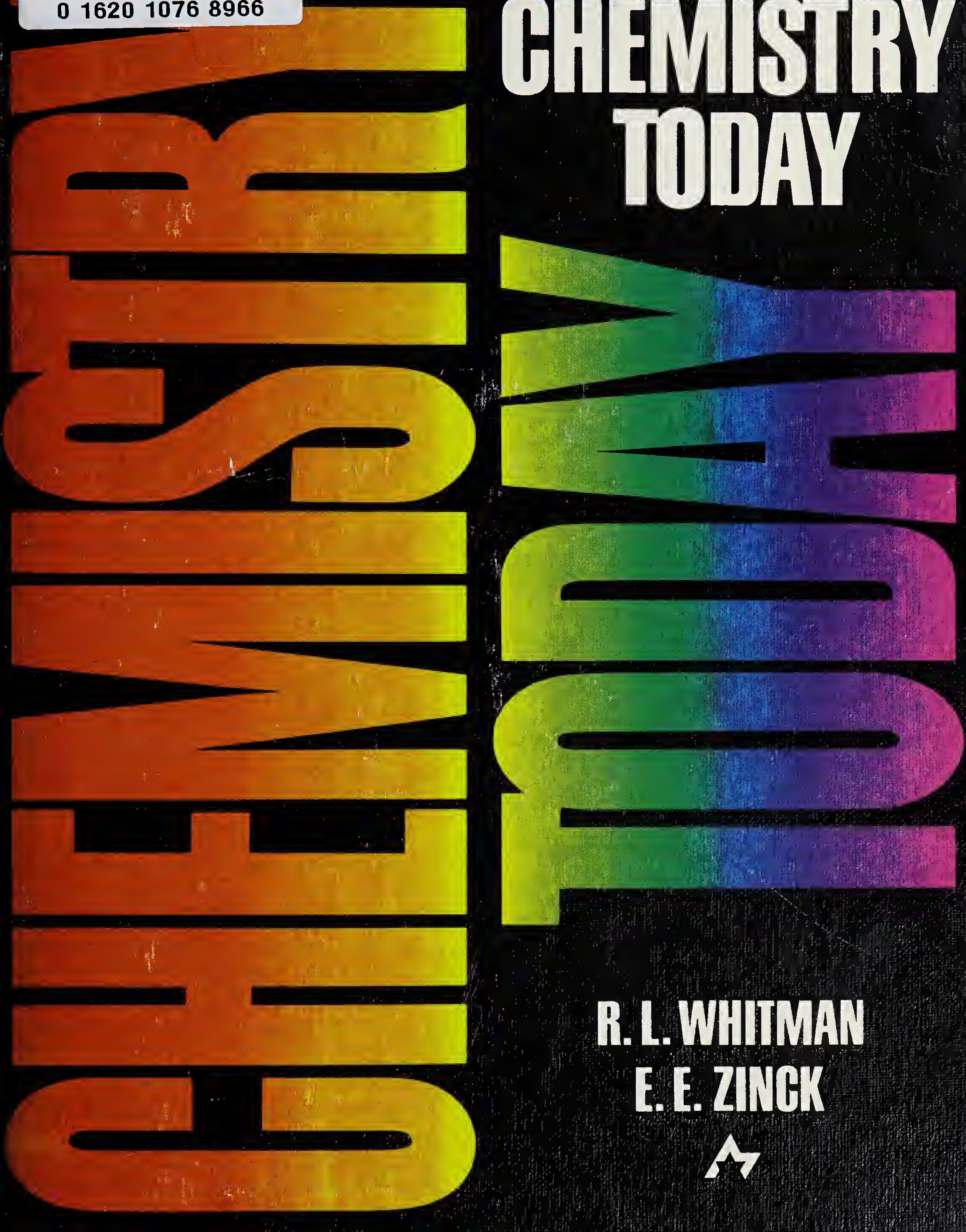
CHEMISTRY TODAY



R. L. WHITMAN
E. E. ZINCK

INTERNATIONAL ATOMIC MASSES

NAME	SYMBOL	ATOMIC NUMBER	ATOMIC MASS
Actinium	Ac	89	(227)
Aluminum	Al	13	27.0
Americium	Am	95	(243)
Antimony	Sb	51	121.8
Argon	Ar	18	39.9
Arsenic	As	33	74.9
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.8
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.1
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.9
Copper	Cu	29	63.5
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(254)

NAME	SYMBOL	ATOMIC NUMBER	ATOMIC MASS*
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	(237)
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.01
Nobelium	No	102	(255)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	(145)
Protactinium	Pa	91	(231)
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4

Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(253)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.2
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.00
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.8
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lawrencium	Lw	103	(256)
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Md	101	(257)
Mercury	Hg	80	200.6

*A value given in parentheses denotes the mass of the isotope with the longest known half-life

Scandium	Sc	21	45.0
Selenium	Se	34	79.0
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Tantalum	Ta	73	180.9
Technetium	Tc	43	(97)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten (Wolfram)	W	74	183.8
Uranium	U	92	238.0
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2
—	—	104**	(260)
—	—	105	(262)

**The names and symbols of elements 104 and 105 have not yet been agreed upon internationally.

CHEMISTRY TODAY

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PREFACE

This book is the result of our contention that an introduction to chemistry can be a valuable, interesting, and enjoyable part of anyone's educational background. We believe that an introduction to chemistry need not be so rigorous that it is suitable for only a small number of people. We also feel that many fundamental ideas in chemistry can be understood without relying on a purely mathematical treatment.

For some people this book may be their first and last look at chemistry. Nevertheless, we hope they will gain an understanding and appreciation of the nature of chemistry and the methods by which chemical knowledge is acquired. For those who will study further chemistry, the book is designed to provide a basic foundation for future studies in secondary and post-secondary programs.

In our presentation we have tried to show that chemical knowledge is gained slowly through the efforts of many people; that it is not an uncontrolled juggernaut rolling along of its own momentum. Chemical knowledge has accumulated through the centuries as a result of the continuing human effort to understand a part of nature.

The book begins with a general examination of science and the scientific method in Chapter 1. The second chapter attempts to show how chemical knowledge is acquired by tracing the development of the theory of combustion. Chapters 3 to 9 follow a relatively traditional pattern of developing chemical concepts such as the atomic theory, the periodic table, chemical bonding, chemical nomenclature, and chemical reactions.

The bulk of the mathematical topics in the book is contained in Chapters 10 to 12. Chapter 10 illustrates the use of the mole concept in chemistry, and Chapter 11 introduces the gas laws, followed by an extension of the mole concept to situations in which gases are involved as reactants or products. Finally, Chapters 13 to 16 (Organic Chemistry, Biochemistry, Chemistry and the Environment, and Nuclear Chemistry) deal with chemical topics which are useful, interesting, and relevant to today's readers.

There is more than enough subject matter in this book for a one-year introduction to chemistry, and it should not limit the scope of an introductory course. The teacher should and undoubtedly will feel free to modify the presentation to fit the needs of students.

For example, some teachers may prefer a less mathematical approach. They may wish to omit certain sections such as Chapters 10 to 12 which cover some of the more quantitative aspects of chemistry. We fully realize that teachers will not expect all their students to cover all the material in this text. It is our hope that CHEMISTRY TODAY will be a book that teachers can use without feeling hemmed in by a prescriptive type of presentation. Furthermore, we hope that students will find it a readable and enjoyable introduction to chemistry.

It is an impossible task for us to completely acknowledge our debt to all those who aided us in one way or another in what seemed at first like an impossible job. Many people made valuable suggestions for improving the book, from the time it was being prepared to its final stages of production. We thank them all for their contributions without holding them responsible for any flaws that still remain. We also thank Ada Crosby for her assistance in reading the final draft.

Lastly, we acknowledge the indispensable contribution of Gwen Whitman for her typing of the manuscript. Without her careful and competent help, our work would have been much more difficult.

R. L. Whitman

E. E. Zinck

1

INTRODUCTION

To live in the modern world is to be surrounded by the products of science. Among these are the color television, the bottle of aspirin, and the polyester shirt. We are exposed to the claims of advertisers: "It's 99 and 44/100% pure," or "Consumes 47 times its own weight in excess stomach acid." We hear conflicting or confusing statements that are supposed to come from scientists. For example, on one day it may be reported that LSD causes chromosome damage; a month later another report will suggest that LSD causes less damage to chromosomes than other common drugs. Some people, when faced with so many conflicting statements, simply close their minds to further scientific pronouncements. One Ontario fisherman, for example, when told about mercury contamination in Great Lakes fish, said that he had eaten the fish for many years, and he was still alive so he did not care at all about mercury poisoning.

Perhaps it would be nice to return to a less complex life style. However, we are citizens of one of the most technologically advanced countries of the world. We owe it to ourselves to become acquainted with the realities of life, and science is one of the most important of those realities.

We shall examine science in general and chemistry in particular. Some of you will be more interested than others. and this is natural. We make only one request. Give science the same chance that you would give to any other subject you have ever read or thought about. You will not be asked to like science, but it will be helpful to you if you develop some understanding of it.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Define and give an example of empirical knowledge.
2. State the differences between pure and applied science; state the value of each type; and give an example of each.
3. Identify examples in a list as examples of pure science or technology.
4. List the steps in the traditional scientific method.
5. Explain why methods other than the traditional scientific method are appropriate for the investigation of nature.
6. List and explain four requirements of scientific observation.
7. Explain what is meant by an anomaly, and why an anomalous event must not be disregarded.
8. Explain the differences between a law, a theory, and a model, and identify examples of each.
9. Explain and give an example of the concept of universality.
10. List four imperfections that make science a human pursuit.
11. Describe the general nature of chemistry and its place among the sciences.

1-1/WHAT IS SCIENCE?

Science is a human activity which is directed towards gaining new knowledge about the composition and the functioning of matter, both living and nonliving. Scientific knowledge is mainly empirical. **Empirical knowledge** is knowledge gained by using the senses (Fig. 1-1). It is knowledge gained by seeing, tasting, feeling, hearing, or smelling. It is not the only type of knowledge. Other types of knowledge are revealed knowledge, authoritative knowledge, intuitive knowledge, and rational knowledge. Revealed knowledge is knowledge we accept on faith, e.g., the Bible. Authoritative knowledge is knowledge gained from experts. Intuitive knowledge is know-

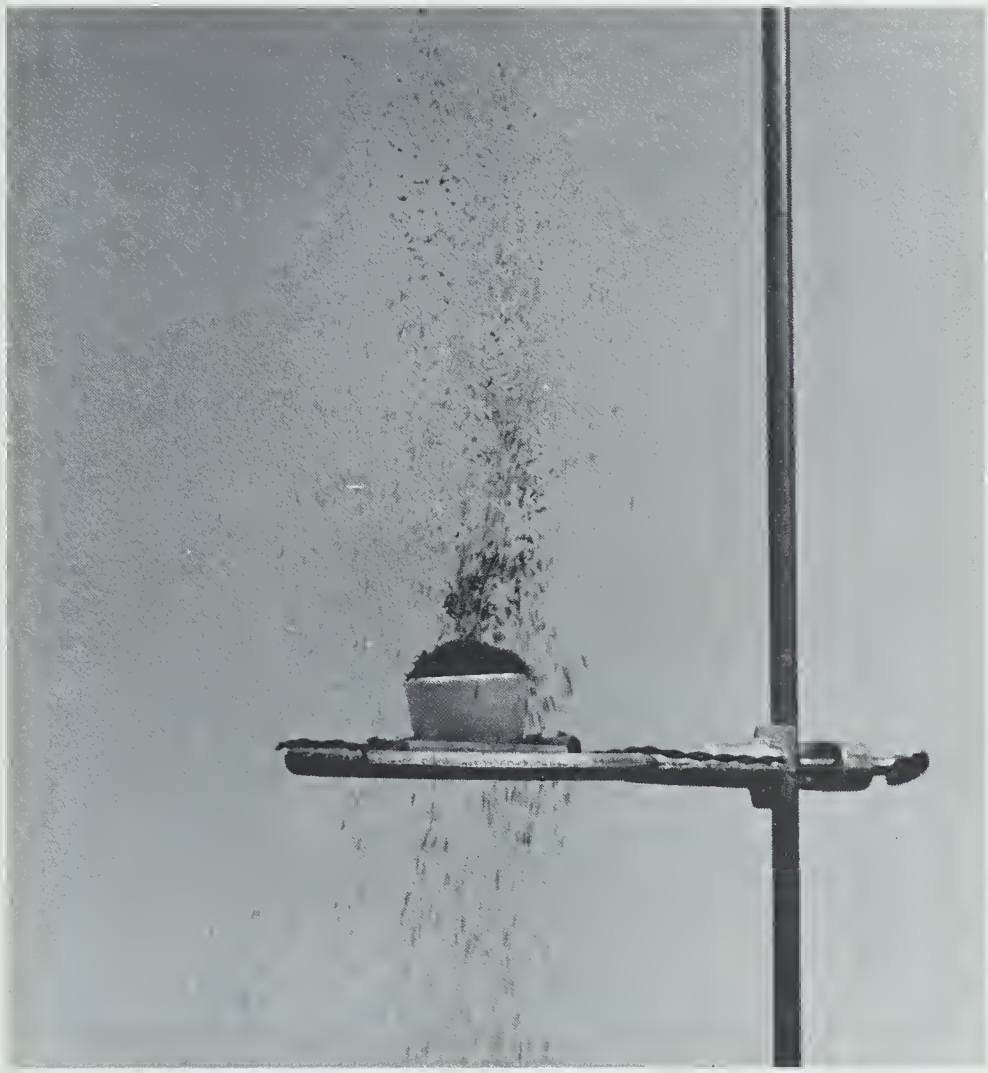


Fig. 1-1 Empirical Knowledge
We can easily see *that a chemical reaction is occurring in this decomposition of ammonium dichromate.*

ledge that you already have but probably do not know from where it came. Rational knowledge is knowledge based on certain logical truths. Scientific knowledge is gained from observation. Observation is the main activity of science, and this is what separates science from other human endeavors.

Let us now establish what science is not. Science is not the telephone or the dacron shirt or the plastic heart valve. In short, science is not gadgetry. Gadgets, in many cases, have improved our lives. In most instances, these improvements have been made possible by scientific knowledge. However, gadgets do not constitute science.

Many accomplishments of science appear to be mysterious to those who are not directly involved in it. Thus, some people regard it as a sort of modern-day witchcraft. These people look at scientific advances with some fear. On the other hand, some people, noting the accomplishments of science, suggest that it will be able to solve all of the problems of mankind. We might hear such statements as, "If the government would spend money for scientific research here on earth instead of wasting it on the moon, scientists could cure the ills of society." It is, in fact, much easier to put a man on the moon than it would be to find a sure way of solving some of mankind's problems, such as poverty or prejudice. Scientists can make great contributions in the field of human welfare, but science will not be able to solve all the problems of mankind. Therefore, science is neither a cure-all nor is it witchcraft.

Finally, science is not merely technology. Technology is directed towards the accomplishment of specific purposes. Getting a man on the moon and building a nuclear power

Fig. 1-2 A Canadian Cancer Therapy Machine
Atomic Energy of Canada Limited (AECL) has been the pacesetter in the development of radiation equipment for cancer therapy. (Photo courtesy of Princess Margaret Hospital)

station are examples of technology. It is true that to a large extent technology depends on scientific knowledge, and in a converse manner, technological problems often stimulate scientific research. However, science is not merely technology.

There are two types and two values of science. First, science is valuable in that it reveals to man the nature of the universe in which he is placed. It helps man to understand. **Pure science** is directly related to this value. The large number of ways in which man's comfort, convenience, and health are enhanced by scientific discoveries indicates the second important value of science (Fig. 1-2). **Applied science** or **technology** is related to this value. However, we must realize that pure science is an essential basis for technology (Is technology an essential basis for pure science?). For example, pure research revealed that the addition of sulfur to rubber improved the durability of the rubber. This information now forms the basis of the process of vulcanization. Vulcanization is part of the technology associated with the rubber industry. In this book, the word *science* will be used to mean pure science or pure research. The word *technology* will denote applied science.

1-2/THE METHODS OF SCIENCE

In the past, writers of introductory texts have, in their desire to clearly describe the scientific method, given readers the impression that there is only one acceptable method. They have implied that all scientists use the same method. This is unfortunate because it makes science look as if it were purely mechanical. Some readers may even feel that using the scientific method is an excuse for not thinking.

The traditional form of the scientific method is first observing nature, then seeking the regularities in the observations, formulating a hypothesis (a tentative explanation of the regularities), experimenting to test the hypothesis, and finally constructing a theory. This is a good method and it may be acceptable to some scientists. However, any method which is a combination of curiosity and imagination and which uses experimentation to look for regularities in nature will be an acceptable method for scientists to use.

Scientists usually call their investigations research projects. One researcher might plan his project very carefully. He might contemplate his method, ideas, and proposed experiments for days. For this man, science is like a chess game—every move is carefully considered. Another scientist might be impatient and wish to get on with the job so that he can test out a hunch. There may be some aspect of the problem that has him so curious that he cannot wait to try and find some answers. Thus, the method that a scientist will use really depends on his personality.

However, there are some rules that scientists must follow if the results of their research projects are to be acceptable to other scientists. Since observation is the very lifeblood of

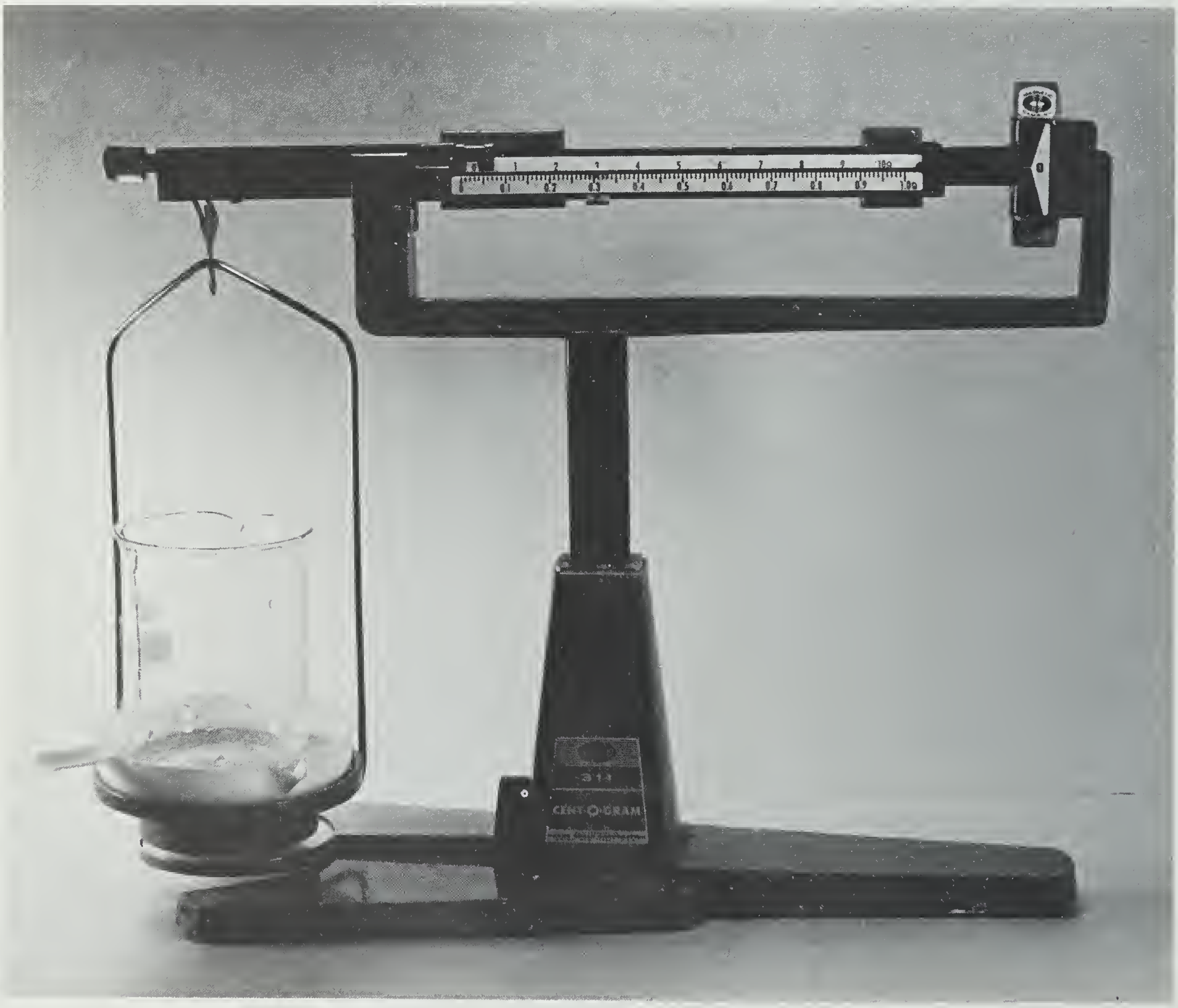


Fig. 1-3 The Importance of Accuracy
Is the mass of this beaker being determined accurately?

science, these rules apply particularly to it.

