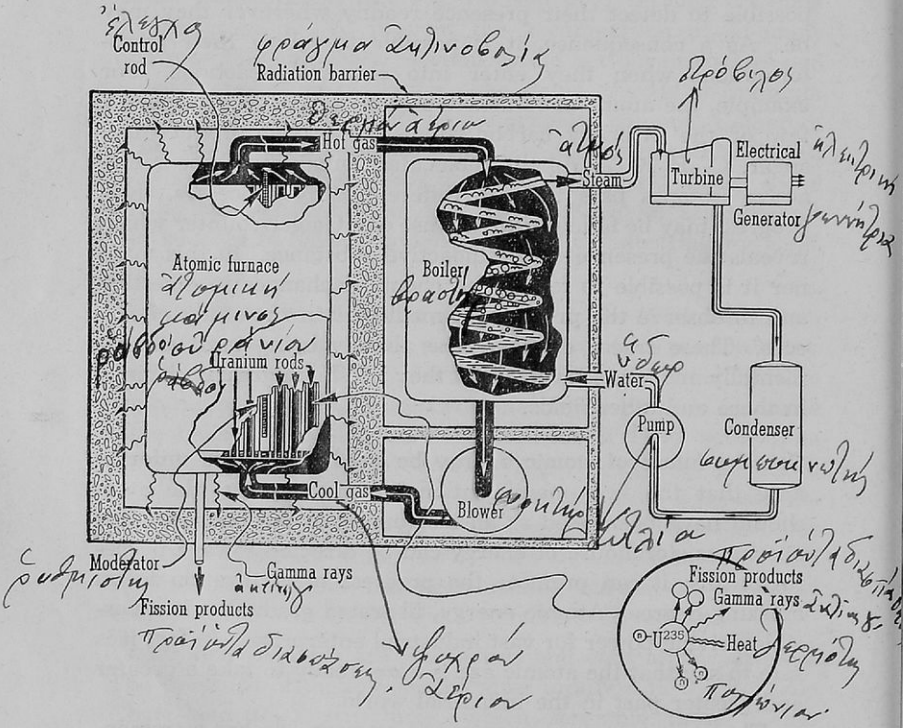

FIG. L. ONE METHOD FOR USING ATOMIC ENERGY TO GENERATE ELECTRICITY. Operators of such a power plant need to be protected from the radioactive rays by heavy installation.

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XXVI. GLOSSARY

(The pronunciation signs used here are the same as those used in Webster's International Dictionary.)

A

Absolute zero: a temperature approximately 273° below zero centigrade (0° A. = −273° C.); at this temperature all molecular activity is supposed to cease.

Acid: a substance which liberates hydrogen ions in water solution; its common properties in water solution are a sour taste, turning litmus red, and action on bases to form water and salt.

Acidic anhydride (ă·sĭd′ĭk ăn·hī′drīd) (acidic oxide): an oxide that reacts with water to form an acid; conversely, the oxide formed when water is removed from the acid.

Acid salt: a salt formed by replacing a part of the hydrogen ions of a dibasic or tribasic acid with metallic ions, such as $NaHSO_4$ and NaH_2PO_4.

Activated charcoal: a specially treated and finely divided form of carbon, which possesses a high degree of adsorption.

Activity series: *of metals*, an arrangement of the metals in the order of their ability to replace other metals from their compounds. *Of nonmetals*, an arrangement of the nonmetals in the order of their ability to replace other nonmetals from their compounds.

Adsorption (ăd·sôrp′shŭn): the adhesion (in an extremely thin layer) of the molecules of gases, of dissolved substances, or of liquids to the surfaces of solid bodies with which they come in contact.

Alcohol: an organic hydroxyl compound formed by replacing one or more hydrogen atoms of the hydrocarbon with an equal number of hydroxyl (OH) groups.

Aldehyde (ăl′dē·hīd): an organic compound formed by dehydrating oxidized alcohol; contains the characteristic CHO group.

Alkali (ăl′kə·lī): usually refers to strong bases, such as sodium hydroxide and potassium hydroxide: *alkaline* pertains to any substance having basic properties.

Allergy (ăl′ĕr·jĭ): the sensitivity of certain persons to contact with substances, usually proteins, such as pollen, bacteria, certain foods, etc., which results in such diseases as hay fever, asthma, and hives.

Allotropic (ăl ō trŏp′ĭk): referring to forms of certain elements which differ in their physical make-up and energy content; the diamond, graphite, and various forms of charcoal are allotropic forms of carbon.

Alloy (ă·loi′; ăl′oi): a substance composed of two or more metals, which are intimately mixed, usually made by melting the metals together.

Alpha rays: a stream of the nuclei of helium atoms shot out from radioactive substances.

Alum: a double sulfate of a monovalent and a trivalent metal, such as $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot (H_2O)_{24}$. This term is also used as a common name for commercial aluminum sulfate.

Amalgam (ə·măl′găm): an alloy of mercury and some other metal.

Amine (ă·mēn′): a compound derived from ammonia by substituting one or more NH_2 groups for the hydrogen, such as CH_3NH_2.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Amorphous (*ȧ*·môr′fŭs): having no definite crystalline structure.