First, a scientist must be **accurate** in his observations. If he is trying to measure the weight of a container, he must be sure that it is clean and dry. If the container holds a few drops of water, then he will obtain the weight of the container plus the weight of the water, not the weight of the container alone. In other words, it is important that he measure what he says he is going to measure, not something else (Fig. 1-3).

Second, observations must be **precise** (Fig. 1-4). If a scientist is trying to measure the volume of a container, a measure-

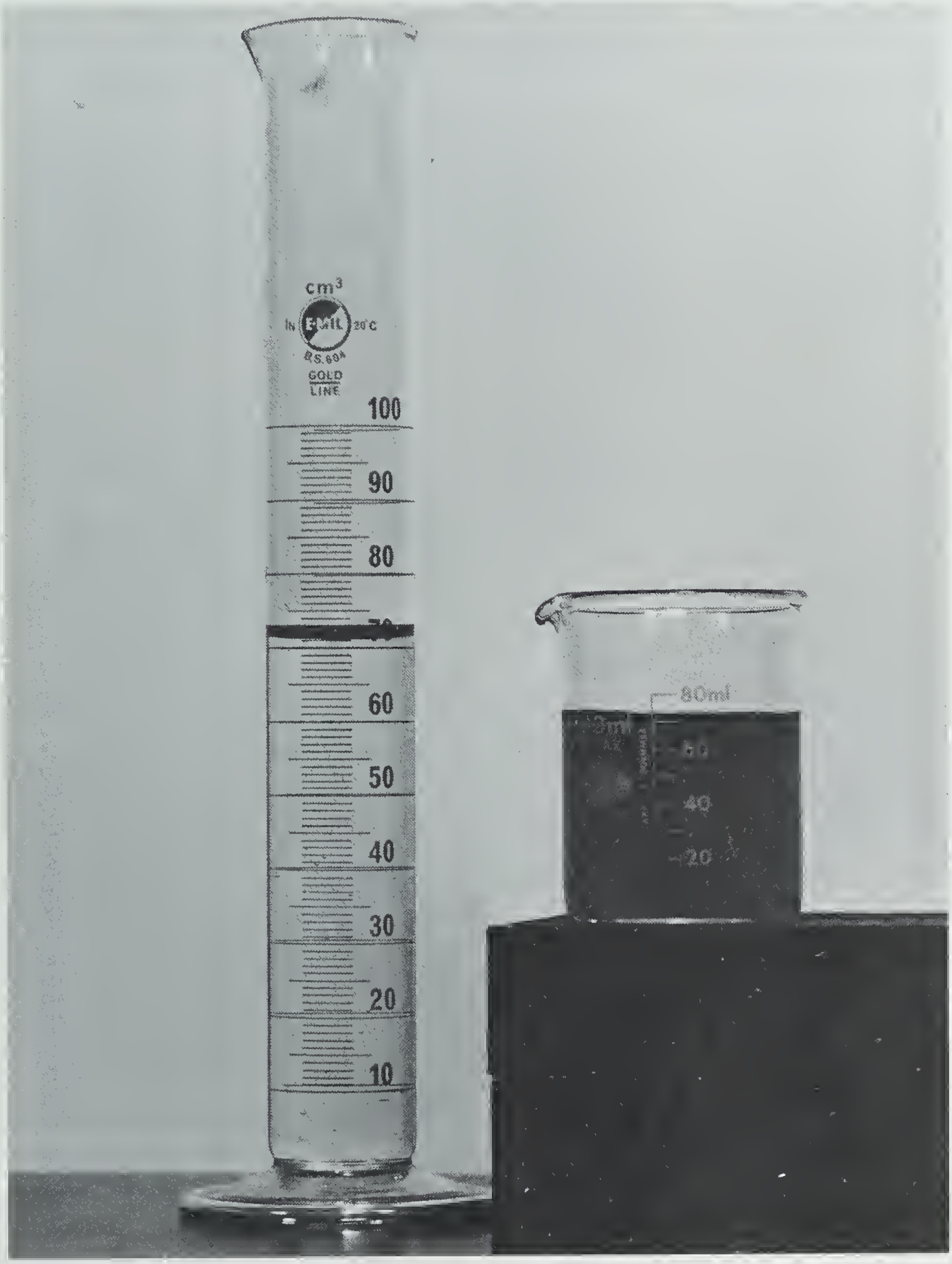


Fig. 1-4 The Importance of Precision
Which of these containers measures volume more precisely?

ment of 1.312ℓ is more precise than a measurement of 1.3ℓ. The distinction between accuracy and precision is important to a scientist.

Third, a scientist is expected to be **objective** in his observations. If he does five similar experiments that all give the same answer, and then does a sixth that gives a different answer, he is not allowed to discard the different or anomalous (irregular) result. Scientists believe that nature is not capricious. That is, nature does not try to trick men by causing events to happen one way on ninety-nine occasions and another way on the hundredth occasion for no reason at all. There must be a logical explanation for an anomalous event. Time and time again scientists have found that what they thought was an anomaly was really due to a lack of knowledge. Often an anomaly will lead to a new set of observations which might well add to our understanding of nature. Consequently, since anomalous events can turn out to be disguised blessings, it is the scientist's duty to report faithfully all of the observations which he makes (unless, of course, he can see that he made a mistake in his experiment).

Fourth, measurements must be **reproducible**. Scientists believe that all measurements made of the same object or event under the same conditions must agree regardless of when or by whom the measurements are made. This concept of reproducibility follows from the idea that nature is not capricious.

Once the scientist has made his observations, he seeks regularities. **Laws** are statements of regularities found in observations made on living and nonliving systems. Laws are a matter of convenience and are not proven beyond a shadow of a doubt. Often scientists accept a law because it is useful in anticipating or predicting what will happen if a certain experiment is performed. Occasionally a law has to be modified to explain some new observation. Scientists are not overly upset that the established law has to be modified. Over the years, they have become used to the necessity of changing or discarding scientific laws as a result of the discovery of new knowledge.

A law is a rule that nature appears to follow. However, a scientist is not satisfied with the law alone. He wants to know more about the underlying principles associated with the law. A **theory** is a guess at the underlying principles which can "explain" the group of related observations (the law).

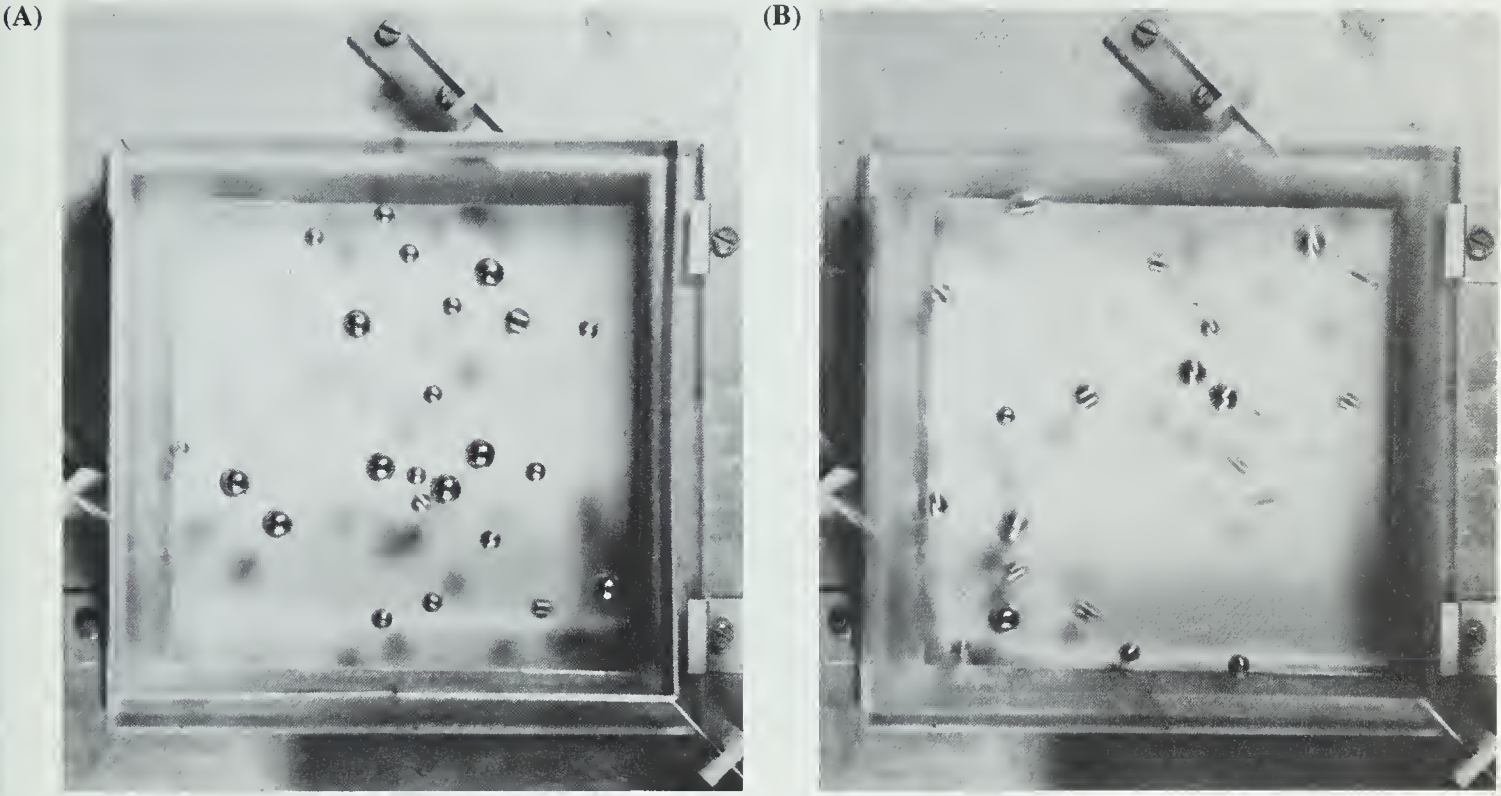


Fig. 1-5 A Model
This model is used to illustrate the movement of gas molecules. Ball bearings are kept in continuous motion by the vibrating walls of the container. **(A)** *This represents slower-moving molecules at a lower temperature.* **(B)** *This represents faster-moving molecules at a higher temperature.*

Many times we must theorize about events that are too small or too large for us to see. A **model** is a visualization of these events (Figs. 1-5A and 1-5B). Thus, models are useful in helping us to understand a theory. For example, the modern theory of gases is the Kinetic Molecular Theory. This theory has, as some of its postulates (basic assumptions), the statements:

(a) Gases are made up of small particles called molecules.
(b) These molecules are in rapid random motion.
(c) They move in straight lines until their directions are changed by collisions.
(d) These molecules are widely separated.

As we cannot see these atomic-sized particles, it may be difficult to visualize them. We may resort to a model. We might visualize a closed room with a few ping-pong balls constantly moving around the room, colliding with the walls of the room and occasionally with one another in a random manner. These never-stopping ping-pong balls might constitute an acceptable model to help us understand the motion of gas molecules in a container. Of course, the model is not perfect. In reality, the ping-pong balls would fall to the floor and remain there.

Let us be clear about one thing. Theories and models, like laws, must come under constant inspection. There may be events that a certain theory cannot explain. The theory may have to be altered or discarded. Models, too, may need revision.

Moreover, models are only visualizations of the real thing. They are products of the scientists' imaginations. There may be an observation that will not fit a model or theory. We again use the word *anomaly*. The anomalous observation may contradict the accepted theory or model, but it cannot be disregarded. If the experiment was performed correctly, and if the observation was made correctly, this irregular behavior may serve as the basis for either a new theory or a modified theory. Scientists have their "pet theories," and often they argue strenuously for them; but in the final analysis, they realize that all theories must be put on display for other scientists to examine. Scientists realize that no theory or model will ever be a perfect explanation of the events it was constructed to explain.

Thus, scientists have found that it is useful to stop and think, to suspend one's prejudices (insofar as it is possible) in order to find relevant facts. They have found that anomalies cannot always be disregarded, and they believe that nature is not capricious. Successful scientists, like successful men in other occupations, possess high standards of honesty, a desire to know the truth, open-mindedness, and focused vision. Needless to say, not all scientists will measure up to these exacting standards; however, those who do are usually the great ones.

1-3/COMMUNICATION AND SCIENCE

One of the main reasons for the recent rapid growth of scientific knowledge is that scientists are now able to communicate with one another very quickly. They are able to exchange experimental observations, and they are able to exchange hunches and theories. Each scientist is obligated to communicate his findings to other scientists. This is most often done by written descriptions which are published in scientific journals. These journals are published in countries

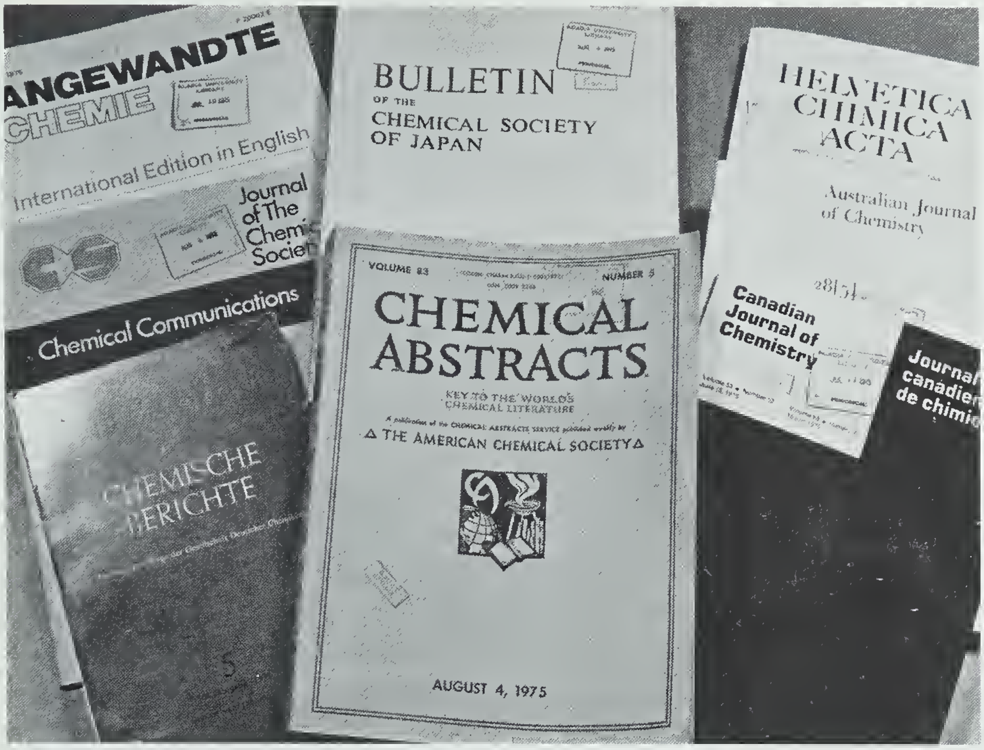


Fig. 1-6 Some International Chemical Journals

all over the world (Fig. 1-6). They contain descriptions of recent scientific research and are published weekly in some cases, but usually monthly. Because they are published frequently, these journals are reasonably up-to-date. Books are also used to communicate scientific information; however, scientific knowledge is growing so rapidly that books are often out-of-date as soon as they are issued. Scientists often communicate their findings by lectures given at annual meetings of the various scientific societies, and occasionally special symposia are organized so that scientists investigating a certain area (e.g., cancer research) can meet and discuss their research.

Thus, because scientists communicate, scientific knowledge is cumulative. Ideas from previous generations are used to construct modern theories. Scientists are not required to start from square one. They are able to build on what has already been learned, and there is much to learn. This is the reason for the long period of training required by a modern scientist.

In order for scientific communication to be effective it must have **universality**. That is, it must be interpreted the same way in London as it is in Tokyo. A work of art need not have this universality; and, in fact, it could lose its appeal if everyone interpreted it the same way.

One of the best ways for scientists to communicate is by mathematical equations. In fact, mathematics is the language of science, and mathematics adds to the universality of science. You have probably heard of Einstein's equation, $E = mc^2$. This is understood by all scientists throughout the world to mean that energy equals mass times the square of the speed of light. It can be restated in the form of a ratio $E/m = c^2$. This means that the ratio of E to m will always be equal to the same value, c^2, regardless of the size of the quantities involved.

For these mathematical ratios to have universality, scientists must all use the same units of measurement. International organizations of scientists have agreed to use SI (from the French name, Le Système International d'Unités) units which include the metre (length), kilogram (mass or quantity of matter), and second (time). There are also units for energy, electric current, pressure, temperature, and others. These units are precisely defined. For example, the Handbook of Chemistry and Physics gives the following definition of the standard kilogram: "the kilogram (unit of mass) is the mass of a particular cylinder of platinum-iridium alloy, called the International Prototype Kilogram, which is preserved in a vault at Sèvres, France, by the International Bureau of Weights and Measures." The metre is defined as 1 650 763.73 wave lengths in vacuum of the orange-red line of the spectrum of krypton-86. By contrast, until recently, railroads all over the world have had no standard measurement for the distance between rails. Consequently, rail cars manufactured in Europe could not be used in North or South America. One could imagine similar difficulties for scientists if each country had its own units of measurement.

Some scientific knowledge cannot be communicated by mathematical equations and must be communicated by means of analogies. An analogy expresses a likeness. We may say that gas molecules in motion are like ping-pong balls bouncing in a room. We may say that radio waves are like water waves. Analogies are useful in science, but they do not have the universality that an equation would have. However, there are times when analogies are the only means of communicating scientific ideas.

1-4/SCIENCE AS A HUMAN PURSUIT

Science has had an impressive number of successes. Physical scientists discovered the planet Pluto by predicting its location from observed anomalies in the orbits of Uranus and Neptune, and then searching that area of the heavens until they were able to find the new planet. They have also begun to explore the mysteries of the atom and have even converted matter to energy. Physical scientists have also used atoms to build many new substances (compounds). As impressive as the achievements of the scientists who deal with matter and energy are, it may be that the scientists who deal with living matter are on the verge of even more spectacular discoveries, possibly the very secret of life.

Perhaps because of its tremendous successes, some people fear science. To these people, science seems to be an all-powerful and all-conquering monster—almost inhuman. There seems to be no end to the mysteries of the universe that are solvable by the methods of science. But is science really so inhuman? We know that human pursuits have their limitations; they are not perfect. Is science perfect? Are there any weaknesses in the way in which science proceeds?

There are a number of imperfections that make science very human indeed. First, science is made up of theories, none of which constitutes an ultimate explanation. For example, merely because we are told that radio waves are like water waves, we are not justified in feeling that we completely understand radio waves. This kind of explanation by analogy is certainly not perfect. Furthermore, explanation by mathematical equation is not perfect either. We may understand that matter is related to energy according to the equation, $E = mc^2$, but that does not explain why matter is related to energy. Thus, science does not have the final answers.

Second, scientists do not all agree about some of the most fundamental aspects of science. This imperfection shows that science is not an inhuman endeavor. It is a very human enterprise, and the disagreements of scientists with one another reflect the same kind of diversity that one finds in art or music.

Third, perfect accuracy in measurements is not possible. If every member of a town were to measure the same object, a number of different measurements would be obtained. Thus, the average measurement would have to be used in any calculations. But who can prove that the average value is the true value?

Fourth, perfect objectivity in scientific measurement is a fond dream of the scientists. No scientist can remain completely objective as he gathers his data. He might have some bias of which he is not even aware. It is a scientist's duty to try to be objective, but scientific knowledge cannot be completely impersonal.

The value of science is real. It is a human activity which attempts to deepen our understanding and our appreciation of nature. It emphasizes honesty and clarity of thinking. It is related to the economic prosperity and the general cultural life of a country. However, science is not hard facts, nor is it unassailable truths.

Even the scientific method, which skeptics suggest hampers creativity, is merely a mind-freeing method. In fact, the method gives the scientist an opportunity to be creative. It has solved the problem of the relationship between freedom and discipline. A scientist is free to test out any hunch knowing that the method will expose any mistakes and will help to guide him on to the next step. Science joins hands with other forms of human activity by learning from its own mistakes.

1-5/ENTER CHEMISTRY

Until now chemistry has not really been mentioned. Science in general has been discussed. No apology is made for this because the division of science into chemistry, physics, geology, and so on is an artificial one. They are all very much alike and very much related. In fact, sometimes it is difficult to distinguish between physical chemistry and chemical physics, or between biochemistry and molecular biology.

However, the divisions have been made because it is really impossible for one person to be a master of all science. Thus, scientists have been forced to specialize. Many of them specialize because of necessity rather than desire.

Therefore, what has been said about science in this chapter applies to that subdivision of science called chemistry. The methods of chemistry are the methods of science.

It might be interesting for us to examine the place of chemistry in science. Imagine a ladder (Fig. 1-7). At the bottom of the ladder, on the first rung, is mathematics. This discipline has selected from the real world only a limited number of simple concepts such as number, order, and dimensionality. This is not to say that mathematics is necessarily simple to learn; however, the concepts that the mathematicians work with are simple.

On the rung above mathematics is placed physics. Physics retains the concepts of mathematics and adds further concepts selected from the real world. Matter, energy, and electricity are some of the concepts that physics adds to those of mathematics.

By including the further concepts of different kinds of matter and of transformation from one type of matter to another, we arrive at the discipline of chemistry. Chemistry makes use of all of the concepts of mathematics and physics. Because chemistry has selected more concepts of study, it is more complex than either mathematics or physics. This does not mean to imply that chemistry is more difficult to learn than either physics or mathematics. Complexity and difficulty are not synonymous. In fact, because chemistry deals with more concepts selected from the real world (a world we all know reasonably well), it is for many people easier to learn than either physics or mathematics.

Let us go up the ladder in order. If we further select the concept of living matter, we leave the physical sciences and enter the area of biology, and if we go one step further to mental behavior, we are dealing with psychology. If we keep adding more concepts selected from the real world, we come to the social sciences.

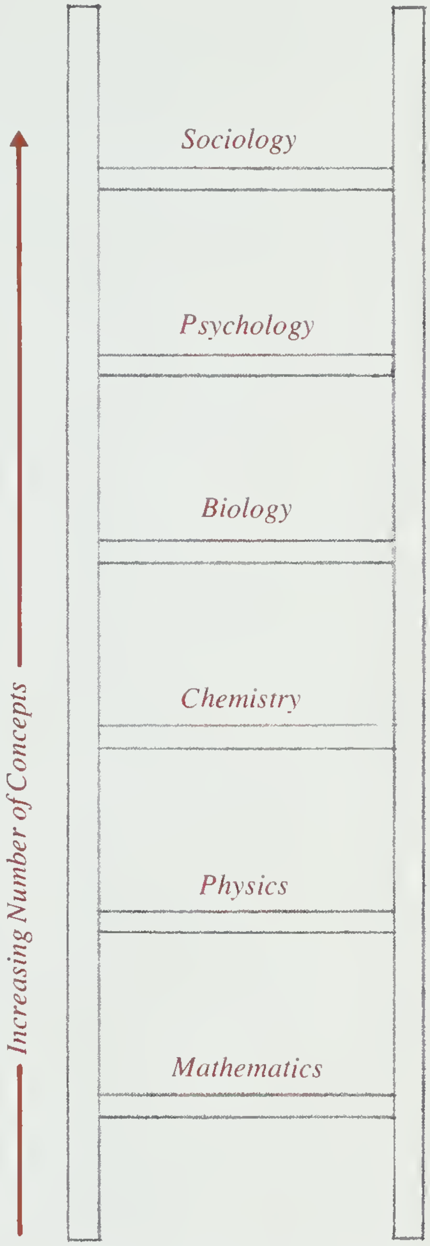


Fig. 1-7 The Science Ladder

QUESTIONS

1. Which of the following are best considered as examples of science, and which as examples of technology? Why?
   (a) The transistor has almost completely replaced the vacuum tube in its applications.

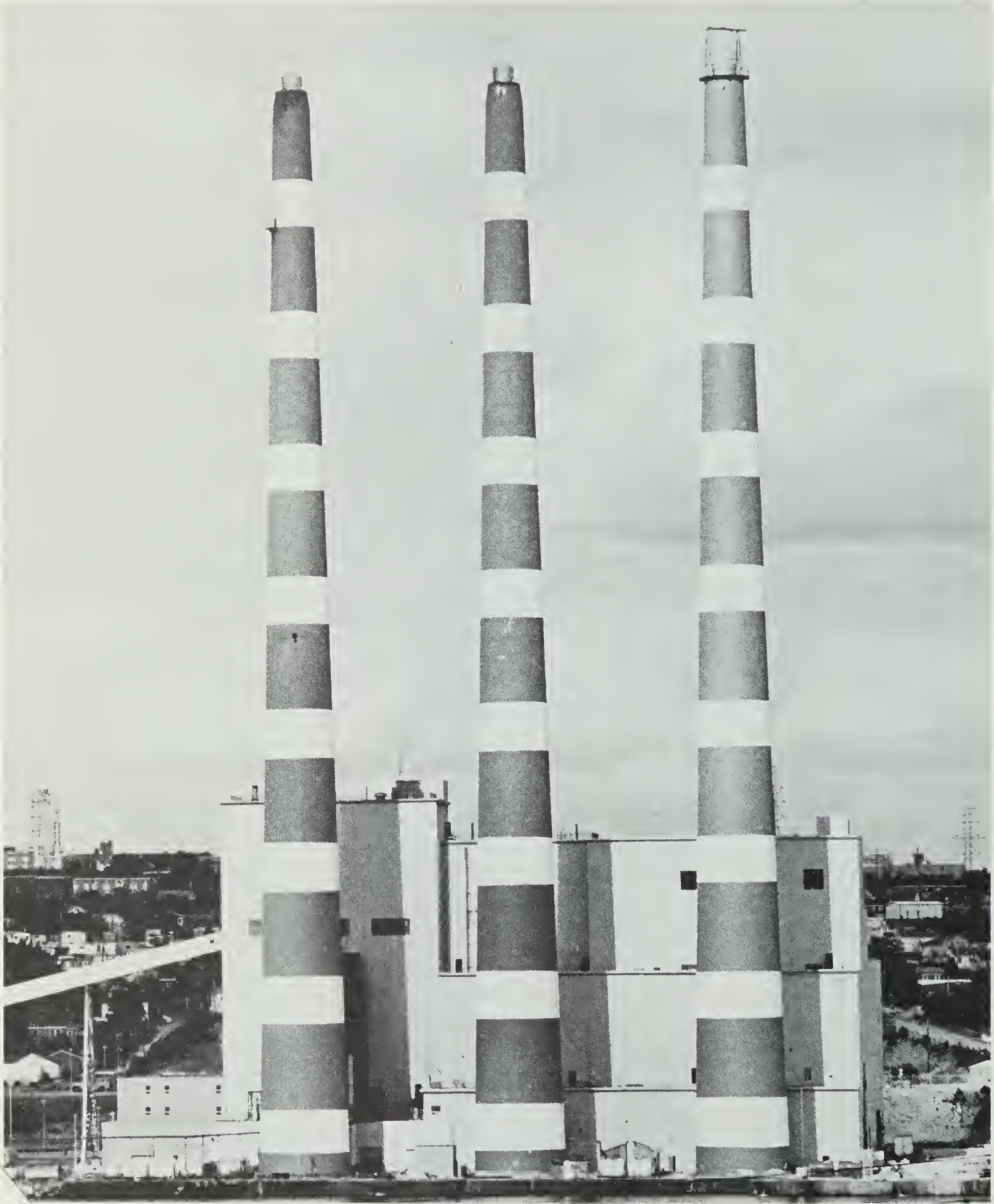
   - (b) It has been found that some of the so-called inert gases will react with fluorine.
   - (c) Fluoridation of drinking water appears to significantly decrease the incidence of tooth decay in children.
   - (d) Safe nuclear reactors will have to be designed to replace thermal electric generating stations due to an increasing scarcity of fossil fuels.
   - (e) In 1942 Enrico Fermi constructed the first atomic pile in order to prove that nuclear fission could be controlled.

2. What are two types of science? What is the value of each type? Give examples of each.
3. What is the most important activity of the scientist?
4. What is an anomaly? Why must an anomaly not be disregarded?
5. What is a scientific method? Are all scientists likely to use exactly the same method? Why or why not? Is there an activity that is common to all scientists?
6. Why are scientists forced to assume that nature is not capricious?
7. Which of the following statements is best considered as a law, and which as a theory?
   - (a) The pressure exerted by a given volume of a gas is directly proportional to its Kelvin temperature, provided the volume remains constant.
   - (b) Gases are made up of small particles called molecules.
   - (c) In all chemical reactions so far studied the total amount of matter remains constant.
   - (d) A solution of salt in water conducts electricity because the salt has dissociated to form mobile positive and negative particles.
   - (e) Carbon monoxide is poisonous because it prevents the hemoglobin in the blood from carrying oxygen to the tissues.
8. Why would one use a model when describing a scientific theory?
9. What is empirical knowledge?
10. Why do scientists feel they must exchange their findings and theories with one another?
11. The concept of universality illustrates one of the differences between science and art. What is this difference?

12. "Even the scientific method, which skeptics suggest hampers creativity, is merely a mind-freeing method." How is the scientific method a mind-freeing method?
13. Briefly discuss three of the imperfections of science which make us realize that science is no better than any other activity of mankind.
14. Why do scientists go to such great lengths to define their units of measurement accurately?
15. What is chemistry?

QUESTIONS TO THINK ABOUT

16. The Nobel prize-winning chemist Linus Pauling has maintained that massive doses of Vitamin C are effective in preventing colds. Other scientists disagree with this hypothesis. What kind of experiments would you plan in order to prove or disprove Pauling's theory?
17. If technology is the application of science to industrial or commercial objectives, can there be a similar technology which applies to either art or music? Support your answer with examples.
18. As opposed to art, science is an activity in which people no longer depend on individuals of ever-increasing genius for progress. Instead they build on the successes of their predecessors. To what extent do you agree with this?



2-1 A Thermal Electric Generating Station

at Dartmouth, Nova Scotia, this oil-fired thermal generating station produces 200 MW of power.

2

A CASE HISTORY OF SCIENCE

Chemists have studied combustion for hundreds of years, and they have used several theories to explain it. The purpose of this chapter is to follow the development of the modern theory of combustion in order to study the strategy of science.

At first fire was undoubtedly terrifying, but as men learned to control it, they discovered its usefulness. For example, fire was used to convert some types of stone into metals, and this allowed mankind the use of metals for weapons and cooking utensils.

Today, fire is a familiar part of our lives. Some of our electric power is generated by means of the burning of fuels (Fig. 2-1). Our cars are powered by internal combustion engines. Many of our homes use heating systems which are oil- or gas-fired.

Combustion is a phenomenon of considerable interest to chemists. After all, one of the main functions of the chemist is to attempt to gain an understanding of nature in general and the transformation of matter in particular. Combustion processes involve transformation of matter. For example, many combustion reactions involve the transformation of solid or liquid matter, such as coal or oil, into the gases carbon dioxide and water vapor.

The chapter will begin with the modern theory of combustion. This will be followed by a description of the efforts made by a number of scientists to develop this theory.

When you have finished studying this chapter you should be able to attain the following objectives:

1. State the assumptions of the modern theory of combustion.
2. Propose explanations for reactions involving oxygen, in terms of the modern view and of the phlogiston theory, and write word equations for these reactions according to both viewpoints.
3. Using the development of the modern theory of combustion, give an example of prejudice preventing the acceptance of a plausible theory.
4. Using the development of the modern theory of combustion, give an example of a delay in the acceptance of a plausible theory due to the lack of suitable experimental techniques to test the postulates of the theory.
5. Using the development of the modern theory of combustion, give an example illustrating that a single contradictory fact does not destroy a complete theory.
6. Describe the experiments by which Lavoisier proved that combustion of a substance involved its combination with oxygen.

2-1/THE MODERN THEORY OF COMBUSTION

Air is mostly a mixture of nitrogen and oxygen, but nitrogen does not play a significant role in combustion. **Combustion** is a process *normally* involving oxygen,* which produces energy in the form of heat and light.

Many combustible materials are substances containing carbon and hydrogen. Acetylene, propane, and gasoline are examples. It is possible to write a word equation which is useful in describing many combustions:

$$\begin{array}{lclclclcl}
\text{Combustible} & + & \text{Oxygen} & \xrightarrow{\Delta} & \text{Carbon} & + & \text{Water} & + & \text{Energy} \\
\text{Material} & & & & \text{Dioxide} & & & & \\
\text{(containing} & & & & \text{(oxide of} & & \text{(oxide of} & & \text{(heat and} \\
\text{carbon and} & & & & \text{carbon)} & & \text{hydrogen)} & & \text{light)} \\
\text{hydrogen)} & & & & & & & &
\end{array}$$

---

* Combustion may also involve other oxidizing substances.

The arrow is read *yields*, and the triangle above the arrow indicates that the substances must be *heated* or *ignited* in order for them to react. This corresponds to lighting a propane torch with a burning match.

Another example of combustion is seen in the reaction of certain metals with oxygen in the air:

$$\text{Metal} + \text{Oxygen} \xrightarrow{\Delta} \text{An Oxide of the Metal} + \text{Energy (heat and light)}$$

This oxide is a compound formed by the combination of a metal and oxygen. The burning of magnesium is an example of the formation of a metallic oxide (Fig. 2-2).

Fig. 2-2 Combustion of Magnesium
Magnesium burns with a brilliant white flame to produce a white powdery product.

A metallic oxide can be converted back to a metal. When a metallic oxide reacts with carbon, the oxygen leaves the metal and moves to the carbon:

$$\text{Metallic Oxide} + \text{Carbon} \xrightarrow{\Delta} \text{Metal} + \text{Carbon Dioxide}$$

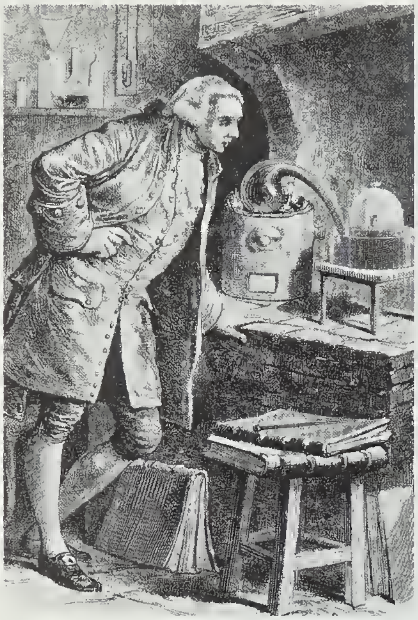


Fig. 2-3 Antoine Lavoisier (1743-1794)
(Photo courtesy of The Bettmann Archive)

Also, when a metallic oxide reacts with hydrogen, the oxygen moves from the metal to the hydrogen forming the oxide of hydrogen, water:

$$\text{Metallic Oxide} + \text{Hydrogen} \xrightarrow{\Delta} \text{Metal} + \text{Water}$$

This may seem easy to understand; however, it would have been impossible two hundred years ago to meet a scientist capable of recognizing fire as being caused by a chemical reaction between oxygen in the air and the substance which was burning. It is not that scientists of that day were ignorant or unconcerned about combustion. Rather, they had a theory of their own which was useful to them. It was left to a French chemist, Antoine Lavoisier (Fig. 2-3), to build up the modern theory of combustion from the information that he and other scientists were able to gather.

Lavoisier has been highly praised for his work in this field. Many consider him to be the father of modern chemistry. In this chapter, as we follow the development of the theory of combustion, we shall start with the phlogiston theory.

2-2/THE PHLOGISTON THEORY

Several early civilizations—Chinese, Hindu, and Egyptian—had developed a form of chemistry which was concerned mainly with practical arts. Metallurgy, fermentation, glass making, and preparation of explosives were techniques that their societies had mastered. A large amount of information was associated with these technologies. Later, the alchemists acquired a large number of facts as they attempted to change some metals into gold (Fig. 2-4). As time passed men tried to systematize this accumulated information.

In 1661 the Englishman, Robert Boyle, published a book entitled "The Sceptical Chymist." He differed from many of the scientists of his day in that he asked questions of nature which took the form of planned experiments. His contemporaries merely made observations and speculated as to their meaning. Boyle's work was an important step in the development of a useful scientific method.

Fig. 2-4 The Alchemist
(Photo courtesy of Fisher Scientific Company)

Some of the observations made by Boyle and his contemporaries were:

(a) Sulfur merely melts and fumes when heated in the absence of air.
(b) Some materials such as sulfur and carbon burn when heated in air.
(c) Metals can be obtained by heating certain materials called earths or **calxes** in the presence of carbon.
(d) Some metals form calxes when they are heated in air. (This process was called *calcination.*)

At the beginning of the eighteenth century (around 1703), two German chemists, Johann Becher and Georg Stahl, proposed a theory which explained these observations. The theory was based on the assumption that a common "something" was involved in the process of converting calxes to metals and vice versa. This common something was called **phlogiston**, and it was thought to be present in all metals and in all combustible materials.

Substances that were supposed to be rich in phlogiston burned easily and produced fire. Thus, because carbon (or charcoal, as it was called) burned in air it was said to be rich in phlogiston:

$$\text{Charcoal} \xrightarrow{\Delta} \text{Phlogiston (escapes into the air)} + \text{Fire}$$

Since calxes were abundant in nature, and metals could be made from calxes, it was believed that calxes were simple materials, and that metals were made by adding phlogiston to calxes. Because charcoal or carbon was so rich in phlogiston, it would readily give the phlogiston to a calx so that a metal could be formed:

$$\text{Calx} + \text{Phlogiston (from carbon)} \xrightarrow{\Delta} \text{Metal}$$

Then, if phlogiston were removed from a metal, a calx was reformed and the phlogiston went into the air:

$$\text{Metal} \xrightarrow{\Delta} \text{Calx} + \text{Phlogiston (escapes into the air)}$$

A lighted candle placed in a bell jar will burn for a while and then go out. An eighteenth century professor would have suggested that the air had received as much phlogiston from the burning candle as it could hold. He would have said that the air in the bell jar had become completely "phlogisticated." (What would we say today?) He would have suggested that the bell jar had prevented the escape of the phlogisticated air and that if the bell jar were lifted, phlogisticated air could leave and allow the candle to burn.

In the same way, a mouse placed under a bell jar soon dies. An eighteenth century professor believed that respiration involved the exhaling of phlogiston. Since the air in the bell jar would soon become saturated with phlogiston, the mouse would not be able to rid its body of phlogiston and death would occur.

2-3/FLAWS IN THE PHLOGISTON THEORY

Often certain observations do not fit a theory. This was true in the case of the phlogiston theory. In fact, one flaw in the phlogiston theory was known to chemists for 150 a (years) before the theory was finally discarded. Around 1630 a French chemist, Jean Rey, noticed that tin calx weighed more than the tin from which it was made.

The equation for the calcination of tin was written by the phlogistonists as:

$$\text{Tin} \xrightarrow{\Delta} \text{Tin Calx} + \text{Phlogiston (escapes into the air)}$$

The tin would not be expected to gain weight as a calx formed because it was losing something (phlogiston). A loss of weight would fit the equation better; however, the experiments were conclusive and showed a gain in weight.

Rey himself said "... this increase in weight comes from the air ... which air mixes to the calx ... and becomes attached to its most minute particles ...." Rey had come very close to the modern theory of combustion before the phlogiston theory had even been proposed! However, it was only a guess; and at that time, nothing could be done with his guess. No experiments could be performed; the techniques did not exist. At that time there was no way to prove or disprove the guess that some material from the air combined with the metal to make a calx. In fact, the nature of air was not understood at all. No one knew about the existence of different gases such as oxygen, nitrogen, or hydrogen. Rey's guess was too far ahead of his time.

When the phlogiston theory was proposed, the fact that a metal gained weight as it formed a calx contradicted the ideas of the theory but was not at all fatal to the theory. This illustrates an important point about the methods and tactics of science. Scientists attempt to develop schemes or theories which will account for a large number of facts. One contradictory fact is almost never enough to destroy an entire theory. A theory may be left as it is, modified, or replaced by a better theory (one which accounts for more of the facts). However, a theory is never abandoned with nothing left to replace it. It takes a new theory to depose an old one. If facts which seem to contradict a theory are discovered, the first reaction of scientists is to try to fit these facts into the theory.

How did the early phlogistonists try to fit into the phlogiston theory the observation that a calx weighed more than the metal from which it was derived? Some of them took refuge in a confusion between weight and weight per unit volume (density). Metals are more dense than their corresponding calxes. However, the idea that a metal gives up its phlogiston to become less dense did not last long. It was decided that weight, not density, was the relevant quantity. The dilemma persisted: when a metal lost phlogiston and became a calx, it gained weight.

Some chemists talked about assigning a negative weight to phlogiston. This would mean that anything that lost phlogiston would gain weight. Does this idea seem to be logical? How can a substance gain weight by losing something?

2-4/EXPERIMENTAL ADVANCES

One of the problems chemists of the eighteenth century had was their inability to distinguish among different gases; they had better luck with solids and liquids. Gases which would not support burning—such as nitrogen or carbon dioxide—were

confused with each other. Gases which would burn—such as hydrogen and carbon monoxide—were also confused with each other. It was only when scientists began to notice that gases differed in other properties and came from different sources that they finally began to understand the chemistry of gases.

From Boyle's time to that of the English chemist Joseph Priestley (around 1772), a number of techniques were developed which simplified the handling of gases. One of these was the pneumatic trough (Fig. 2-5).