Amphoteric (ăm fō·tĕr′ĭk): referring to an element whose hydroxide may have either acidic or basic properties, depending on the substance with which it reacts.

Analysis (*ȧ*·năl′ĭ·sĭs): breaking down of a compound into two or more simpler substances.

Anesthetic (ăn ĕs·thĕt′ĭk): an agent which deadens pain or produces unconsciousness.

Anhydrous (ăn·hī′drŭs): containing no water.

Annealing: the heating and subsequent slow cooling of glass or metal to render it less brittle and more resistant to shock.

Anode (ăn′ōd): the positive electrode of an electrolytic cell to which the negative ions are attracted.

Antichlor (ăn′tī·klōr): a substance used to remove the excess of chlorine in the bleaching process.

Antiseptic: a substance used to slow up or stop the growth or action of microorganisms.

Aqua regia (ăk′wȧ rē′jĭ·*ȧ*): a mixture of three volumes of concentrated HCl and one volume of concentrated HNO_3.

Atom: a chemical unit of matter; the smallest particle of an element able to enter into a chemical reaction.

Atomic (*ă*·tŏm′ĭk) **number:** for any element, it represents the total number of planetary electrons in the atom, or the number of free protons in the nucleus.

Atomic (*ă*·tŏm′ĭk) **weight:** the weight of an atom of an element compared with the weight of an atom of oxygen, having an atomic weight of 16.

B

Baking powder: a mixture of sodium hydrogen carbonate and some acid salt or salt which will hydrolyze to form an acid; used as a leavening agent in baking.

Barometer (bȧ·rŏm′ē·tĕr): an instrument used for measuring atmospheric pressure.

Base: a substance which tastes flat or bitter, turns litmus blue, and produces OH ions in water solution; reacts with acids to form water and salt.

Basic anhydride (ăn·hī′drīd) (basic oxide): an oxide that reacts with water to form a base; conversely, the oxide formed when water is removed from a base.

Basic salt: a salt which contains a hydroxyl group, such as $Bi(OH)_2Cl$ or a salt derived from such a compound as BiOCl.

Beta rays: streams of fast moving electrons, given off by radioactive substances.

Binary (bī′nȧ·rĭ): referring to a compound composed of two elements, such as H_2O and KCl.

Boiler scale: a formation of insoluble calcium and magnesium compounds (usually) that precipitates out in boilers and teakettles when hard water is used.

Boiling point: the temperature at which the vapor pressure of a liquid just exceeds the atmospheric pressure.

Brownian movement: continuous zigzagging movement of colloidal particles, as viewed through an ultramicroscope.

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B. T. U. (British thermal unit): the amount of heat necessary to raise the temperature of one pound of water one degree Fahrenheit.

C

Calorie (kăl′ō·rĭ): amount of heat necessary to raise the temperature of one gram of water one degree Centigrade.

Calorimeter (kăl ō·rĭm′ē·tĕr): an instrument used for the measurement of the amount of heat liberated or absorbed.

Carat: a unit of weight (200 mg) for diamonds and precious stones; also the fineness of gold, based on a standard of 24 carats for pure gold.

Carbohydrate (kär bō hī′drāt): a compound of carbon, hydrogen, and oxygen, with hydrogen and oxygen usually in the ratio of 2 to 1, as in H_2O; sugars, starches, and cellulose are carbohydrates.

Catalyst (kăt′ȧ·lĭst) (catalytic agent): a substance used to speed up or slow down a reaction, but it itself is unchanged at the end of the reaction.

Cathode (kăth′ōd): the negative electrode of an electrolytic cell to which positive ions are attracted.

Centigrade: a temperature scale to measure intensity of heat on which 0° represents the freezing point of H_2O and 100° the boiling point of H_2O (at standard pressure).

Chemical change: change that takes place in the composition of a substance.

Chemistry: the science that treats of the composition of substances and the changes which they undergo.

Coagulum (kō·ăg′ū·lŭm): applied to the aluminum hydroxide (or others), formed in water purification, which settles and removes bacterial and suspended matter from the water.

Colloidal (kŏ·loi′dăl; d′l) **state:** a condition obtained by dispersing ultramicroscopic particles of gases, liquids, or solids, in a medium, which may be gaseous, liquid, or solid; (gas dispersed in gas is not colloidal, but a diffusion).

Combining (equivalent) **weight:** the number of grams of an element that will combine with or displace one gram of hydrogen or eight grams of oxygen.

Combustion: a chemical action in which both heat and light are given off.

Compound: a substance composed of chemically united elements in definite proportions by weight.

Copolymerization (cō·pŏl′ĭ·mĕr·ī·zā′shŭn): the process of combining several molecules of two different substances, to form one large molecule.

Cottrell precipitator (kŏt rĕl′prē·sĭp′ĭ·tā tĕr): an electrical device to precipitate dispersed dust (smoke) particles which carry an electrical charge.

Covalence (kō·vā′lĕns): when atoms combine by sharing electrons and not by electron transfer; no ions are formed.