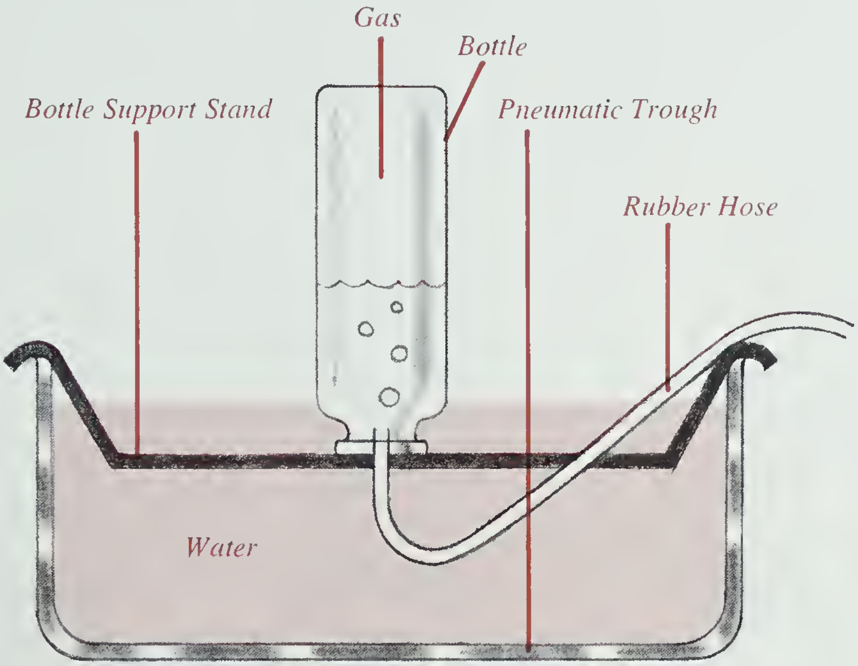


Fig. 2-5 The Pneumatic Trough
On the left page is a photograph of a pneumatic trough; at right, a diagram of how it is set up.

By using a pneumatic trough, gases which are insoluble (or sparingly soluble) in water can be collected by allowing them to displace water from a previously filled bottle. Gases can be collected in a nearly pure state in this way.

Gradually chemists began to understand the difference between ordinary atmospheric air and various other gases or "airs." One air, *fixed air* (now called carbon dioxide), was recognized as being the gas produced when charcoal burns. Another air, *inflammable air* (now called hydrogen) was also recognized. Before Priestley's work, only three different airs were known, but in a few years he alone discovered 11 more. One of these was oxygen.

2-5/LAVOISIER'S EXPERIMENTS

Lavoisier started his work with experiments involving the burning of two nonmetals, sulfur (Fig. 2-6) and phosphorus. He wrote his observations and conclusions in what is now his famous note to the French Academy of Sciences in 1772:

> About eight days ago I discovered that sulfur in burning, far from losing weight rather gains it . . . . It is the same in the case of phosphorus. The gain in weight comes from the prodigious quantity of air which is fixed during the combustion and combines with the vapours.
>
> This discovery, which I have established by experiments which I consider decisive, has made me believe that what is observed in the combustion of sulfur and phosphorus may equally well take place in the case of all those bodies which gain weight on combustion or calcination. I am persuaded that the gain in weight of the metallic calxes is due to the same causes. Experiment has completely confirmed my conjectures . . . .

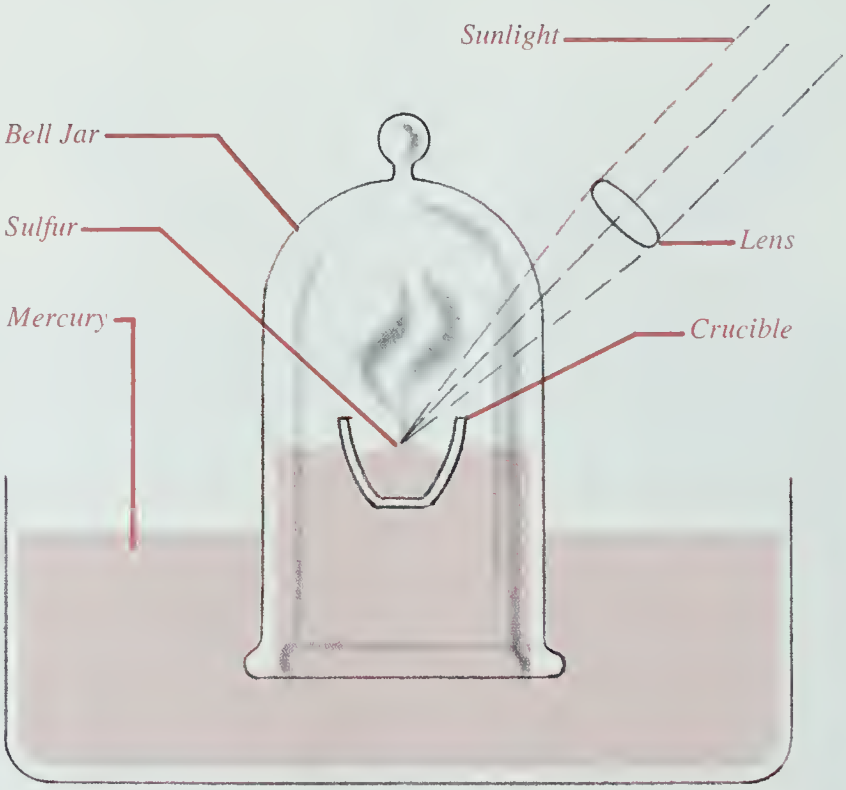


Fig. 2-6 Burning Sulfur

Notice that Lavoisier had worked with only two combustible substances, sulfur and phosphorus. He extended his idea of part of the air combining with these burning materials to include all calcination processes.

As we have seen already, a phlogistonist would have written the equation for the calcination of a metal like tin as:

$$\text{Tin} \xrightarrow{\Delta} \text{Tin Calx} + \text{Phlogiston (escapes into the air)}$$

This would suggest that the calx should weigh no more than the metal, thus contradicting experimental evidence. However, Lavoisier felt that the equation should be written:

$$\text{Tin Metal} + \text{Something from the Air} \xrightarrow{\Delta} \text{Tin Calx}$$

Notice that Lavoisier was presenting the same theory that Jean Rey had considered 142 a before. However, in Rey's time, the techniques of chemistry were not developed to the extent necessary to prove or disprove his idea. In Lavoisier's time, chemists were beginning to understand more about gases, and their techniques of weighing and handling gases were far enough advanced so that Lavoisier would eventually be able to support his theory with experimental evidence.

Lavoisier felt sure that the large weight increase of the nonmetals phosphorus and sulfur, when they burned, was due to something absorbed from the air. However, the weight changes which occurred when a metal was converted to a calx were so small that it was difficult for Lavoisier to demonstrate that something in the air had combined with the metal during calcination. The weighing techniques available to Lavoisier were just not precise enough for these experiments.

It may be useful to review what had happened up to this point, and also to look at Lavoisier's plans for future work.

First, Lavoisier developed the idea that something was absorbed from the air during the combustion process and during the calcination of metals. Second, he began to look for that something. Third, he was unsuccessful in proving that metals absorbed something from the air during calcination. Fourth, he had heard about one metallic calx, mercury calx, which he hoped might aid him in his search.

2-6/LAVOISIER'S THEORY OF COMBUSTION

It was Priestley who introduced Lavoisier to mercury calx—at a dinner party! Priestley told Lavoisier of a red calx of mercury which decomposed at high temperature to give a gas.

At that time, Priestley mistakenly believed this gas to be laughing gas (now known to be an oxide of nitrogen). He thought it was laughing gas because a candle burned brightly in it just as a candle burned brightly in laughing gas.

It was fortunate that Lavoisier did find out about mercury calx. Mercury was the only metal known in Lavoisier's time which could have been useful to him. It is one metal that will form a calx at one temperature and revert to the metallic state at a higher temperature. Lavoisier might have been slowed down, or perhaps stopped, if he had not begun to use mercury calx. At that time, the development of chemistry depended on discovering the right substance to study, and to some extent, this principle holds good even today.

Lavoisier duplicated Priestley's experiments with mercury calx after performing a new one of his own. Lavoisier heated mercury in a closed retort. The neck of the retort was bent so that there was free access to the air in a bell jar placed in a pneumatic trough containing mercury (Fig. 2-7). As the mercury was heated, it was gradually converted to red mercury calx, and mercury rose from the trough into the bell jar. This indicated that something had disappeared from the air, and had combined with the mercury. After twelve days, about one-sixth of the air had disappeared and there was no further rise of mercury into the bell jar.

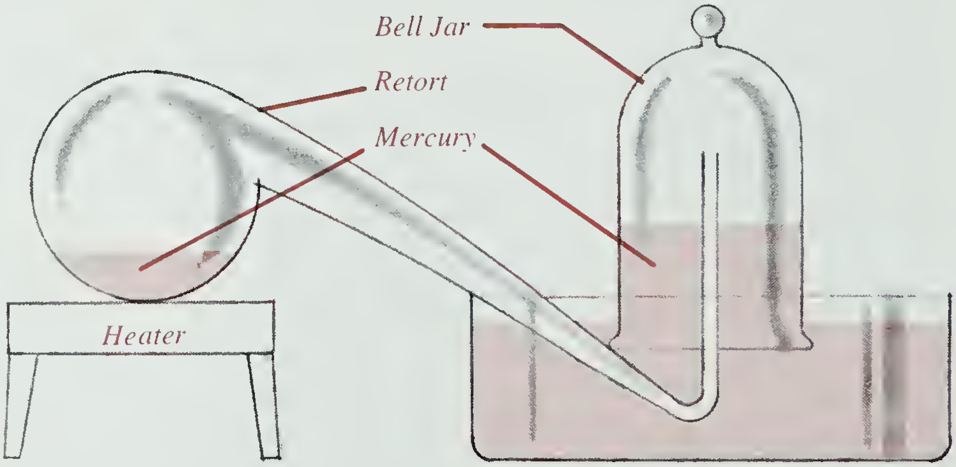


Fig. 2-7 Lavoisier's Apparatus

Lavoisier established that the gas left in the bell jar was no longer suitable for respiration or combustion. Animals placed in it perished within a few moments, and a flame placed in it was extinguished at once.

Lavoisier then wanted to recover the gas which had left the air and combined with the mercury. He placed the red calx of mercury in an apparatus similar to the one that Priestley had used and heated the calx by focusing sunlight on it (Fig. 2-8).

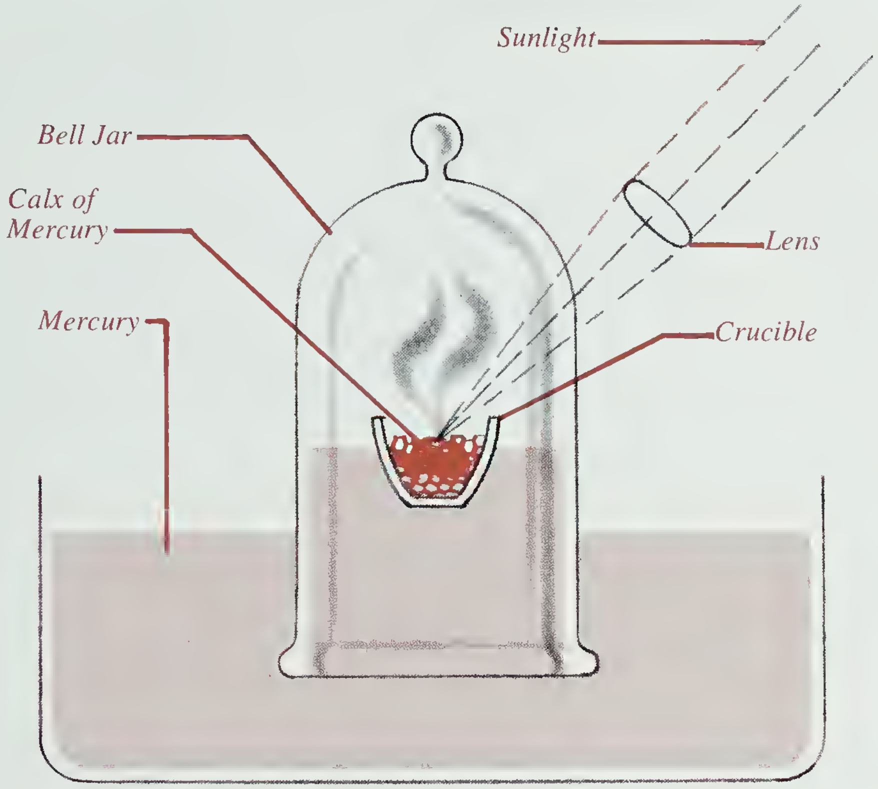


Fig. 2-8 Priestley's Apparatus

The metal was regenerated. A gas was evolved; and it forced the mercury out of the bell jar. The same quantity of gas was produced in the second experiment as was used up in the first experiment. Furthermore, when the gas produced in the second experiment was mixed with the remaining gas from the first experiment, the resulting mixture was the same as ordinary air.

Lavoisier believed that the gas obtained from mercury calx was a type of ordinary air "but that it was more respirable, more combustible and consequently that it was more pure than even the air in which we live." For example, charcoal burned in this gas much more brightly than it did in ordinary air. Lavoisier did not realize that he and Priestley were working with a new gas. He thus lost his opportunity to become the discoverer of oxygen.

In the meantime Priestley realized that the gas was a new gas, not laughing gas after all. Since Priestley was a phlogistonist, he believed that phlogiston left the air and went to the calx forming mercury and dephlogisticated air. Priestley wrote the following equation to explain his results:

$$\begin{array}{l}\text{Mercury Calx} + \text{Air (containing Phlogiston)} \xrightarrow{\Delta\Delta} \text{Mercury} \\ \qquad + \text{Completely Dephlogisticated Air}\end{array}$$

Priestley also pointed out to Lavoisier that the latter was wrong in suggesting that this gas was merely high quality ordinary air. Lavoisier was quick to recognize his error, and was then able to straighten out his own theories regarding combustion. He published his theory in his "Easter Memoir," without even mentioning the unsolicited help that he had received from Priestley.

Lavoisier knew that he had found the 'something in the air' for which he had been looking. It was Priestley's "dephlogisticated air" (now called oxygen). Lavoisier's new scheme can be summarized by the following equations:

$$\text{Carbon} + \text{Oxygen} \xrightarrow{\Delta} \text{An Oxide of Carbon}$$

$$\text{Phosphorus} + \text{Oxygen} \xrightarrow{\Delta} \text{An Oxide of Phosphorus}$$

$$\text{Sulfur} + \text{Oxygen} \xrightarrow{\Delta} \text{An Oxide of Sulfur}$$

$$\text{Mercury} + \text{Oxygen} \xrightarrow{\Delta} \text{An Oxide of Mercury}$$

$$\text{Oxide of Mercury} \xrightarrow{\Delta\Delta} \text{Mercury} + \text{Oxygen}$$

$$\text{Oxide of a Metal} + \text{Carbon} \xrightarrow{\Delta} \text{Metal} + \text{Oxide of Carbon}$$

Lavoisier's new theory was not immediately accepted by everyone even though his experiments were simple and elegant. The results would seem to prove Lavoisier's theory about as well as it is possible to prove any theory of chemistry; however, the phlogistonists were still completely convinced that the phlogiston theory was correct. In a controversy of this sort, both sides tend to put aside experimental evidence that does not fit their respective schemes. Slowly, French chemists began to accept Lavoisier's theory, but Priestley, Cavendish, and others were not convinced. In fact, Priestley was still a confirmed phlogistonist at the time of his death 29 a later.

We now know that combustion does not have to involve oxygen. For example, it is possible to burn hydrogen gas in an atmosphere of pure chlorine. It is also possible to burn magnesium in carbon dioxide. While combustion must be carefully defined in order to accommodate these observations, they do not change the fact that Lavoisier's work was and is the basis of the modern theory of combustion. Modifying a theory to accommodate new information is a common occurrence in science. While combustion normally involves oxygen, any process which is rapid and produces energy in the form of heat and light can be a "combustion."

Hopefully, a number of concepts became apparent as you read this account of the birth of the modern theory of combustion. First, an established theory may be a road-block in the development of a better theory. This is particularly true if the established theory has been a popular and useful one. Second, occasionally a new theory is not successful because the scientists of the day have not developed the experimental techniques necessary to test the theory. Third, a theory is never abandoned with nothing to replace it. It is either modified or replaced by a better theory.

QUESTIONS

1. For each of the following observations give the two contradicting explanations for each observation, that of the phlogistonist and the modern view:
   (a) When a candle burns in a closed container the flame is eventually extinguished.
   (b) Burning is more rapid in pure oxygen than in air.
   (c) Methane, an organic compound containing carbon and hydrogen, burns in air.
   (d) Some metal calxes can be heated in methane to produce the metal.
   (e) A mouse will suffocate in a closed container of air.
2. Complete the following word equations according to the modern theory of combustion:
   (a) Metallic oxide + hydrogen →
   (b) Metallic oxide + carbon →
   (c) Organic compound containing carbon and hydrogen + oxygen →

3. What discovery of Jean Rey later turned out to be a flaw in the phlogiston theory?
4. When Priestley first prepared oxygen from mercury calx, he thought that oxygen was completely dephlogisticated air. Write the word equation that Priestley would have used to explain his results.
5. How did Lavoisier prove that Priestley's oxygen was the substance in air that is involved in all combustions and calcinations?
6. Was the phlogiston theory really a useful theory? Why or why not? Is the modern theory of combustion a useful theory? Why or why not?
7. Can a useful theory be proved incorrect by one contradictory fact?

QUESTIONS TO THINK ABOUT

8. How would a phlogistonist explain the burning of hydrogen in an atmosphere of chlorine?
9. How would a phlogistonist explain the observation that sulfur merely melts and fumes when heated in the absence of air?
10. How would a phlogistonist explain the observation that when charcoal or sulfur is added to hot molten niter an explosion occurs?

3

MATTER

Chemistry is the study of matter, the transformations it undergoes, and the energy that is absorbed or released during these changes. In this chapter we will introduce the basic concepts and background material required for an introductory study of matter. In Chapter 2 the development of the modern theory of combustion was traced. In this chapter the development of another theory, the atomic theory, will be examined.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Define matter and inertia.
2. Distinguish between mass and weight; between work and energy; between kinetic and potential energy.
3. Identify examples of kinetic and potential energy.
4. State the Law of Conservation of Mass and Energy.
5. State the characteristics of solids, liquids, and gases.
6. Distinguish between physical and chemical properties and identify examples of each.
7. Distinguish between physical changes and chemical changes and identify examples of each.
8. Distinguish between pure substances and mixtures; elements and compounds; homogeneous and heterogeneous mixtures.

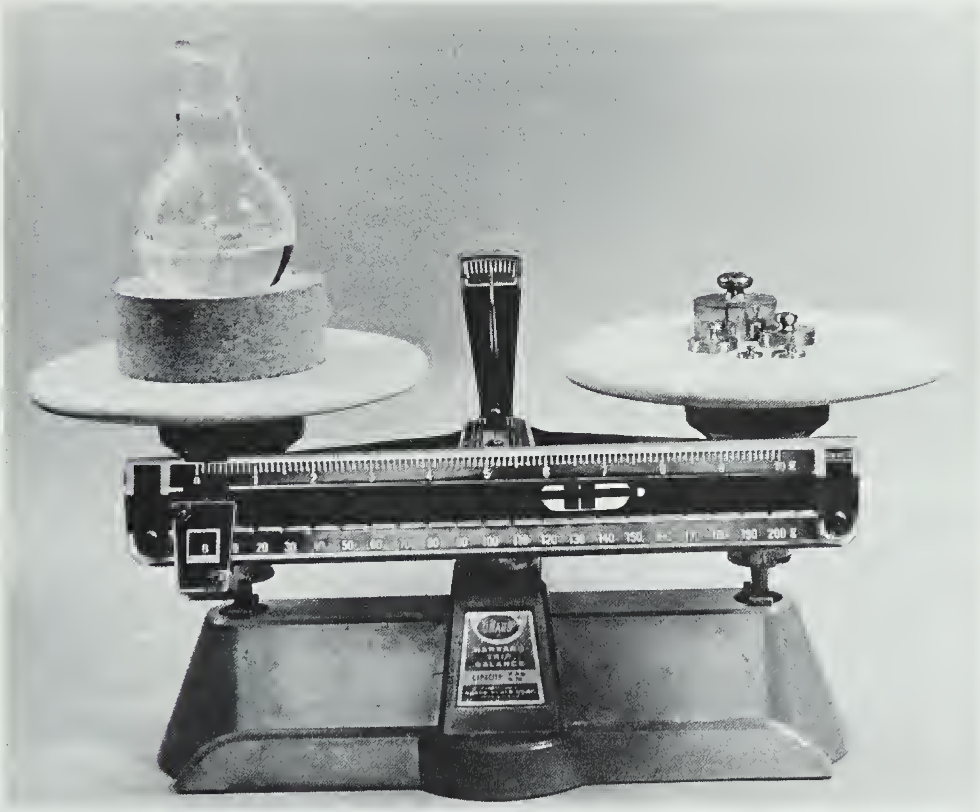
9. State the characteristics of a solution and show how solutions differ from pure substances and from heterogeneous mixtures.
10. State the properties of metals and nonmetals and give examples of each.
11. State the laws of chemical change.
12. Calculate the mass of one element required to react with a given mass of another element to form a compound of known composition.
13. State the postulates of Dalton's atomic theory.
14. Show how Dalton's atomic theory explains the laws of chemical change.
15. Explain the difference between an atom and a molecule.
16. Define atomic mass, isotope, mole.
17. Calculate the mass of an atom of any element, given its mass as a multiple of the mass of a carbon-12 atom.
18. Given the atomic mass of an element, calculate the mass of a given number of moles of the element.
19. Given the atomic mass of an element, calculate the number of moles of atoms present in a given mass of the element.
20. Given the number of moles in a given mass of an element, calculate the atomic mass of the element.

3-1/MATTER, MASS, AND ENERGY

The physical universe is made up of matter and energy. **Matter** is defined as anything that has mass and occupies space. Matter possesses **inertia**—the tendency for a moving body to remain in motion and the tendency for a stationary body to remain stationary. For the most part, matter is easily recognized, e.g., wood, bricks, and water. Some forms of matter such as air are slightly more difficult to recognize as being matter until one remembers that a hovercraft is supported by a blanket of compressed air or that the high winds of a hurricane can destroy a huge building.

Mass is the term applied to the quantity of inertia that is possessed by an object. Mass can also be defined as the quantity of matter; however, since matter possesses inertia, these definitions mean the same thing. The greater the mass of a body, the more inertia it contains. For example, a large object such as a boulder is difficult to move; however, once the boulder is moving it is difficult to stop. The boulder has a great deal of inertia (mass). The unit of mass used in chemistry is the kilogram. Since the kilogram is a relatively large unit of mass, the gram (1/1000 kg) is more commonly used in practice.

Weight is a term which is frequently confused with mass. These two terms are related, but technically they mean different things. The **weight** of an object is the force with which it is attracted to the earth (Figs. 3-1A and 3-1B). This force depends on the earth's gravitation and the mass of the object. The mass of an object is constant, but the pull of the earth's gravity is not the same everywhere on the earth's surface. Therefore, the weight of a given object does change. If that object is taken far enough from the surface of the earth, the pull of gravity becomes negligible, and the object becomes essentially weightless. However, the object still possesses the same amount of mass that it has always possessed.



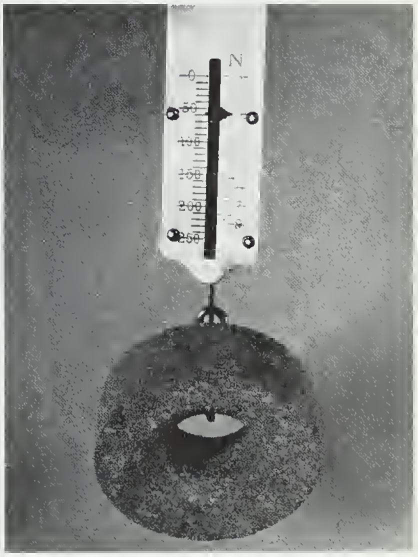


Fig. 3-1A Measurement of Mass
The mass of the objects on the left pan of the balance is equal to the total mass on the right pan; the position of the pointer does not change with a change in gravitational force.

Fig. 3-1B Measurement of Weight (Force of Earth's Attraction)
The position of the pointer on the spring scale is subject to some variation from place to place on the earth's surface due to gravitational changes.

Energy is the ability to do work. **Work** can be defined as the moving of matter against a force which opposes the motion. A hummingbird hovers, a worm burrows through the earth, oil burns in a furnace, you turn the pages of a book—all these actions involve energy. Energy is subdivided into two main categories: kinetic energy and potential energy. **Kinetic energy** is energy of motion. A moving object can pass through a glass window if it has enough kinetic energy to shatter the glass. **Potential energy,** on the other hand, is the energy of position. A book held above a desk has potential energy. If the book is allowed to fall, it acquires kinetic energy. The potential energy grows smaller and the kinetic energy grows larger as the book nears the surface of the desk. When the book hits the desk, its kinetic energy is used to increase the temperature of both the book and the desk.

The potential energy of the book depends on the definition of zero potential energy. For example, we can define the potential energy of the book, when it is placed on the desk, to be zero. When the book is above the desk, its potential energy is larger than zero. As the book falls to the desk, its potential energy decreases to zero. However, if the book were to fall past the desk to the floor, its potential energy would become less than zero. Thus the potential energy can have values greater than zero, equal to zero, or less than zero. The actual value depends on where we have defined the zero level of potential energy to be. In this example negative values of potential energy can be eliminated simply by defining floor level rather than desk level as zero potential energy.

The total energy of any system is equal to the sum of its kinetic and potential energies. Mechanical, heat, light, sound, electrical, and chemical energies are forms of both kinetic and potential energy. Energy can be transformed from one form to another. For example, the kinetic energy of rushing water turning the blades of a turbine produces the mechanical energy necessary to generate electrical energy which can be used to toast bread (heat energy) and light a room (light energy).

At one time it was believed that there was a constant quantity of matter (i.e., mass) in the universe. It was also believed that there was a constant quantity of energy in the universe. These generalizations were known as the Laws of Conservation of Mass and Conservation of Energy respectively. The study of nuclear reactions has led to the discovery that in some cases mass can be converted into energy, and vice versa. This knowledge gave rise to the **Law of Conservation of Mass and Energy.** This law states that there is a constant total quantity of matter and energy in the universe. An increase in the total quantity of matter must be balanced by an equivalent decrease in the total quantity of energy, and vice versa. In chemical processes, the change of mass into energy is too small to be detected. However, in nuclear processes, the change in the quantity of matter is large enough to be measured.

3-2/THE THREE STATES OF MATTER

The three states of matter are the solid, liquid, and gaseous states. Matter in the **solid** state has a definite shape and volume. A solid object will have a constant size and shape regardless of the container in which it is placed. Factors such as temperature and pressure have little effect on solids. That is, solids do not expand or contract very much when they are heated or cooled, and they are not easily compressed.

Matter in the **liquid** state has a definite volume, but it does not have a definite shape. A liquid takes the shape of the container into which it is poured. Liquids may be compressed slightly; but for most purposes, it is safe to assume that they do have a constant volume. This incompressibility of liquids means that a pressure exerted on a liquid will be transmitted equally in all directions. Use is made of this property in the automotive hydraulic brake system. When the brake pedal is depressed, the pressure is transmitted from the master-cylinder by the brake fluid to the slave-cylinders connected to the brake shoes which in turn press against the revolving brake drums to slow or stop the car.

Matter in the gaseous state has neither definite volume nor a definite shape. A **gas** takes both the shape and the volume of the container in which it is placed. Factors such as temperature and pressure have such a large effect on a gas that it is pointless to consider a given volume of gas unless both its temperature and pressure are known. The tank on a scuba diver's back would contain enough air to supply his lungs for only a very short time if it were at normal atmospheric pressure. By forcing more air into the tank at pressures of one thousand to two thousand times that of the atmosphere, the supply of air can be enormously increased with no change in the size of the container. This principle is also used by firefighters, mine rescue personnel, and others who require a self-contained supply of air for work in the presence of toxic gases.

3-3/PHYSICAL AND CHEMICAL PROPERTIES

The **physical properties** of a substance are those properties which can be determined without changing its composition. Mercury, for example, is an odorless liquid with a characteristic silvery luster. It does not dissolve in water. It is an excellent conductor of electricity. It freezes at −39°C and boils at 357°C. Properties such as color, odor, hardness, melting point, boiling point, electrical conductivity, and many others are examples of physical properties. They do not involve changing the composition of the mercury to that of some other substance. Thus, the density of mercury is also one of its physical properties. **Density** is defined as the mass of an object per unit volume of the object. One cubic centimetre of mercury has a mass of 13.6 g. Hence the density of mercury is 13.6 g/cm^3. Since density can be measured using only devices for determining mass and volume, and without changing the mercury into some other substance, it is a physical property.

The **chemical properties** of a substance are those properties which can be observed only when the substance undergoes a change in composition. It is difficult to distinguish pyrite (fool's gold) from gold because they are physically so much alike. Yet it is quite easy to distinguish them chemically. Concentrated nitric acid has no effect on gold, but it reacts with pyrite to give a soluble product, iron(III) nitrate, and a residue of insoluble sulfur. Charcoal (carbon) burns in air to give a mixture of two gases, carbon monoxide and carbon dioxide. An iron nail immersed in water gradually becomes coated with a layer of rust. These properties are all chemical properties because they involve changing various kinds of matter into other substances with different compositions, different structures, and different properties. Such changes or transformations are called **chemical reactions.** The formation of iron(III) nitrate and sulfur by the action of nitric acid on pyrite is an example of a chemical reaction. Burning charcoal involves a reaction between carbon and oxygen; the rusting of iron involves a chemical reaction between iron and oxygen.

A substance can often be identified by observing its chemical and physical properties. Silver and platinum are both beautiful silvery white metals used extensively in jewelry. Silver melts at 961°C, boils at 2212°C, and has a density of 10.50 g/cm^3. Platinum melts at 1769°C, boils at 3827°C, and has a density of 21.4 g/cm^3. They can be distinguished and identified by these differences in their physical properties. For a chemist, perhaps the easiest way to distinguish them would be to test a small amount of each metal with nitric acid. Silver dissolves readily in nitric acid with a vigorous chemical reaction, whereas platinum is completely unaffected by the acid.

3-4/PHYSICAL AND CHEMICAL CHANGES IN MATTER

A **physical change** is a change which alters one or more of the properties of the substance with no change in its composition or identity. When liquid water freezes to ice, one of its properties changes: it no longer pours—but it is still water. When water boils and is converted into water vapor, another property changes: it no longer has a definite volume—but again it is still water. Water retains the same chemical composition whether it is in the form of a solid, a liquid, or a gas. Changes of state, such as melting, freezing, or boiling are physical changes because they do not change the composition or chemical identity of the substance. The tungsten filament in a light bulb becomes white hot when electricity is passed through it, but it is still tungsten. This is again a physical change because the tungsten filament is not converted to any other substance during the passage of the electric current.

A **chemical change** is a change in a substance which converts it into a different kind (or different kinds) of matter each with a different composition and new properties. When paper burns, it is converted mainly into two gases, carbon dioxide and water vapor, both of which differ in composition and properties from the original paper. The rusting of iron gives a product, rust, which is different in composition and properties from the original iron. At least one new substance, different in composition and properties from the original substances, must be produced whenever a chemical change occurs. The burning of gasoline in an automobile engine and the preparation of caramel by heating sugar are other examples of chemical changes.

3-5/PURE SUBSTANCES AND MIXTURES

A **pure substance** is a homogeneous (uniform) material. It consists of only one particular kind of matter and has the same properties throughout. It always has the same composition. Diamond is a pure substance. It consists only of carbon. Pure substances are classified into two categories: elements and compounds.

Elements are pure substances that cannot be broken down into simpler substances by ordinary chemical methods. Carbon, oxygen, and iron are examples of elements.

Compounds are pure substances, consisting of two or more elements in combination. Compounds may be decomposed into two or more simpler substances by ordinary chemical methods. Pure water is a *pure substance* by virtue of the fact that it is homogeneous and consists of only one kind of matter. It is a *compound* by virtue of the fact that it can be broken down into hydrogen and oxygen.

When a compound is prepared, the original components lose their identities, and they can then be separated only by chemical means. When compounds are prepared, evidence of chemical reaction (e.g., heat or light) can usually be observed.

A **mixture** is a combination of two or more pure substances each of which retains its own physical and chemical properties. Many mixtures are heterogeneous (nonuniform). A **heterogeneous mixture** consists of more than one phase. The word **phase** is used to mean any region with a uniform set of properties. For example, a mixture of sand and water is composed of two phases. One phase is the solid sand. The second phase is the liquid water. A mixture of pieces of iron and lumps of sulfur is a two-phase system consisting of a solid iron phase and a solid sulfur phase.

A heterogeneous mixture is not uniform throughout. Different portions have different properties. Also, a heterogeneous mixture of iron and sulfur can be prepared using any quantity of iron and any quantity of sulfur. Mixtures can have a variable composition. There is no evidence of a chemical reaction when a mixture is prepared. The materials that have been mixed retain their own identities, and they may be separated by physical means. Figure 3-2 illustrates a number of heterogeneous mixtures consisting of different numbers of phases.

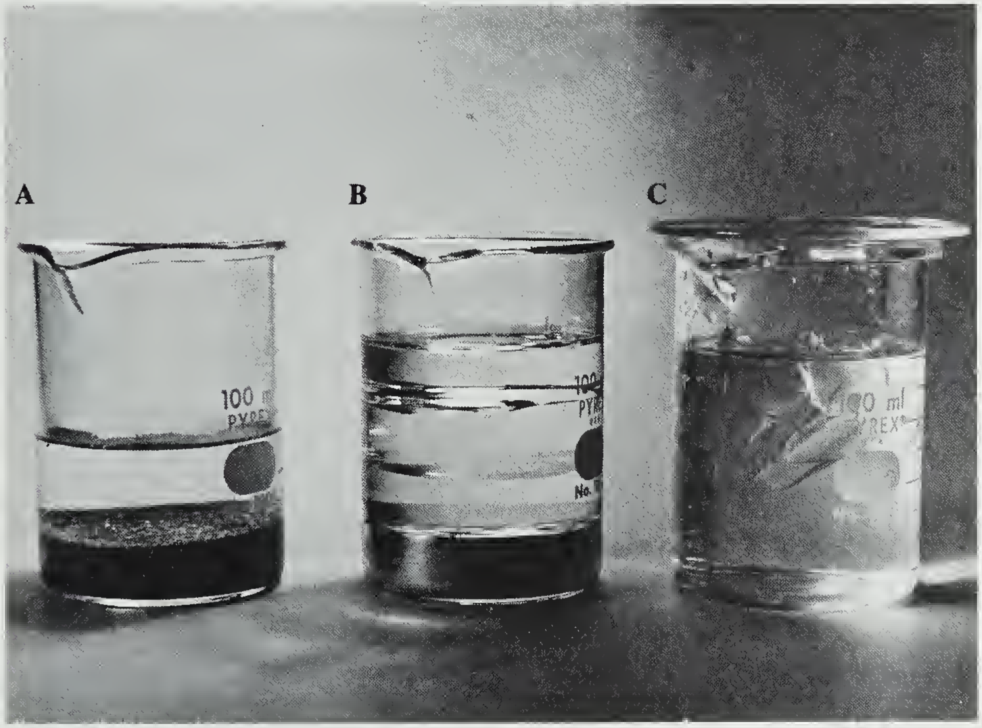


Fig. 3-2 Heterogeneous Mixtures **(A)** *A two-phase system consisting of a solid and a liquid;* **(B)** *A four-phase system consisting of four different liquids;* **(C)** *A three-phase system consisting of solid ice, liquid water, and water vapor in air.*

A **homogeneous** or one-phase mixture is called a **solution.** A homogeneous mixture is uniform throughout. A solution of sugar dissolved in water is an example of a homogeneous mixture. What has been said about heterogeneous mixtures can also be said about homogeneous mixtures or solutions but with one caution. A homogeneous mixture of sugar and water cannot be prepared using *any* quantity of sugar and *any* quantity of water. One can not dissolve one kilogram of sugar in a drop of water.

Except for certain solutions (e.g., ethyl alcohol and water) the solubility of one substance in another is limited (or has a maximum value). A solution of one metal (or several) in another is called an **alloy.** Mixtures do have variable composition, but usually the composition of a solution can vary only within certain limits. The various ways in which matter can be classified are summarized in Fig. 3-3.

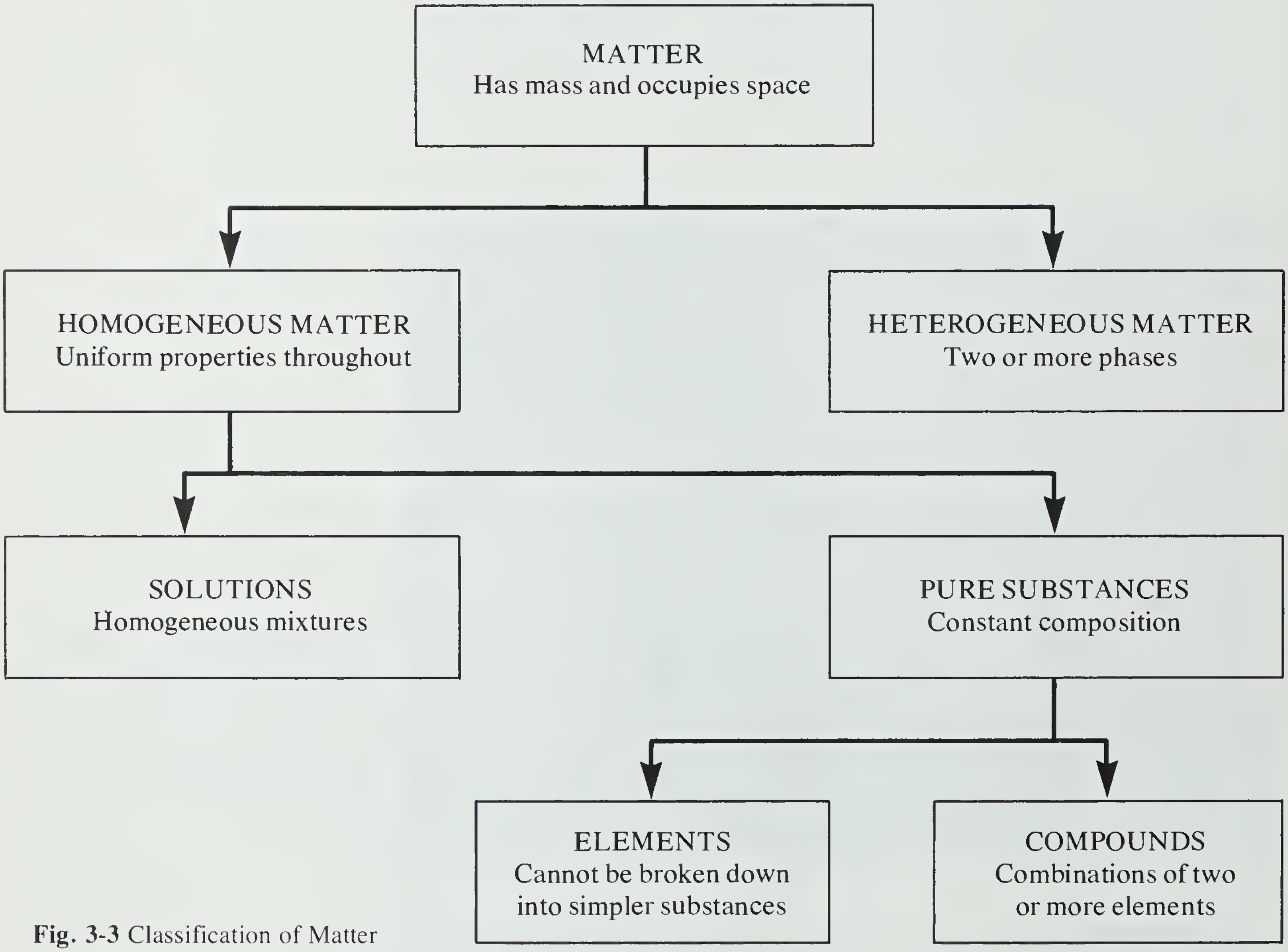


Fig. 3-3 Classification of Matter

3-6/ELEMENTS

At present 105 elements have been identified. Of these, 103 have been named. The other two are unnamed due to conflicting claims of discovery by Russian and American scientists. Eighty-eight elements occur naturally and the other 17 are man-made. Only about a quarter of the elements occur in the free or elemental state. The others are all found combined with one another in compounds. The more abundant elements found in the earth's crust and atmosphere are listed in Table 3-1.

TABLE 3-1

OCCURRENCE OF ELEMENTS IN THE EARTH'S CRUST AND ATMOSPHERE

Oxygen	49.20%	Chlorine	0.19%
Silicon	25.67%	Phosphorus	0.11%
Aluminum	7.50%	Manganese	0.09%
Iron	4.71%	Carbon	0.08%
Calcium	3.39%	Sulfur	0.06%
Sodium	2.63%	Barium	0.04%
Potassium	2.40%	Nitrogen	0.03%
Magnesium	1.93%	Fluorine	0.03%
Hydrogen	0.87%	Strontium	0.02%
Titanium	0.58%	All others	0.47%

3-7/METALS, METALLOIDS, AND NONMETALS

Stone Age man had only stone and wooden implements. Some time around 8000 years ago he discovered **metals,** probably accidentally, by heating rocks containing them. The first metals to be discovered were probably silver, gold, and copper. These were easily hammered into various shapes and could be used to make pieces of jewelry, tools, or weapons. Later tin was discovered. It was found that an alloy of tin and copper, called bronze, made superior tools and weapons, and thus began the Bronze Age about 5000 a (years) ago. There was a thriving tin trade between Phoenicia and the tin mines in Cornwall, England, at least as long ago as 1000 B.C. At about that time, however, iron began to supplant bronze in general use.

During the past 3000 a many other metals have been discovered. A majority of the known elements are metals. They all share similar properties. They are good conductors of heat and electricity. They have a characteristic luster. They are malleable and ductile, that is, they can be hammered into sheets and drawn into wires. They usually have high densities and high boiling points. Many metals have other useful properties such as resistance to stretching and twisting (Fig. 3-4).

Fig. 3-4 Resistance of Metals to Stretching
The suspension cables of this bridge between Halifax and Dartmouth show the resistance to stretching possessed by many metals.