C. P. chemicals: *chemically pure*; chemicals with a high degree of purity.

"Cracking": the process of breaking up the large complex hydrocarbon molecules in petroleum into short chain hydrocarbons, thus increasing the yield of gasoline.

Crystalline: having a definite geometric shape.

Crystallization: process of forming definitely shaped crystals as when water is evaporated from a solution of the substance.

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D

Decomposition: the breaking down of a compound into simple substances or into its constituent elements.

Decrepitation (dē·krĕp′ĭ·tā′shŭn): crystals, containing droplets of inclosed water, give off miniature explosions when they are heated.

Dehydrate (dē·hī′drāt): to take water from a substance.

Dehydrating agent: a substance which is able to withdraw water from another substance, consequently drying it.

Deliquescent (dĕl′ĭ kwĕs′ĕnt): referring to a substance that absorbs water from air; the substance may dissolve in the water so absorbed.

Denatured alcohol: grain alcohol which has been "poisoned" in order to produce a cheaper alcohol for industrial purposes.

Density: the weight of a solid or liquid in grams per ml; for a gas, the weight of a liter of the gas.

Destructive distillation: the process of heating an organic substance, such as coal, in the absence of air to break it down into solid and volatile products.

Deuterium (dū·tēr′ĭ·ŭm): the isotope of hydrogen, sometimes called heavy hydrogen, with atomic weight of 2.

Dialysis (dī·ăl′ĭ·sĭs): the process of separating a true solution from a colloidal dispersion by means of a membrane; colloidal particles will not pass through the membrane.

Diffusion: the tendency of gases or liquids to mix freely of their own accord.

Disaccharid (dī·săk′ā rĭd): a sugar, as $C_{12}H_{22}O_{11}$, which will hydrolyze to form two molecules of simpler sugars.

Disinfectant: a substance that will destroy disease germs.

Disintegration: The separation or breaking up of a substance into parts.

Displacement: A change by which an element takes the place of another element in a compound.

Displacement series: see activity series.

Distillation: the process of first vaporizing a liquid and then condensing the vapor into a liquid, leaving behind the nonvolatile impurities; the liquid condensed is called the *distillate.*

Double decomposition (displacement): a reaction in which two chemical substances exchange "partners:" $NaCl+AgNO_3 \rightarrow NaNO_3+AgCl$.

Dry Ice: solid carbon dioxide.

E

Effervescence (ĕf ēr·vĕs′ĕns): the rapid escape of excess gas which has been dissolved in a liquid.

Efflorescent (ĕf lō·rĕs′ĕnt): referring to any hydrate which gives up its water of hydration on standing and becomes a powder.

Elastomer (ē·lăs′tō-mēr): an elastic substance resembling natural rubber; commonly called "artificial rubber."

Electrode (ē·lĕk′trōd): a terminal of a battery or electrolytic cell; the positive pole is the anode, the negative pole is the cathode.

Electrolysis (ē·lĕk trŏl′ĭ·sĭs): the decomposition of a compound by passing an electric current through a dissolved or melted electrolyte.

Electrolyte (ē·lĕk′trō·līt): a substance in solution or melted that will conduct the electric current.

Electron: a negatively charged particle, one of the units of atomic structure.

Ψηφιοποιήθηκε από το Ινστιτούτο Εκπαιδευτικής Πολιτικής

Element: one of the 92 "building blocks" of which all matter is composed.

Emulsifying agent: a colloidal substance which forms a film about the particles of immiscible liquids, so that they remain suspended in each other.

Emulsion (ē·mŭl′shŭn): a suspension of fine particles or droplets of one liquid in another, the two liquids being immiscible in each other; droplets are surrounded by some colloidal (emulsifying) agent.

Endothermic (ĕn dō·thûr′mĭk): referring to a chemical reaction in which heat is necessary to bring the reaction about heat being taken up in the reaction.

Energy: the ability to do work; in every chemical change energy is either given off or taken in; forms of energy are heat, light, motion, sound, electrical, and chemical.

Enzyme (ĕn′zīm): an organic catalyst occurring in plants and animals.

Equation: a shorthand method of showing the change which takes place in a chemical reaction.

Equilibrium (ē kwĭ·lĭb′rĭ·ŭm): *chemical or ionic*, the state of balance between reacting substances in which a continuous chemical change is going in each direction, a reversible reaction.

physical, in a saturated solution the rate of dissolving is just balanced by the rate of crystallizing.

Ester (ĕs′tēr): an organic salt formed by the action between an alcohol ("organic base") and an organic acid.

Eudiometer (ū dĭ·ŏm′ē·tēr): a graduated tube into which gases are placed and subjected to an electric spark; volume relations between the combining gases are determined.

Evaporation: process in which molecules of a liquid (sometimes a solid) leave the surface in the form of vapor.

Exothermic (ĕk sō·thûr′mĭk): referring to a chemical reaction in which heat is given off, such as the burning of paper.

F

Fahrenheit (fär′ĕn·hīt): a common temperature scale in which 32° represents the freezing point of water and 212° the boiling point of water (at standard conditions).

Fermentation: process in which a chemical change is brought about by enzymes, bacteria, and other living organisms.

Filtration (fĭl·trā′shŭn): the process in which suspended matter is removed from a liquid by passing the liquid through a porous material; the *residue* remains, the *filtrate* passes through.

Fixation of nitrogen: converting atmospheric nitrogen by various processes into useful commercial products, such as ammonia and nitric acid.

Flame: more or less luminous appearance produced by the burning of a substance.

Flammable (flăm′ă·b'l): applied to a substance capable of being easily set on fire; combustible; (same as inflammable).

Flotation (flō·tā′shŭn): the process of separating low-grade metallic ores (usually sulfides) from foreign materials by mixing with oil and water; the ore particles stick to oil and "float" off.

Flux (flŭks): *in metallurgy:* a substance that helps to melt and remove the solid impurities as slag.

in soldering: a substance that will clean the surface of the metal to be soldered.

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Formula: a combination of symbols used to denote the composition of a molecule, as H_2O.

Fractional distillation: method of separating mixtures of liquids having different boiling points.

Freezing point: the definite temperature at which a liquid changes to a solid state.

Fuel: any substance used to furnish heat by combustion.

Fungicide (fŭn'jĭ·sīd): chemicals used to kill fungous diseases on plants.

Fusion (melting): changing a solid to the liquid state by heating.

G

Galvanizing: applying a coating of zinc to iron or steel as a protective coat.

Gamma rays: "super X rays," which travel with the speed of light and are very penetrating, as they are given off by radioactive substances.

Gel (jĕl): a colloidal solution whose dispersed substance coalesces and precipitates forming a jelly.

Glass: ordinary glass is a mixture of silicates, made by fusing together silica sand and sodium carbonate and lime; the various forms of glass contain many other silicates.

Gram: unit of weight in metric system; weight of 1 ml of water at 4° C.

Gram-molecular (grăm mô·lĕk'ū·lēr) **volume:** 22.4 l (at standard conditions), or the volume occupied by one gram-molecular weight of any gaseous substance.

Gram-molecular (grăm mô·lĕk'ū·lēr) **weight:** the relative weight in grams of a molecule of a compound (or element); the sum of all the atomic weights of the elements in the compound.

H

Haber (hä'bĕr) **process:** method for union of atmospheric nitrogen with hydrogen to form ammonia; named for the German chemist, Haber, its inventor.

Halogen (hăl'ô·jĕn): salt producer; referring to any member of the chlorine family.

Hard water: Water that will not easily produce a lather with soap because of dissolved calcium and magnesium salts.

carbonate ("temporary") *hardness:* water containing dissolved bicarbonates.

noncarbonate ("permanent") *hardness:* water containing dissolved salts other than bicarbonates.

Heat of decomposition: the amount of heat (calories) necessary to decompose one gram-molecular weight of a substance.

Heat of formation: the amount of heat (calories) liberated (or absorbed) in the formation of one gram-molecular weight of a substance from its elements.

Heat of fusion: the amount of heat (calories) required to melt one gram of a substance; for water, 80 calories.

Heavy water: (deuterium oxide, D_2O) water in which the hydrogen atoms are replaced by the isotope of hydrogen, deuterium.

Homologous (hŏ·mŏl'ô gŭs): (meaning *alike in structure*) referring to series of compounds, such as hydrocarbons, in which each member differs from the

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next by the same group. CH_2 is the increment (increase) in several homologous hydrocarbon series.

Hormone (hôr'mōn): a secretion from one of various glands of the body which acts catalytically in regulating the action of many of its organs.

Humidity: amount of moisture in the air.

Hydrate: a crystalline compound, usually a salt, loosely combined with a definite number of molecules of water, such as $CuSO_4 \cdot (H_2O)_5$.

Hydrocarbon (hī drō·kär'bŏn): a binary compound of hydrogen and carbon.

Hydrogenation (hī drō·jĕn ā'shŭn): process in which hydrogen is made to combine with another substance in the presence of a catalyst.

Hydrolysis (hī·drŏl'ĭ·sĭs): *of carbohydrates:* action of water in presence of a catalyst upon one carbohydrate to form simpler carbohydrates.

of salts: action of water on a salt to form an acid and a base.

Hydroxyl (hī·drŏk'sĭl): referring to the OH radical.

Hypothesis (hī·pŏth'ê·sĭs): a theory that has not been fully proved by experimentation.

I

Immiscible (ĭ·mĭs'ĭ·b'l): referring to liquids which are not soluble in each other or do not mix.

Indicator: a dye that has one color in the presence of the hydrogen ion (acid) and a different color in the presence of the hydroxyl ion (base).

Inert (ĭn·ûrt'): inactive.

Insecticide (ĭn·sĕk'tĭ·sīd): a chemical substance used to destroy insects.

Inversion of sucrose: action of water (hydrolysis) on sucrose in the presence of a catalyst to form dextrose and levulose (invert sugar).

Ion (ī'ŏn): an atom or a radical that carries an electrical charge.

Ionic (ī·ŏn'ĭk) **equation**: an equation showing the ions formed by a compound; such as $Na_2SO_4 \rightleftarrows 2\ Na^+ + SO_4^{--}$.