Gold, silver, and copper are called the **coinage metals** because they are part of the alloys used to make coins. Lithium, sodium, and potassium are members of the **alkali metal** family. Other well-known metals are iron, aluminum, platinum, zinc, and mercury. Mercury is the only metal that is a liquid at room temperature.

The elements which are not metals are called **nonmetals.** They do not usually have a luster. They are usually brittle and are poor conductors of heat and electricity. Iodine, phosphorus, and carbon are examples of solid nonmetals. Bromine is the only nonmetal that is a liquid at room temperature. Oxygen, chlorine, and fluorine are examples of gaseous nonmetals.

There is no sharp dividing line between metals and nonmetals. Certain elements have some properties of metals and some properties of nonmetals. They are called **metalloids.** Boron, silicon, and arsenic are examples of this type of element.

3-8/SYMBOLS OF THE ELEMENTS

The alchemists of the Middle Ages spent much of their time trying to find methods of transforming iron and lead into gold. They were naturally rather secretive in this hopefully profitable pursuit and developed secret notations to represent the substances with which they experimented. Eventually more or less standard symbols evolved to represent the elements then known. Among these symbols were such diagrams as:

☾ or ☽	Silver	♄	Lead	 or ○	Gold
♀	Copper	🜍	Sulfur	☿	Mercury

The crescent symbolized the silvery color of the moon; both the horn of plenty and the circle, symbolizing the golden sun, were used to represent gold.

In the early nineteenth century the English schoolteacher John Dalton simplified these symbols by means of drawings related to circular designs. Among his symbols were:

⊙	Hydrogen	●	Carbon	⌽	Nitrogen
○	Oxygen	⊕	Sulfur		Mercury

Chemists now use a system of abbreviations devised by the Swedish chemist Jöns Jakob Berzelius in 1814. The **symbols** usually consist of the first one or two letters in the name of the element. If the second letter is used, it is not capitalized. The symbols are so useful that they are used in all languages, even in Russian and Chinese which do not use our Roman alphabet. Examples are:

H	Hydrogen	B	Boron	C	Carbon
N	Nitrogen	O	Oxygen	F	Fluorine
He	Helium	Be	Beryllium	Ne	Neon

For some elements the symbols consist of the first letter followed by a letter from the middle of the name:

Mg	Magnesium	Mn	Manganese
Cl	Chlorine	Cr	Chromium

The symbols of many elements reveal the time when they were discovered. Many of the elements were known to the Romans or were discovered by the alchemists, when Latin was the language of educated persons. Hence the symbols of many elements are based on their Latin names:

Na	Sodium	(Latin *natrium*)
Cu	Copper	(Latin *cuprum*)
Sn	Tin	(Latin *stannum*)
Au	Gold	(Latin *aurum*)
Pb	Lead	(Latin *plumbum*)
K	Potassium	(Latin *kalium*)
Ag	Silver	(Latin *argentum*)
Sb	Antimony	(Latin *stibium*)
Hg	Mercury	(Latin *hydrargyrum*)
Fe	Iron	(Latin *ferrum*)

One element, tungsten, has a symbol, W, derived from the German name, Wolfram.

A list of the elements and their symbols is given on the inside front cover of this book.

3-9/CHEMICAL REACTIONS AND CONSERVATION OF MASS

Oxygen can be produced when potassium chlorate ($KClO_3$) is heated. This reaction will not proceed unless the potassium chlorate is strongly heated, and the reaction is said to be **endothermic** (Greek *endo*, within) because heat is absorbed. The reaction is somewhat dangerous because of the high temperature required to cause the potassium chlorate to decompose. To lower the decomposition temperature of the $KClO_3$ it is customary to use a small amount of a catalyst such as manganese dioxide (MnO_2), though slow, careful heating is still required to avoid a possible explosion. A **catalyst** is a substance that speeds up or aids a chemical reaction without being consumed itself. The manganese dioxide can be recovered unchanged after the decomposition of the $KClO_3$ is complete. If heat had been evolved, the reaction would have been **exothermic** (Greek *exo*, out of).

Observations of chemical reactions are summarized in certain generalizations called the **laws of chemical change.** Two of these are the Law of Conservation of Mass and the Law of Definite Composition. They will be used to develop a theory of the atom. The **Law of Conservation of Mass** states that during a chemical reaction matter is neither created nor destroyed to any significant extent. That is, there is a negligible conversion of mass into energy. Thus, the products of a chemical reaction have the same mass as the starting materials or reactants.

The constancy of mass during chemical reaction can be investigated experimentally by carrying out a reaction in a closed container and obtaining the mass of the system before and after the reaction. Lavoisier showed that it was necessary to have a closed system for the reaction of tin and oxygen so that nothing is lost to or gained from the surroundings. A good example of a reaction in a closed system is the ignition of the magnesium wire in a flash bulb. In the bulb, very fine magnesium wire is heated by an electric current. The hot magnesium reacts explosively with the oxygen in the bulb to form magnesium oxide, light, and heat. This combustion produces a compound having the same mass as the reactants. No change in the mass of the bulb takes place after ignition.

3-10/DEFINITE COMPOSITION

When Lavoisier showed that the total mass remains constant during chemical reactions, he became one of the first people to apply mathematics to chemical processes successfully. Not long afterward, in 1792, the German chemist Jeremias Richter suggested that it should be possible to calculate the composition of the products of a reaction if the composition of the reactants were known. His prose was so difficult to read, however, that chemists paid little attention to his suggestion. Seven years later, in 1799, the French chemist Joseph Proust showed that copper carbonate always had the same chemical composition no matter how it was prepared. In doing so he had discovered the **Law of Definite Composition**—compounds always have the same composition by mass.

For example, when hydrogen and oxygen are ignited, the product is water. Oxygen and hydrogen can be mixed in any proportion desired: 50/50, 25/75, 75/25, etc. No matter what the proportions of oxygen to hydrogen, the resulting water will always have the same composition. By mass, the water will contain 11.19% hydrogen and 88.81% oxygen. Any excess hydrogen (or oxygen) will remain unreacted. In the same way, when sodium reacts with chlorine to form sodium chloride, salt, 1.00 g of sodium uses up only 1.54 g of chlorine and forms only 2.54 g of sodium chloride even if 100 g of chlorine are available.

Thus, in the formation of a compound, the mass of one element needed to combine with a given mass of another is always the same. This is another way of stating the Law of Definite Composition.

SAMPLE PROBLEM/3-1

Lithium and fluorine always react so that 7.00 g of lithium and 19.2 g of fluorine combine to give 26.2 g of lithium fluoride. If 1.00 g of lithium is reacted with 3.00 g of fluorine to form lithium fluoride, how much fluorine combines with the lithium? How much fluorine remains unreacted?

$$7.00 \text{ g of lithium combine with } 19.2 \text{ g of fluorine}$$

$$1.00 \text{ g of lithium combines with } 19.2/7.00 = 2.74 \text{ g of fluorine}$$

$$3.00 \text{ g} - 2.74 \text{ g} = 0.26 \text{ g of fluorine}$$

∴ 2.74 g of fluorine react with 1.00 g of lithium, and 0.26 g of fluorine remain unreacted.

EXERCISE/3-1

Potassium and iodine react so that 3.00 g of potassium and 9.74 g of iodine combine to give 12.74 g of potassium iodide. If 1.00 g of potassium is reacted with 4.00 g of iodine to form potassium iodide, how much iodine combines with the potassium? How much iodine remains unreacted? (*Answers:* 3.25 g; 0.75 g)

EXERCISE/3-2

Magnesium oxide contains one magnesium atom for every oxygen atom, and a magnesium atom has a mass 1.52 times that of an oxygen atom. How many grams of magnesium will react with 10.0 g of oxygen to form magnesium oxide? How many grams of oxygen will react with 10.0 g of magnesium to form magnesium oxide? (*Answers:* 15.2 g magnesium; 6.58 g oxygen)

3-11/ATOMIC THEORY

The Law of Conservation of Mass and the Law of Definite Composition summarize the experimental facts known about reactions. There should exist a satisfactory theory which will explain these facts. Logically, there are two possibilities: either matter is continuous or matter is discontinuous. If matter is continuous, one could theoretically subdivide a piece of iron without limit. On a submicroscopic scale, the iron would appear to be continuous like jelly. If matter is discontinuous, eventually extremely small indivisible particles would be obtained. On a submicroscopic scale, the iron would appear to be discontinuous like a group of marbles.

One school of Greek philosophers, who lived in the fourth and fifth centuries B.C., believed that matter is composed of tiny indestructible particles which they called atoms (from the Greek word *atomos*, meaning uncut). However, this theory was never verified by experiments and was discarded. More than two thousand years later, in 1803, John Dalton, an English schoolteacher, reintroduced and developed the model, or theory, to such an extent that it was able to explain the Laws of Conservation of Mass and Definite Composition.

To some extent, Dalton's ideas arose from a great controversy between the French chemist J. L. Proust and his compatriot C. M. Berthollet. The argument lasted from 1799 to 1806, and it was carried out in the journals with great brilliancy and extreme courtesy. For example, Berthollet argued that copper and sulfur would combine in an infinite number of proportions, depending on the proportions of each substance used. Proust maintained that the "compounds" of variable composition prepared by Berthollet were simply mixtures of two compounds, each of which had its own constant copper to sulfur ratio. Berthollet and his colleagues worked for more than seven years. Yet every time they prepared a "compound" that they thought showed continuously variable composition, Proust and his colleagues were able to demonstrate that the compound was a mixture of two pure substances, each of which had its own composition.

Gradually the tide of opinion shifted in favor of Proust's arguments. The important result, however, was that scientists on both sides of the controversy collected large amounts of data concerning substances, and this information was all available to Dalton. Earlier scientists had occasionally speculated on the atomic nature of matter, but Dalton was able to put all the latest information together and construct a theory which explained the laws of chemical change.

Dalton's theory consisted of several statements or postulates:

1. All matter is composed of extremely small particles called atoms.

2. Atoms can be neither subdivided nor changed into one another.
3. Atoms cannot be created or destroyed.
4. All atoms of one element are the same in shape, size, mass, and all other properties.
5. All atoms of one element differ in these properties from atoms of all other elements.
6. Chemical change is the union or separation of atoms.

If all chemical reactions are unions or separations of atoms, and if atoms are indestructible, a chemical reaction would not involve the creation or destruction of atoms or mass. Thus, Dalton's theory explains the Law of Conservation of Mass. When oxygen and hydrogen atoms unite to form water, no atoms are created and none are destroyed. Thus, the mass of the atoms before reaction must be the same as the mass of the atoms after reaction.

Dalton's atomic theory also explained the Law of Definite Composition. When carbon atoms react with oxygen atoms to form carbon monoxide, each carbon atom reacts with one oxygen atom to form one molecule of carbon monoxide (a **molecule** is the smallest particle of a compound). If there were 15 carbon atoms present, only 15 oxygen atoms would react to form 15 carbon monoxide molecules, even if 100 oxygen atoms were available for reaction with the carbon. According to the atomic theory, all carbon atoms have the same mass, and all oxygen atoms have the same mass. Therefore, each carbon monoxide molecule will have the same mass—the sum of the atomic masses of carbon and oxygen. The fraction of the molecular mass contributed by carbon will be the mass of a carbon atom (always the same) divided by the mass of the molecule of carbon monoxide (always the same). This fraction will be constant. Thus, when carbon and oxygen unite to form carbon monoxide, the molecule will always have the same fraction of carbon uniting with the same fraction of oxygen. That is, carbon monoxide has a definite composition by mass.

Dalton's atomic theory was a positive contribution to our knowledge of matter; however, some postulates have had to be altered in the light of later discoveries. For example, atoms of the same element may have different masses. Atoms of the same elements which have different masses are called **isotopes.**

Dalton's theory was valuable because it was able to predict other laws. It stimulated chemists to do still more experiments to verify the predictions, and thus began an enormous advance in chemical knowledge and in chemical understanding.

3-12/ATOMIC MASS

One of the most important concepts to arise from Dalton's theory is that all atoms of one element have the same mass and that this mass is different from the masses of the atoms of other elements. Chemists immediately began to try to determine the masses of atoms. It was impossible, of course, for them to determine the masses of individual atoms or even to *prove* that atoms existed at all. But if atoms did exist, they had definite masses, and chemists attempted to assign relative atomic masses that agreed with the known compositions of compounds. There was much confusion because chemists confused atoms and molecules. Dalton, for example, believed (incorrectly) that one atom of hydrogen combined with one atom of oxygen to form one atom of water:

$$H + O \rightarrow HO$$

Since analysis tells us that the mass of oxygen in water is eight times the mass of hydrogen, Dalton thought that atoms of oxygen had eight times the mass of hydrogen. Using similar arguments for other compounds, it was possible to construct a table of relative atomic masses of most of the elements then known. There were many errors due to faulty analyses of compounds and to wrong guesses as to the number of atoms of each element in a molecule of the compound. Gradually the errors were discovered and corrected, and we now have the modern table of *relative atomic masses* which is reproduced at the front of this book.

In this table the most common isotope of carbon (carbon-12) is chosen as a reference standard. An atom of carbon-12 is arbitrarily assigned a mass of 12 atomic mass units (u). The masses of all other atoms are compared to the mass of this type of carbon atom. According to this definition, one **atomic mass unit** (u) is 1/12 the mass of a carbon-12 atom. The choice of an atomic mass of 12 u for carbon conveniently gives atomic masses for most of the other elements that are very nearly whole numbers.

An atom of ordinary hydrogen, for example, has an atomic mass which is about 1/12 as great as the mass of carbon-12. Therefore, the mass of an atom of ordinary hydrogen is about 1 u ($12 \times 1/12 = 1$). A more precise value of the atomic mass of an atom of ordinary hydrogen is 1.007 825 u. The mass of an atom of ordinary oxygen is about 4/3 as great as the mass of carbon-12. Therefore, the mass of an atom of ordinary oxygen is about 16 u ($12 \times 4/3 = 16$). A more precise value is 15.994 91 u.

SAMPLE PROBLEM/3-2

An atom of neon has a mass which is 3/2 the mass of an atom of carbon-12. What is the atomic mass of neon?

$$\text{Mass of carbon-12 atom} = 12.0\ \text{u}$$

$$3/2 \times \text{mass of carbon-12 atom} = 3/2 \times 12.0 = 18.0\ \text{u}$$

$$\therefore \text{The atomic mass of neon is } 18.0\ \text{u.}$$

EXERCISE/3-3

An atom of sodium has a mass which is 1.92 times the mass of a carbon-12 atom. What is the atomic mass of sodium? (*Answer:* 23.0 u)

3-13/THE MOLE CONCEPT

The atomic mass unit (u) is defined as being 1/12 of the mass of a single carbon-12 atom. This is an extremely small unit of mass. No balance is capable of determining such a small quantity of matter. However, it is often necessary to measure out a certain number of atoms of an element such as carbon.

The **mole** (mol) is a certain quantity or number of atoms called Avogadro's number of atoms. Avogadro's number has been selected carefully. If a single atom of carbon-12 has a mass of 12 u, one mole (or *Avogadro's number*) of carbon-12 atoms will have a mass of 12 g. Similarly, if a single oxygen atom has a mass of 16 u (4/3 × the mass of a single carbon-12 atom), and if Avogadro's number (1 mol) of carbon atoms has a mass of 12 g, then Avogadro's number of oxygen atoms will have a mass of 16 g ($4/3 \times 12\ \mathrm{g} = 16\ \mathrm{g}$). In the same way, if a single hydrogen atom has a mass of 1 u (1/12 × the mass of a single carbon-12 atom), and if Avogadro's number of carbon-12 atoms have a mass of 12 g, then Avogadro's number of hydrogen atoms will have a mass of 1 g ($1/12 \times 12\ \mathrm{g} = 1\ \mathrm{g}$).

A mole is Avogadro's number of atoms or molecules. Avogadro's number is very large: 6.023×10^{23}. Thus the mole is just a special number. Just as a "dozen" is a special name for 12 and "a gross" is a special name for 144, "a mole" is a special name for 6.02×10^{23} particles. A mole is a collection of atoms whose total mass in grams is numerically equal to the atomic mass of an atom in atomic mass units. A mole is also a collection of molecules whose total mass is the number of grams numerically equal to the molecular mass, in atomic mass units. These are all correct definitions of the mole. However, a simple, useful definition of the mole is: the atomic or molecular mass of an atom or molecule expressed in grams. One atom of sulfur has a mass of 32 u. Therefore, one mole of sulfur atoms has a mass of 32 g. Remember that 32 g of sulfur is not made up of a single sulfur atom. Thirty-two grams of sulfur is composed of *many* sulfur atoms—Avogadro's number of sulfur atoms. However, 32 u of sulfur is the mass of a single sulfur atom. The atomic mass unit is a *much* smaller unit of mass than the gram. The mole concept is treated in more detail in Chapter 10 and Chapter 12.

SAMPLE PROBLEM/3-3

If three moles of a monatomic element have a mass of 12.0 g, what is the mass of a single atom of that element?
A monatomic element is one which consists only of single atoms.

$\therefore$ 3 mol of the element contain 3 mol of atoms and

1 mol of the element contains 1 mol of atoms.

Since 3 mol of atoms of the element have a mass of 12.0 g, 1 mol of atoms of the element has a mass of $12.0/3 = 4.00$ g

$\therefore$ 1 atom of the element has a mass of 4.00 u.

SAMPLE PROBLEM/3-4

If a certain element has an atomic mass of 9.0 u, what is the mass of one-third mole of atoms of the element? Of three moles of atoms of the element?

One atom has a mass of 9.0 u

One mole of atoms has a mass of 9.0 g

1/3 mol of atoms has a mass of $1/3 \times 9.0 = 3.0$ g

3 mol of atoms have a mass of $3 \times 9.0 = 27$ g

SAMPLE PROBLEM/3-5

A certain monatomic element has an atomic mass of 20.2 u. How many moles of atoms are present in 50.5 g of the element? How many in 3.00 g of the element?

20.2 u is the mass of 1 atom

20.2 g is the mass of a mole of atoms

1 g is the mass of 1/20.2 mol of atoms

$\therefore$ 50.5 g is the mass of $50.5 \times 1/20.2 = 2.50$ mol of atoms, and 3.00 g is the mass of $3.00 \times 1/20.2 = 0.149$ mol of atoms.

EXERCISE/3-4

If 2.50 mol of a monatomic element have a mass of 60.8 g, what is the average mass of a single atom of that element? (*Answer:* 24.3 u)

EXERCISE/3-5

A certain monatomic element has an atomic mass of 39.9 u. What is the mass of 3.13 mol of the element? (*Answer:* 125 g)

EXERCISE/3-6

How many moles of atoms are present in 100 g of a monatomic element of atomic mass 39.1 u? (*Answer:* 2.56 mol)

QUESTIONS

1. What is inertia?
2. Distinguish between mass and weight; between work and energy; between kinetic and potential energy.
3. What type of energy, kinetic or potential, is illustrated in the following examples: a speeding bullet; a skier poised at the top of a ski jump; water held behind a dam; the mainspring in a recently wound watch; a sky-diver in free fall?
4. What is the difference between a solid and a liquid? Between a gas and a liquid?
5. On which state of matter do temperature and pressure have the greatest effect?
6. Why is a moving automobile more difficult to stop than a moving baby carriage?
7. Are the following statements examples of physical properties or chemical properties?
    (a) Gold does not tarnish.
    (b) Lead is useful in making weights for scuba divers.
    (c) Copper is easily drawn into thin wires.
    (d) Laughing gas supports combustion.
    (e) Gallium metal melts in your hand.
8. Are the following statements examples of physical changes or chemical changes?
    (a) A platinum wire becomes red when held in the flame of a Bunsen burner.
    (b) Nitroglycerine explodes on impact or with heating.
    (c) Propane burns.
    (d) Milk sours on standing at room temperature.
    (e) Zinc sulfide glows when exposed to gamma radiation.
9. Distinguish between a pure substance and a mixture.
10. List two ways in which a solution differs from a compound.

11. What properties distinguish metals from nonmetals?
12. If 1.00 g of hydrogen uses up 8.00 g of oxygen when water forms from these two elements, even if 25.0 g of oxygen are available, which law is illustrated? How many grams of hydrogen are required to react with the 25.0 g of oxygen? (*Answer:* 3.12 g)
13. How did Dalton's atomic theory help to explain the Law of Conservation of Mass and the Law of Definite Composition?
14. What is the mass of an atom which has a mass 7/3 times as much as that of a carbon-12 atom?
15. What is the mass of an atom that has 4/5 the mass of a calcium atom? The mass of a calcium atom is 10/3 times the mass of an atom of carbon-12. (*Answer:* 32 u)
16. If four moles of an element have a mass of 128 g, what would be the atomic mass of a single atom of that element?
17. If a certain element has an atomic mass of 40 u, what is the mass of 0.20 mol of that element? Of 6.5 mol of the element? (*Answers:* 8.0 g; 260 g)
18. A certain element has an atomic mass of 195 u. How many moles of atoms are present in 39.0 g of the element? In 250 g of the element?

QUESTIONS TO THINK ABOUT

19. Why is the concept of continuous matter inconsistent with the Law of Definite Composition?
20. The Law of Definite Composition is true for all compounds, yet we know that most elements consist of mixtures of isotopes. Explain why these two statements do not contradict each other.
21. What mass in grams is represented by 1 u?

4

THEORIES OF THE ATOM

John Dalton had viewed atoms as being tiny, indivisible particles. However, almost a century after Dalton proposed his theory, a series of experiments performed in the late 1800s demonstrated that the atom can be subdivided into even smaller particles. It is now known that atoms are composed of several fundamental particles. Chemists have been most interested in three of these: electrons, protons, and neutrons.

This chapter describes some of the experiments that resulted in the discovery of electrons, protons, and neutrons and traces the development of the modern theory of the atom through several model modifications. When you have finished studying this chapter, you should be able to attain the following objectives:

1. Describe a discharge tube and what happens when a high voltage is applied to its terminals.
2. State the mass, charge, and behavior in an electric field of electrons, protons, and neutrons.
3. Describe the J. J. Thomson model of the atom.
4. Describe Rutherford's gold foil experiment.
5. Describe the nuclear model of the atom.
6. Given the atomic number and mass number of an atom, state the number of electrons, protons, and neutrons contained in the atom.

7. Explain the difference between a continuous spectrum and a line spectrum.
8. Describe the Bohr model of the atom and state the evidence in support of the Bohr model.
9. Given the isotopic composition of an element, calculate the average atomic mass of the element.
10. Distinguish between an orbit and an orbital.
11. State the symbols and numerical restrictions on the principal, secondary, magnetic, and spin quantum numbers, and state the property of the electron which each identifies.
12. Describe the shapes of the *s* and *p* orbitals.
13. Write the orbital names corresponding to different sets of the quantum numbers n, ℓ, and m.
14. Write a set of the quantum numbers n, ℓ, and m corresponding to a given orbital.
15. State the Aufbau principle, the Pauli exclusion principle, and Hund's rule.
16. Using the principles outlined in Section 4-7, draw a predicted energy level diagram for any of the first 38 elements.
17. Write predicted electronic configurations for the first 38 elements.

4-1/ELECTRONS

Observations of the behavior of discharge tubes gave the first indications that atoms can be subdivided into even smaller electrically charged particles.

A discharge tube (Fig. 4-1) consists of two metal plates sealed into the ends of a glass tube. The electrodes, called the cathode and the anode, are attached to the negative and the positive sides of a high voltage source, respectively. When most of the air is pumped from the tube and a high voltage is applied to the electrodes, current flows and the air left in the tube begins to glow. Certain minerals such as zinc sulfide give off light when placed between the electrodes of an operating discharge tube. This light is emitted in flashes. This suggests that the electricity is moving through the tube as a beam of discrete (individual) particles.

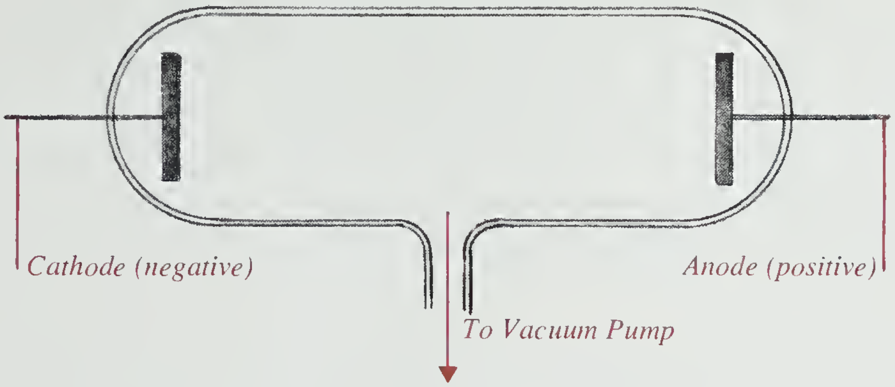


Fig. 4-1 A Discharge Tube

Experiments indicate that charged particles originate at the cathode and travel toward the anode. They are called **cathode rays**. If electrically charged plates are placed above and below the discharge tube, the cathode ray is deflected towards the positive plate (Fig. 4-2). Since opposite charges attract and like charges repel, it seems that cathode rays consist of negative particles. Other experiments prove that these negative particles, now called **electrons,** are identical no matter what material the cathode is made of and no matter what gas is present in the tube. These electrons are considered to be part of all matter. In the case of a discharge tube having a platinum cathode, the electrons would come from the platinum atoms. In the case of a discharge tube having a copper cathode, the electrons would come from the copper atoms. "Replacement" electrons are supplied to the cathode from the high voltage source.

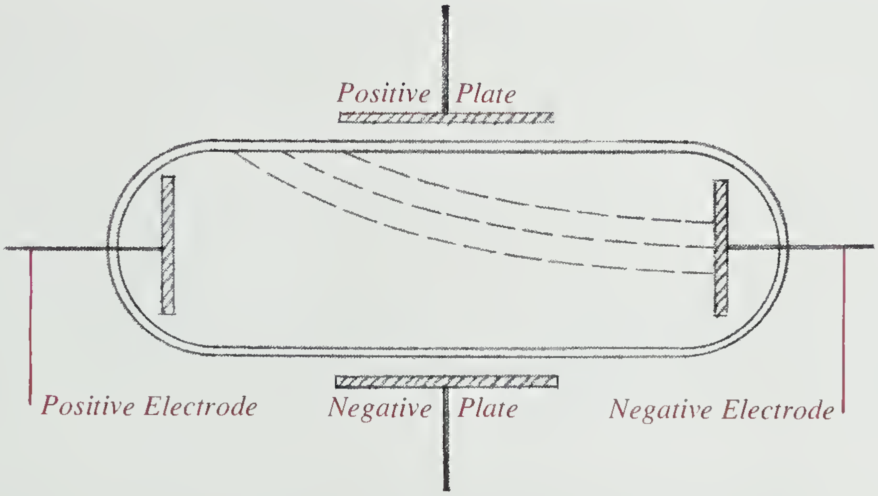


Fig. 4-2 Deflection of Cathode Rays

In an attempt to discover more about the nature of cathode rays the British physicist J. J. Thomson studied their deflection by electric and magnetic fields. By 1897 he was able to determine the ratio of the charge, *e*, to the mass, *m*, of an electron. He found that this ratio, e/m, had the same value for electrons produced in all discharge tubes. The ratio, however, told him nothing about the actual charge or the actual mass of an electron. If either one of these values could be measured experimentally, the other could then be calculated. Twelve years later, in 1909, Robert Millikan, an American physicist, determined the charge of an electron. Using the values of e/m and *e*, he was able to calculate the mass of an electron. He found that an electron had an atomic mass of 0.000 55 u. This means that electrons contribute very little to the mass of an atom.

4-2/PROTONS

In Germany, E. Goldstein had earlier modified the discharge tube by moving the cathode toward the middle of the tube (Fig. 4-3). He found that a zinc sulfide detecting screen glowed when it was located on either side of the cathode. The screen glowed when located between the electrodes because it was being struck by the negatively charged cathode rays. But why did it glow when located on the other side of the cathode? The explanation is that occasionally, as electrons left the cathode and traveled towards the anode, some of them

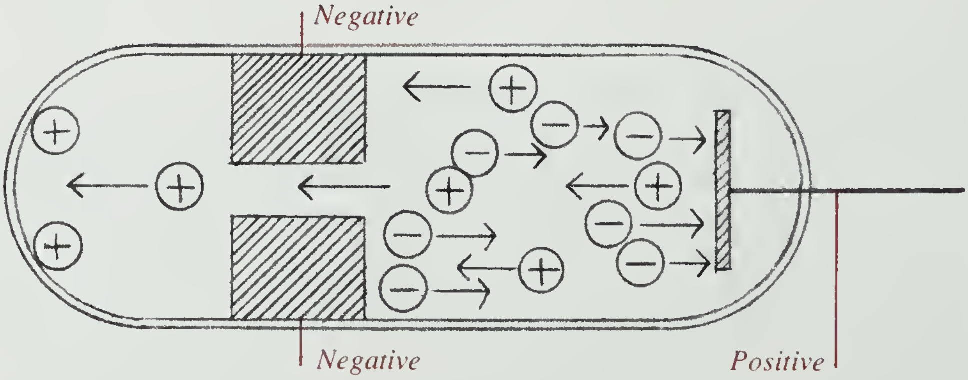


Fig. 4-3 Goldstein's Discharge Tube

struck neutral gas particles with such force that one or more electrons was knocked off. This loss of electrons converted a gas particle into a positively charged *ion* which was attracted to the cathode. Most of the ions picked up electrons at the cathode and were converted back to neutral particles. Occasionally, however, a positive ion passed through the hole in the cathode and was detected by the zinc sulfide screen on the other side.

The charge-to-mass ratio was found to be much smaller for positive ions than for electrons. This indicated that a positive ion had a much larger mass than an electron. Furthermore, the charge-to-mass ratio of the positive fragments, unlike the charge-to-mass ratio for electrons, varied according to the nature of the gas in the tube. However, the unit positive charge was found to be equal but opposite in sign to the negative charge of an electron. The smallest mass for a positive ion was the mass of the hydrogen ion, 1.0073 u. A hydrogen ion is called a **proton.** It is one of the fundamental particles of the atom. Every atom must contain one or more protons. A hydrogen atom is the simplest atom. It consists of one proton and one electron.

4-3/NEUTRONS

The third fundamental particle of the atom was not discovered until 1932 when the British physicist James Chadwick observed that atoms of beryllium emitted uncharged particles on being bombarded with high-speed positive helium ions (alpha particles). These uncharged particles were called **neutrons.** The atomic mass of a neutron was found to be 1.0087 u.

4-4/THE NUCLEAR ATOM

It had been shown earlier that the atom was not a solid, indestructible particle. In 1898, before the discovery of the neutron, J. J. Thomson proposed a model to explain the arrangement of protons and electrons in the atom. Thomson

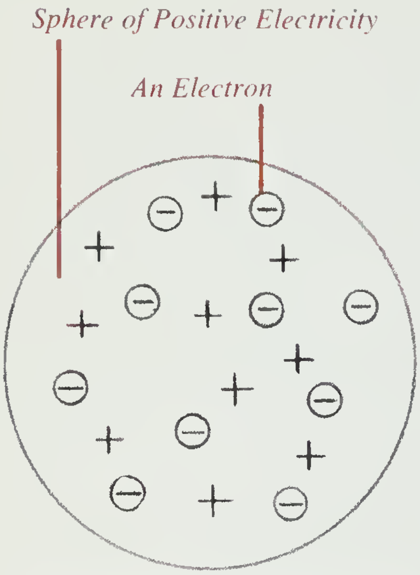


Fig. 4-4 J. J. Thomson's Plum Pudding Model of the Atom

considered the atom to be a sphere of positive electricity in which negative electrons were embedded like raisins in a plum pudding (Fig. 4-4). It had been demonstrated that protons had more mass than electrons, and therefore most of the atom's mass was thought to be associated with the positive charge.

In 1911, Lord Rutherford investigated the scattering of alpha particles (positive helium ions) by thin sheets of gold metal (Fig. 4-5). Alpha particles from a polonium source passed through a hole in a lead plate and were allowed to strike a sheet of gold foil. The movable zinc sulfide detector gave off a flash of light whenever it was struck by an alpha particle.

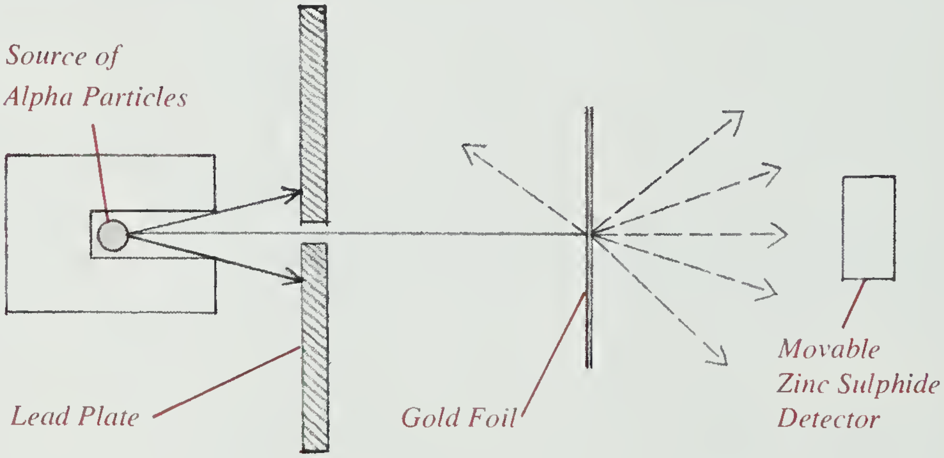


Fig. 4-5 Rutherford's Gold Foil Experiment

According to the Thomson model of 1898, atoms are essentially a sphere of uniform positive charge in which the negative particles are embedded. Since alpha particles have high speed, they should penetrate the foil. If the positive charge of an atom is uniformly distributed, an alpha particle would have little reason to swerve from its original path. It should pass through the foil without being deflected (Fig. 4-6).

Rutherford found that most of the alpha particles did pass through the gold undeflected, but some were deflected quite a lot. In fact, some were reflected back towards the lead plate. Rutherford was astonished. He said "it was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

The Thomson model could not explain this result. According to that model, an alpha particle would never encounter a

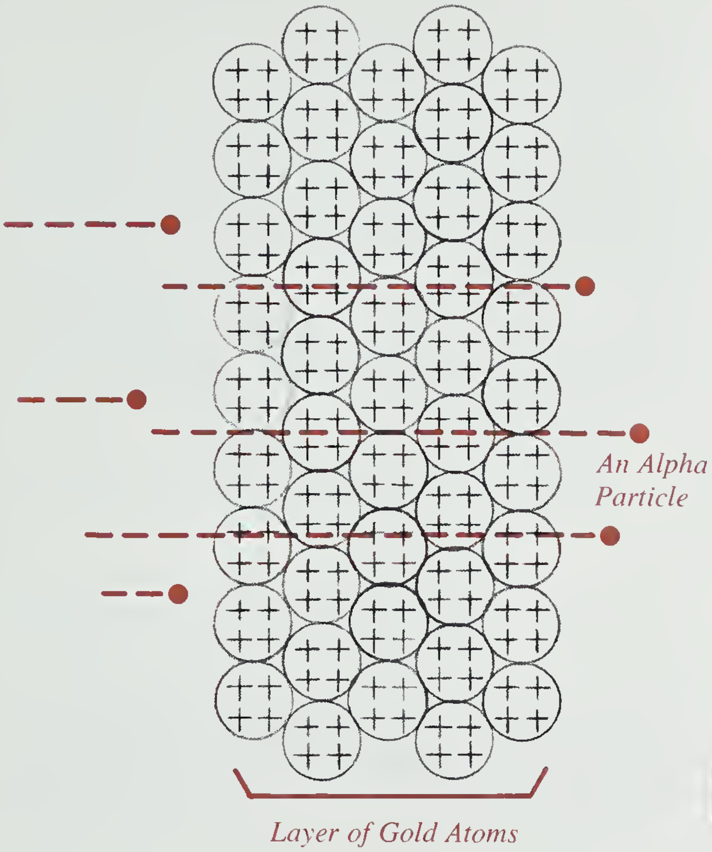


Fig. 4-6 Predicted Passage of Alpha Particles Through a Thomson Model of the Atom

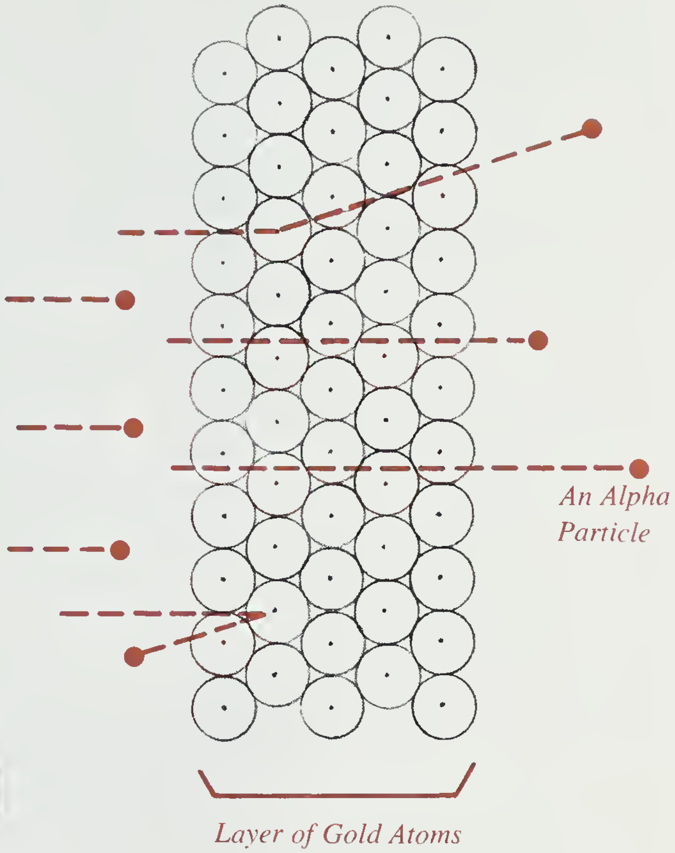


Fig. 4-7 Passage of Alpha Particles Through a Nuclear Atom

large enough obstacle to force it to be reflected. Rutherford proposed his own model to account for his experiment. He suggested that the mass and the positive charge in the gold atoms must be concentrated in very small regions. Most of the alpha particles could pass through; however, occasionally one came close to a high concentration of positive charge and mass. The large amount of mass made the positive charge immovable. As the positive alpha particles came near these positive particles in the atom, the repulsion of like charges caused the alpha particles to swerve (Fig. 4-7).

Rutherford suggested that an atom had a **nucleus** or center in which the positive charge and most of the mass were located. This nucleus occupied only a tiny portion of the volume of the entire atom. If a large football stadium were to represent the volume of the entire atom, a flea in the center of the stadium could represent the size of the nucleus.

4-5/THE STRUCTURE OF THE ATOM

The nuclear atom is the basis of our present theory of atomic structure. The protons and neutrons are called **nucleons.** Together they reside in the nucleus which is a minute but very dense part of the atom. The positive charge of the protons is balanced by the negative charge of the electrons in a neutral atom. The neutrons have no charge. The extranuclear (outside the nucleus) region, which makes up virtually all of the volume of the atom, contains only the electrons. The nucleus contributes almost no volume to the atom, but it contains essentially the entire mass of the atom.

The number of protons in the nucleus is called the **atomic number** (Z). Every atom of each element has a particular number of protons. That is, all oxygen atoms have 8 protons. If an atom has a number of protons other than 8, it is not an oxygen atom. In a neutral atom, Z is also the number of electrons. Oxygen is element number 8, and a neutral oxygen has 8 protons and 8 electrons.

The atomic mass of the proton is 1.0073 u. The atomic mass of the neutron is 1.0087 u. Thus, the approximate masses of the proton and of the neutron are 1 u. The mass of the electron is 0.000 55 u or approximately 0 u. The total number of protons and neutrons in an atom is called the **mass number**, A, and it is numerically equal to the approximate mass of the whole atom. A specific atom may be referred to by using a symbol incorporating both the atomic number and the mass number. For example, the symbol $^{12}_{6}C$ indicates a carbon atom that has $Z = 6$ and $A = 12$. The atom has 6 protons and a total mass of 12 u. The atom contains a total of 12 protons and neutrons, but it contains 6 protons. Therefore, it must also contain 6 neutrons. This atom is the carbon-12 mentioned in Chapter 3.

SAMPLE PROBLEM/4-1

How many electrons, protons, and neutrons are in an atom for which the atomic number is 92 and the mass number is 235?

The atomic number is the number of protons in the atom.

∴ There are 92 protons.

There must be the same number of electrons as of protons.

∴ There are 92 electrons.

The mass number is the sum of the number of protons and the number of neutrons.

∴ The number of neutrons is $235 - 92 = 143$.

EXERCISE/4-1

How many electrons, protons, and neutrons are in an atom for which the atomic number is 103 and the mass number is 257?

All atoms of the same element must have the same number of protons, but they need not all have the same number of neutrons. Atoms which have the same number of protons but different numbers of neutrons are called **isotopes.** Isotopes are atoms that have the same atomic number but different mass numbers. For example, there are two isotopes of chlorine: $^{35}_{17}Cl$ and $^{37}_{17}Cl$. The first isotope has 18 neutrons and the second one has 20 neutrons. These isotopes have the same chemical properties, but they have slightly different physical properties.

The atomic mass for chlorine, found in the tables, is derived from the masses of the two isotopes: $^{35}_{17}Cl$ makes up 75.40 percent of all chlorine atoms, and $^{37}_{17}Cl$ makes up the other 24.60 percent. Of 1000 chlorine atoms, 754 have a mass number of 35 (actual mass 34.97 u) and 246 have a mass number of 37 (actual mass 36.97 u). The average mass is $(754 \times 34.97 + 246 \times 36.97) \div 1000 = 35.46$ u. This explains why some elements have average atomic masses that are not close to whole numbers.

SAMPLE PROBLEM/4-2

Natural carbon consists of 98.89% carbon-12 and 1.11% carbon-13 (actual mass 13.0033 u). What is the average atomic mass of natural carbon?