Ionization (ī ŏn·ĭ·zā'shŭn): setting free the ions of a chemical compound so they are free to move about in solution.

Isomer (ī'sô·mĕr): any compound having the same percentage composition, but different properties, as another compound.

Isotope (ī'sō·tōp): One of two or more forms of the same element differing in atomic weight but having the same atomic number and the same chemical properties.

J

Javelle (zhȧ·vĕl') **water**: a solution of sodium hypochlorite.

K

Kindling point: the temperature to which any substance must be raised before it can burn.

Kinetic-molecular (kĭ·nĕt'ĭk mô·lĕk'ū·lĕr) **theory**: the hypothesis that all molecules are in motion; this motion is most rapid in gases, less rapid in liquids, and very slow in solids.

L

Lake: the combination resulting from the action between dyestuffs and the insoluble hydroxides.

Law: a generalized statement that summarizes a large number of facts or principles.

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Laws:

Avogadro (ä vô·gä′drô): Equal volumes of gases under the same conditions of temperature and pressure contain an equal number of molecules.

Boyle: The volume of a confined gas is inversely proportional to the pressure to which it is subjected, providing the temperature remains the same.

Charles: The volume of a confined gas is directly proportional to the absolute temperature, providing the pressure remains the same.

Conservation of matter: Matter can neither be created nor destroyed, but can be changed from one form to another.

Definite composition: All compounds are composed of two or more elements chemically combined in a definite ratio by weight.

Gay-Lussac (gā lü sàk′): The ratio between the combining volumes of gases and the product, if gaseous, can be expressed in small whole numbers.

Henry: The solubility of a gas (unless it is very soluble) is directly proportional to the pressure applied to it.

Multiple proportions: When any two elements, A and B, combine to form more than one compound, the different weights of B, which unite with a fixed weight of A, bear a small whole-number ratio to each other.

Periodic: The chemical properties of elements are periodic functions of their atomic numbers.

Properties: Under constant conditions, a substance always has a definite and characteristic set of properties by which it can be described.

Litmus: an organic substance, obtained from the lichen plant, and used as an indicator; red in acidic solution and blue in basic solution.

Lye: sodium or potassium hydroxide.

M

Malleable (măl′ē·*ă*·b′l): capable of being hammered or pounded into thin sheets.

Mass: a definite quantity of matter; as it represents the molecules in a substance it is unchangeable in quantity, while weight, measured in like units, varies with the pull of gravity on the substance.

Matter: any thing that has weight and occupies space.

Melting point: the definite temperature at which a solid changes to a liquid.

Meta-acid: an acid containing one less molecule of water than an ortho-acid.

Metal: (a) an element whose oxide combines with water to form a base; (b) an element which readily loses electrons and acquires a positive valence.

Metallurgy (mĕt″l·ûr jĭ): the processes involved in obtaining a metal from its ores.

Micron (mī′krŏn): 1/1000 part of a mm; *millimicron*—1/1,000,000 part of a mm.

Mineral: an inorganic substance found in nature.

Miscible (mĭs′ĭ·b′l): referring to liquids which are soluble in each other (will mix with each other).

Mixture: an association of substances not chemically combined.

Molar (mō′lēr) **solution:** a solution containing one gram-molecular weight (mole) of the dissolved substance in one liter of solution.

Mole (mōl): a term used to represent a gram-molecular weight of a substance.

Molecular (mō·lĕk′ū·lēr) **weight:** relative weight of a substance compared with the weight of a molecule of oxygen, which is 32.

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Molecule (mŏl′ē·kūl): the combination, chemically, of two or more like or unlike atoms, as O_2 and H_2O; the smallest quantity of a compound which can exist in the free state.

Monobasic acid: an acid having only one hydrogen atom which can be replaced by a metal or a positive radical.

Monosaccharid (mŏn ō·săk′ă·rĭd): a simple sugar, as $C_6H_{12}O_6$.

Mordant: a chemical, such as aluminum sulfate, used for fixing colors upon textiles.

Mustard gas: a substance used in chemical warfare. It attacks the skin, forming blisters; dichloro-diethyl sulfide, $(ClC_2H_4)_2S$.

N

Nascent (năs′ĕnt; nā′sĕnt) (atomic): referring to an element in the atomic form as it is just liberated in a chemical reaction; very active.

Neutralization: the union of the hydrogen ion of an acid and the hydroxyl ion of a base to form water; incidentally a salt is formed.

Neutron (nū′trŏn): an electrically neutral particle, thought to be composed of an electron and a proton; it is within the nucleus of an atom and has a mass of approximately 1.

Nonelectrolyte (nŏn ē·lĕk′trō·līt): a substance whose solution will not conduct a current of electricity.

Nonmetal: (a) an element whose oxide reacts with water to form an acid; (b) an element which takes on electrons and acquires a negative valence.

Normal salt: a salt in which all of the hydrogen of the acid has been displaced by a metal.

Normal solution: a solution one liter of which contains one gram-molecular weight of dissolved substance divided by the hydrogen equivalent of the substance.

Nucleus: the central part of an atom; it is made up of protons and neutrons, is positively charged, and contains practically all the weighable portion of the atom.

O

Octane (ŏk′tān) **rating:** an artificial rating for gasoline based upon its behavior as compared with iso-octane.

Ore: a natural mineral substance from which a useful element, usually a metal, may be obtained.

Organic chemistry: the chemistry of carbon compounds.

Ortho-acid: an acid containing the normal amount of water, as orthophosphoric acid, H_3PO_4.

Oxidation (ŏk sĭ dā′shŭn): (a) chemical union of oxygen with any substance; (b) a chemical reaction in which an element loses electrons and thus increases in (positive) valence.

Oxidizing agent: a substance that gives up its oxygen readily, removes hydrogen from a compound, and takes electrons from a metal.

Ozone (ō′zōn): an allotropic and very active form of oxygen, formula O_3.

P

Paraffin series: a term applied to the methane series of hydrocarbons.

Pasteurization (păs tĕr·ĭ·zā′shŭn): a partial sterilization of organic liquids, as milk, by heating to approximately 65° C. and for one half-hour.

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Penicillin (pĕn·ĭs′ĭl·ĭn *or* pĕn-ĭ-sĭl′-ĭn): a beneficial drug more powerful than the "sulfa" drugs.

Petroleum: (meaning oil from stone)—a complex mixture of gaseous, liquid, and solid hydrocarbons; common refined products are benzine, naphtha, gasoline, kerosene, vaseline, paraffin, lubricating oils, etc.

Phenolphthalein (fē nōl·thăl′ēn; -ē ĭn): an organic indicator which is colorless in acid solution and red in presence of OH ions.

Phlogiston (flō·jĭs′tŏn) **theory:** belief, just preceding the discovery of oxygen, that a substance, phlogiston, escaped from all burning materials; if absent, the material would not burn.

Photosynthesis (fō·tō·sĭn′thē·sĭs): the reaction taking place in all green plants which produces glucose from carbon dioxide and water under the catalytic action of chlorophyll in the presence of light.

Physical change: does not involve a change in chemical composition.

Pigment: finely divided, insoluble coloring material, suspended in paints.

Plasticizer (plăs′tĭ·sī·zĕr): a substance added in order to increase or preserve flexibility and adhesive power.

Plastics: a group of synthetic organic materials, which are shaped when pliable and then hardened to useful articles.

Polar compound: a compound formed when one element (a metal) gives up one or more electrons to another element (a nonmetal), forming ions.

Polymerization (pŏl ĭ·mĕr·ĭ·zā′shŭn): the process of combining several like molecules to form one large molecule.

Positron (pŏz′ĭ·trŏn): a positively charged particle of electricity with about the same weight as the electron.

Potash: an old term applied to potassium hydroxide or potassium carbonate.

Precipitate (prē·sĭp′ĭ·tāt): an insoluble compound that is formed in the chemical reaction between two or more substances in solution.

Primary cell: an arrangement for transforming chemical energy into electricity. It usually contains an electrolyte in which is suspended an active metal like zinc and an inactive element like copper or carbon.

Proteins (prō′tē·ĭn; prō′tēn): large complex organic molecules, with nitrogen a very essential part, found in the structure of plants and animals.

Proton (prō′tŏn): a positively charged particle which acts as one of the units of atomic structure.

Q

Qualitative analysis: a term applied to the methods and procedures used in finding out any or all of the constituent parts of a substance.

Quantitative analysis: a term applied to the methods and procedures used in finding out the definite quantity or percentage of any or all of the constituent parts of a substance.

R

Radical: a group of atoms which act as a unit in a reaction, such as SO_4.

Radioactive: referring to substances which have the ability to emit radiations (alpha or beta particles) thereby producing spontaneous transmutation.

Rayon: a textile made from cellulose to resemble silk.

Reaction: indicating a chemical change has taken place and represented by an equation.

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Recrystallization: a series of crystallizations, repeated for the purpose of greater purification.

Reducing agent: a substance that is readily oxidized, therefore used to withdraw oxygen from a compound; from electron standpoint, a substance which loses its valence electrons to another element.

Reducing sugar: any sugar which will reduce copper or silver salts in alkaline solution.

Reduction: (a) process in which oxygen is removed from a substance; (b) a chemical reaction in which an element gains electrons and therefore decreases in valence.

Relative humidity: ratio, expressed in per cent, between the amount of water vapor in a given volume of air and the amount this same volume can hold when saturated at the same temperature.

Relative weights: same as atomic weights; the weight of an atom of an element compared with the weight of an atom of oxygen, having an atomic weight of 16.

Replacement: same as displacement.

Reversible reaction: any reaction that reaches an equilibrium, or which can be made to proceed from right to left as well as from left to right.

Roasting: heating an ore (usually a sulfide) in an excess of air to convert the ore to an oxide, which then can be easily reduced.

S

Saccharin (săk′*ȧ*·rĭn): $C_6H_4COSO_2NH$, a white, crystalline, organic compound derived from coal tar, and 400 times sweeter than cane sugar.

Salt: a compound resulting from the reaction between an acid and a base; or a compound of a metal or positive radical and nonmetal or negative radical.

Saponification (sȧ·pŏn *ĭ* fĭ·kā′shŭn): the reaction taking place when an alkali reacts with a fat or oil; the process of soapmaking illustrates this.

Saturated solution: a solution which contains all the solute it can hold in the presence of undissolved solute of the same kind; the rate of dissolving is just balanced by the rate of crystallizing.

Sharing electrons: two atoms may share one (or more) pair of electrons with each other and have them in common, thus forming a non-polar compound, such as CH_4. Molecules of some elementary gases share their electrons, as O_2.

Slag: the product formed when the flux reacts with the impurities of an ore in metallurgical processes.

Sol (sŏl): a colloidal solution whose dispersed substance does not coalesce; that is, it does not "gel" but remains "thin" like a true solution.

Solder: a low-melting metal or alloy that is used to join two adjacent surfaces of less fusible metals or alloys.

Solubility: the weight in grams of a substance needed to saturate 100 grams of the solvent at a given temperature.

Solute: (sŏl′ūt; sō′lūt): a substance that dissolves in a solvent to produce a solution.

Solution: a molecular dispersion (scattering) of one substance in another substance.

Solvent: a liquid that dissolves another substance (solute).

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Specific heat: the ratio between the number of calories needed to raise the temperature of a certain weight of a substance 1° C. and the number of calories needed to raise the same weight of water 1° C.

Specific weight (gravity): the number which expresses the ratio between the weight of a certain volume of a substance and the weight of an equal volume of water.

Spectroscope: an instrument for analyzing light by separating it into its component wave lengths.

Spectrum: The image formed when radiant energy is dispersed by a prism or grating into its various wave lengths.

Spontaneous combustion: the process in which slow oxidation produces enough heat to raise the temperature of a substance to its kindling point.

Stable: referring to a substance not easily decomposed into its component parts.

Standard conditions: the atmospheric pressure of 760 mm (mercury pressure) and temperature of 0° C., used in connection with measurement of gas volumes.

Stratosphere: the upper portion of the atmosphere, in which the temperature changes but little with altitude, and clouds of water never form.

Strong acids (or bases): acids (or bases) capable of a high degree of ionization in water solution.

Structural (graphic) **formula**: a pictured representation of the atomic arrangement of molecules.

Sublime: to vaporize directly from the solid to the gaseous state; vapor then condenses back to the solid.

Substance: referring to any kind of matter, elements, compounds, or mixtures.

Substitution products: products formed by the substitution of elements or radicals for hydrogen in hydrocarbons.

Sulfadiazine (sŭl·fah·dī′az·ĭn): a sulfanilamide vitamin B_1 compound used in certain infections.

Sulfaguanidine (sŭl·fah·gwan′ĭ·dĭn): a relative of sulfanilamide, an intestinal bacteriacide.

Sulfanilamide (sŭl·făn·ĭl′ăm·ĭd): para-amino-benzine-sulfon-amide, a powerful drug.

Sulfapyridine (sŭl·fah·pĭr′ĭd·ĭn): a pyridine derivative of sulfanilamide.

Sulfathiazole (sŭl·fah·thī′ă·zōl): a proprietary drug related to sulfapyridine and sulfanilamide.

Supersaturated solution: a solution that contains a greater quantity of solute than is normally possible at that temperature.

Suspension: a mixture of finely divided solid material in a liquid from which the solid will settle on standing.

Symbol: the letter or two letters that are used to represent one atom of an element, such as Hg for mercury.

Synthesis (sĭn′thĕ·sĭs): the union of two or more elements to form a compound.

T

Temperature: the intensity or the degree of heat of a body, measured by a thermometer.

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Tempering: the reheating and cooling of a metal to increase its hardness; used especially in connection with the hardening of steel.

Ternary (tûr'nȧ·rĭ): referring to a compound composed of three different elements such as H_2SO_4, $NaNO_3$, etc.

Theory (chemical): a general principle offered to explain certain phenomena.

Thermal (thûr'mȧl) **equation:** a balanced chemical equation which states the number of calories of heat given off or taken on in a chemical reaction.

Tincture: an alcoholic solution of a substance, such as a tincture of iodine.

Transmutation: the change which any radioactive element undergoes as it disintegrates into other elements.

Tribasic acid: an acid that contains three replaceable hydrogen atoms in its molecule, such as H_3PO_4.

U

Ultramicroscope: a powerful microscope specially designed to show the movement of some of the larger colloidal particles.

Ultraviolet light: the portion of the spectrum that lies just beyond the violet, and therefore of short wave length.

U. S. P. Chemicals: (*United States Pharmacopeia*)—referring to the standard of purity of chemicals which shows their fitness for medicine.

V

Valence (vā'lĕns): (a) the number of hydrogen atoms that an atom of an element will combine with or displace from a compound;
(b) the number of electrons that an atom gives up or adds when it combines with other atoms;
(c) the number of pairs of electrons which an atom shares with another atom.

Vitamins (vī'tȧ·mĭnz): complex organic compounds which are present in small amounts in certain foods; they act as catalysts in controlling certain body functions.

Volatile (vŏl'ȧ·tĭl): referring to a substance that evaporates readily.

Vulcanized rubber: crude rubber heated with sulfur to give it more desirable properties.

W

Water gas: a mixture of hydrogen and carbon monoxide, formed when steam reacts with glowing coal or coke.

Water of hydration (crystallization): water that is held in loose chemical combination with crystals; it can be driven off by heating to moderate temperature; an example is $CuSO_4 \cdot (H_2O)_5$.

Weak acids (or bases): acids (or bases) which show only a low degree of ionization in water solution.

Weighted silk: silk to which has been added a quantity of metallic salts.

X

X rays: radiations of very short wave length produced by the impact of electrons from the cathode of a vacuum tube striking a target.

Z

Zeolite (zē'ô·līt): any of a group of hydrated aluminum and calcium or sodium silicates, used to remove from hard water those compounds which produce hardness; used in home water-softening plants.

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APPROXIMATE ATOMIC WEIGHTS FOR CALCULATIONS

Element	*Symbol*	*Approximate atomic weight*	*Element*	*Symbol*	*Approximate atomic weight*
Aluminum	Al	27	Iodine	I	127
Antimony	Sb	122	Iron	Fe	56
Arsenic	As	75	Lead	Pb	207
Barium	Ba	137	Magnesium	Mg	24
Bismuth	Bi	209	Mercury	Hg	200
Boron	B	11	Nickel	Ni	58.7
Cadmium	Cd	112	Nitrogen	N	14
Calcium	Ca	40	Oxygen	O	16
Carbon	C	12	Phosphorus	P	31
Chlorine	Cl	35.5	Potassium	K	39
Chromium	Cr	52	Silicon	Si	28
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	63.6	Sodium	Na	23
Fluorine	F	19	Sulfur	S	32
Gold	Au	197	Tin	Sn	119
Hydrogen	H	1	Zinc	Zn	65

TABLE OF COMMON VALENCES

+1		*+2*		*+3*	
Ammonium	NH_4	Barium	Ba	Aluminum	Al
Hydrogen	H	Calcium	Ca	Antimony	Sb
Potassium	K	Copper	Cu	Arsenic	As
Silver	Ag	Ferrous	Fe	Bismuth	Bi
Sodium	Na	Lead	Pb	Ferric	Fe
		Magnesium	Mg		
		Mercuric	Hg		
		Zinc	Zn		

−1		*−2*		*−3*	
Acetate	$C_2H_3O_2$	Carbonate	CO_3	Phosphate	PO_4
Bicarbonate	HCO_3	Oxide	O		
Bisulfate	HSO_4	Sulfate	SO_4		
Bromide	Br	Sulfide	S		
Chlorate	ClO_3	Sulfite	SO_3		
Chloride	Cl				
Hydroxide	OH				
Iodide	I				
Nitrate	NO_3				
Nitrite	NO_2				

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293 - 300
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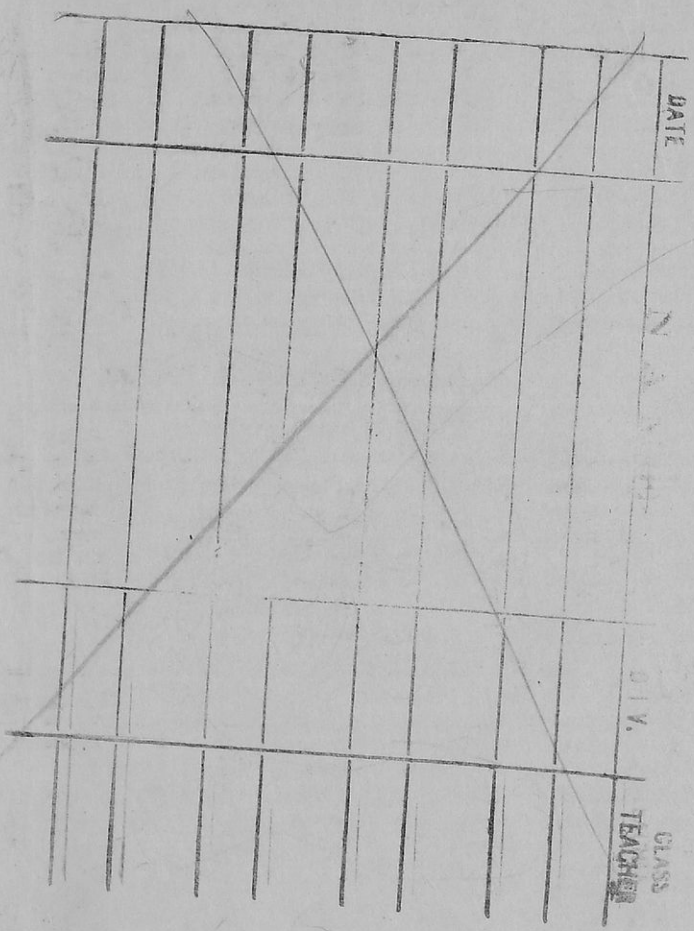

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