Assume you have 10 000 atoms of carbon. Then there will be 9889 atoms of $^{12}_{6}C$ and 111 atoms of $^{13}_{6}C$.

$$\begin{aligned}\text{Total atomic mass} &= 9889 \times 12.000 + 111 \times 13.0033 \\ &= 120\,111\ \text{u} \\ \text{Average atomic mass} &= 120\,111\ \text{u}/10\,000 = 12.0111\ \text{u}\end{aligned}$$

EXERCISE/4-2

Natural neon contains 90.92% $^{20}_{10}Ne$ (mass 20.0 u), 0.26% $^{21}_{10}Ne$ (mass 21.0 u) and 8.82% $^{22}_{10}Ne$ (mass 22.0 u). Show that this gives an average atomic mass for neon of 20.2 u.

4-6/THE BOHR MODEL OF THE ATOM

The nuclear model of the atom raises some interesting questions. Why are the negative electrons not pulled into the positive nucleus because of the attraction of unlike charges? The electrons must be in some type of motion which counterbalances this attraction. It is observed that an electric charge moving under the influence of attractive forces gives off or loses energy. Do electrons give off energy? If so, the loss of energy would cause electrons to slow down and to be more strongly attracted to the nucleus, and they would gradually spiral into the nucleus. The result would be the collapse of the atom. However, atoms do not collapse. Therefore, there must be a flaw in the argument.

A clue to the problem is obtained from a study of the light given off from high energy substances. If a tungsten wire is in a high energy state due to the heating effect caused by an electric current, it releases the extra energy in the form of white light. White light is composed of all colors or frequencies of light. Each frequency has a characteristic energy. White light is composed of all frequencies and all energies of visible light. White light can be broken down into its component colors by passing it through a prism or a diffraction grating. A spectrum of colors is obtained. It is called a **continuous spectrum** because it consists of all the colors or frequencies of visible light (red, orange, yellow, green, blue, indigo, violet).

If hydrogen gas is excited (forced into a high energy state), it will emit some of the extra energy in the form of visible light. However, the visible light will be violet, not white. When this violet light is passed through a prism, it is broken into its component colors. The visible spectrum of hydrogen atoms consists of only certain colors, each of which corresponds to a characteristic energy. This is called a **line spectrum,** because it is made up of only certain frequencies of visible light (Fig. 4-8).

Fig. 4-8 A Schematic Line Spectrum of Hydrogen

When different elements are excited (as hydrogen is excited) by passing an electric current through gaseous samples of the elements, it is found that each element has a characteristic line spectrum.

Niels Bohr, a Danish physicist, proposed a model for the atom in 1913. The Bohr model explained why atoms do not collapse, and it also explained line spectra. Bohr developed his model using the line spectrum of the hydrogen atom, but it was necessary to change his model later so that other atoms could be included.

Bohr suggested that the total energy of an atom is restricted to certain values, that is, the energy is **quantized.** The electron in a hydrogen atom cannot have just any energy value; it can have only certain allowed energy values. The only way an electron can change its energy value is to "jump" from one allowed energy level to another. The jump cannot be gradual; it must occur all at once. An analogous situation is a person climbing or descending a flight of stairs: he might take one, two, or even three steps at a time, but he can never land between the steps.

When a hydrogen atom is excited, the electron gains energy and is promoted from a lower allowed energy level to a higher allowed energy level. When the electron drops back to the lower energy level, the previously gained energy is given off in the form of light of a certain frequency. If the electron is already at the lowest energy level, no more energy can be emitted, and thus the atom does not collapse. This is analogous to being at the foot of the flight of stairs. One can descend no further.

Bohr had found the flaw in the argument which began this section. The laws of Newtonian mechanics (which govern particles of large mass) do not govern particles that have a very small mass. These small particles obey a new set of laws of motion called **quantum mechanics.**

The basic principle of quantum mechanics is that electrons are allowed to have only certain energy values when they are in atoms. No electrons can have energy values that lie between these allowed energy values. When an electron shifts from one allowed energy value (or energy level) to another allowed energy level, the shift must be instantaneous.

Bohr suggested that the electron revolves about the nucleus of the hydrogen atom in one of a series of circular paths called **orbits.** This is analogous to our solar system: planets revolve around the sun in orbits. Only certain radii and certain energies are possible. The energy of the electron in a hydrogen atom can have only certain values that are allowed by the equation:

$$E_\mathrm{n} = -R/\mathrm{n}^2 \quad \text{where} \quad \mathrm{n} = 1, 2, 3, \ldots$$

and R is a constant called the Rydberg constant.

The equation means that the energy of an electron in the first orbit (or energy level) equals $-R/1$. The energy of an electron in the second orbit equals $-R/4$. In the third orbit, the energy of an electron equals $-R/9$ and so on (Fig. 4-9).

From the equation, it is possible to show that the larger the value of n, the more energy an electron possesses. If an electron is promoted from the first, second, or third orbit to

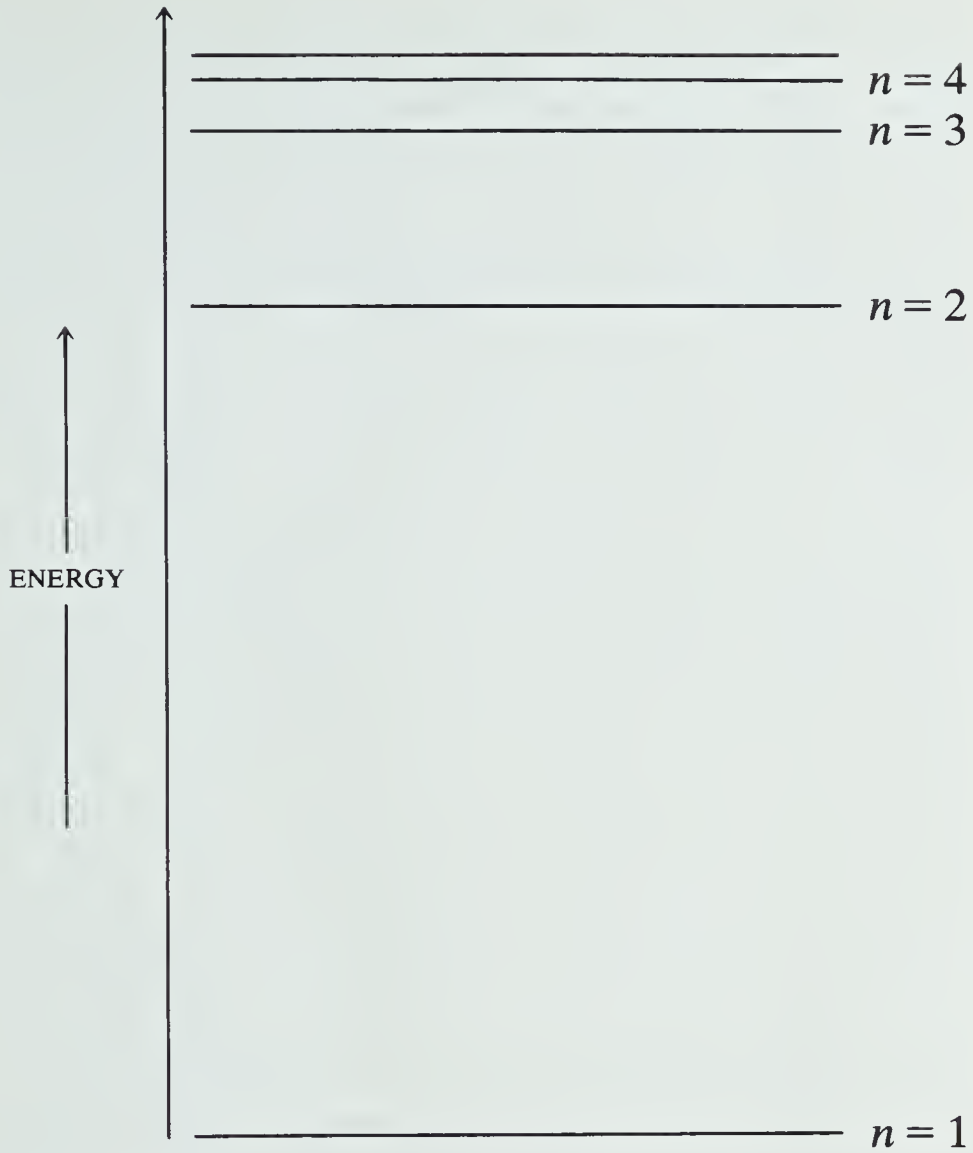


Fig. 4-9 Allowed Energy Levels for a Hydrogen Atom

the second, third, or fourth orbit, energy is absorbed by the atom. When an electron goes from an orbit with a larger radius (larger energy) to an orbit with a smaller radius (smaller energy), energy is emitted by the atom (Fig. 4-10).

Since there are only certain energy levels or orbits in the atom, only certain energies can be absorbed or emitted as the electron changes orbits.

Bohr's model supposed that the electron is a particle whose position and motion could be specified exactly at a given time. The electron was believed to move around the nucleus in one of many possible circular orbits. For each orbit there was supposed to be one energy value. This is the theory of quantization, and it came from a study of the line spectrum of hydrogen.

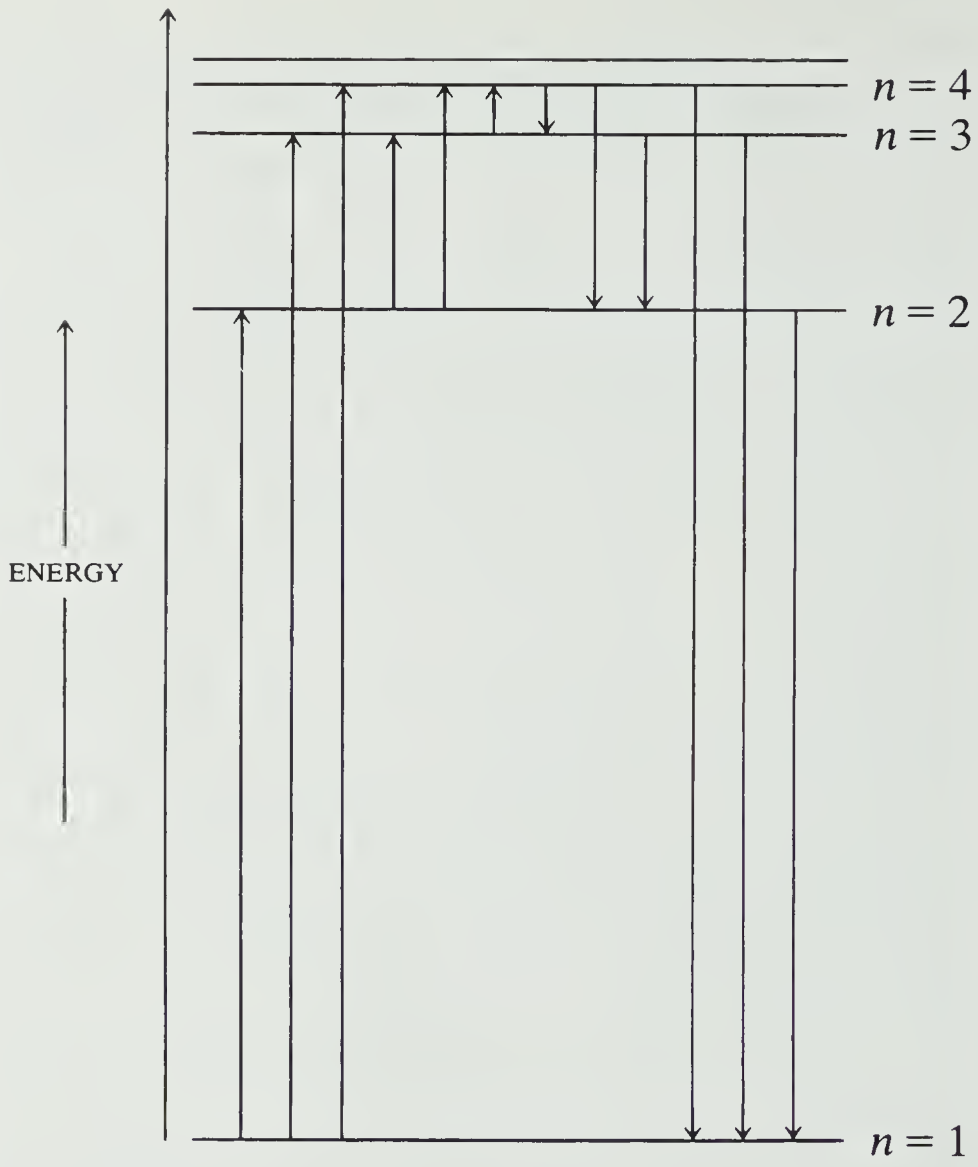


Fig. 4-10 Allowed Transitions Between Energy Levels

4-7/WAVE MECHANICS—THE PRESENT MODEL

Bohr's theory held for the hydrogen atom, but it did not work for any atom having more than one electron. The Bohr model was abandoned but the idea of quantization remained. The idea of quantization was Bohr's great contribution to our growing knowledge of the atom.

One of the problems that led to the discarding of the Bohr model was that in some experiments electrons behaved as particles while in other experiments electrons behaved as waves. That is, they could be reflected and diffracted just as light waves can be. In order to describe the motion of atomic electrons in terms that recognized both their wave nature and their particle nature, the German mathematician Erwin Schrödinger in 1924 devised a type of mathematics called **wave mechanics.**

The basic idea of wave mechanics is that one cannot determine simultaneously the position and velocity of a body as small as an electron. The best one can do is to calculate the probability of an electron being in a certain place at a certain time. This may seem to be rather vague, but much can be learned about an atom by studying electron position probabilities. Many problems of atomic and molecular structure can be solved by use of wave mechanics.

A **wave equation** is a mathematical expression describing the energy and motion of an electron around a nucleus. Such a wave equation exists for the hydrogen atom. It is possible to solve this wave equation and obtain a three-dimensional **wave function**. This wave function is related to the probability of finding an electron in a certain volume of space around the nucleus. Just as -2 and $+3$ are both solutions for the equation $x^2-x-6=0$, there are a number of wave functions which are all solutions to the wave equation for the hydrogen atom. There are many wave functions for the hydrogen atom. They describe regions in space where the electrons are most likely to be found. These regions are called **orbitals.** This word was coined to resemble the term *orbit* used in the Bohr model. Each of the orbitals can be identified by its **quantum numbers:** n, ℓ, and m. (The quantum numbers come from the solution of the wave equation.)

The first quantum number, n, is the **principal quantum number.** It is the same as the n used in the equation: $E_n = -R/n^2$. Again it identifies the energy of any electron in the orbital under study. Also, n goes from 1 to infinity by units: $n = 1, 2, 3, \ldots \infty$.

The second quantum number, ℓ, is the **secondary** or **azimuthal quantum number.** It identifies the shape of the orbital. For any given value of n, ℓ can start at 0 and go to the number which is one unit smaller than n:

$$\ell = 0, 1, 2, \ldots, n-1$$

If $\ell = 0$, the orbital is called an *s* orbital and has a spherical shape. If $\ell = 1$, the orbital is called a *p* orbital (Fig. 4-11).

If $\ell = 2$, the orbital is a *d* orbital, and it has a more complicated shape. If $\ell = 3, 4, 5, \ldots$, the orbitals are called *f, g, h*, . . . orbitals, and they have even more complicated shapes.

The third quantum number, m, is the **magnetic quantum number.** It identifies the direction of orientation (pointing) of the orbital with respect to an external magnetic field. For a given value of ℓ, m takes every integral value starting at $-\ell$, and going to $+\ell$. For example, if $\ell = 0$, then $m = 0$; if $\ell = 1$, then $m = -1$ or 0 or 1; if $\ell = 2$, then $m = -2$ or -1 or 0 or 1 or 2.

We will consider the orbitals which have n equal to 1, 2, and 3. If $n = 1$, then ℓ must equal 0 and m must also equal 0. There is only one orbital for the first energy level. This orbital is called the 1*s* orbital. It is a spherically shaped orbital. If an electron is in this orbital, it is possible to calculate its energy, but it is not possible to calculate its position or motion. The electron is moving so fast that it seems to occupy all the space in a sphere around the nucleus. It is possible to say only that an electron in the 1*s* orbital of a hydrogen atom spends 95 percent of its time somewhere in a sphere with a radius of about 1×10^{-10} m around the nucleus, and that it is most likely to be at a distance of 5×10^{-11} m from the nucleus.

If $n = 2$, ℓ can equal both 0 and 1. If $\ell = 0$, $m = 0$, and the orbital is the 2*s* orbital. This orbital is much like the 1*s* orbital except that it is larger. However, if $\ell = 1$, then there are three acceptable values of m (−1, 0, 1). There are three *p* orbitals in the second energy level. They all have the same shape, size, and energy, but they point in different directions and are called p_x, p_y, and p_z orbitals (Fig. 4-11).

For every value of n, there are n types of orbitals and n^2 actual orbitals. That is to say, the third energy level has three types of orbitals and nine (3^2) orbitals. This is easily computed. If $n = 3$, ℓ can equal 0, 1, and 2. Now if $\ell = 0$, then $m = 0$, and this is the 3*s* orbital. Like all *s* orbitals, the 3*s* orbital is spherical; however, it is larger than either the 1*s* or the 2*s* orbital. An electron in the 3*s* orbital has more energy than it would have if it were in the 1*s* or 2*s* orbital, and it can move further from the nucleus. If $\ell = 1$, m can have three values (−1, 0, 1). There are three 3*p* orbitals. The 3*p* orbitals are like the 2*p* orbitals except that an electron in a 3*p* orbital

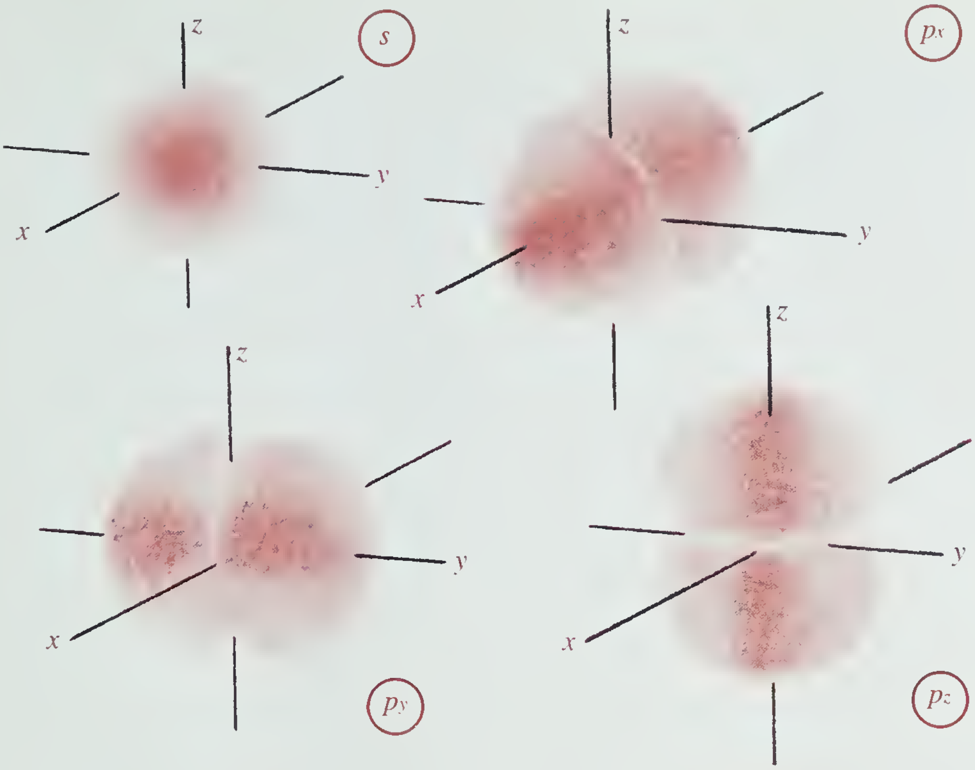


Fig. 4-11 Shapes of *s* and *p* Orbitals *It is impossible to draw a picture of an orbital since theoretically it extends through all space. However, 95 percent of the time the electron can be found in some small region near the nucleus. The shapes drawn here represent contour boundaries within which the electron can be found 95 percent of the time.*

is more likely to be further from the nucleus than an electron in a 2*p* orbital. Also it would have more energy than an electron in a 2*p* orbital. If $\ell = 2$, the orbitals are *d* type, and m can have five values $(-2, -1, 0, 1, 2)$. Thus, there are five 3*d* orbitals. In the third energy level, there are *s*, *p*, and *d* type orbitals. There is a total of 9 orbitals. (1 *s*-type + 3 *p*-type + 5 *d*-type = 9 orbitals). Table 4-1 summarizes the use of quantum numbers.

SAMPLE PROBLEM/4-3

What orbital has quantum numbers $\mathrm{n} = 3$, $\ell = 2$, $\mathrm{m} = 1$?

If $\ell = 2$, the orbital is *d* type. Since $\mathrm{n} = 3$, it must be a 3*d* orbital. The values of m simply serve to differentiate one 3*d* orbital from each of the other four 3*d* orbitals.

EXERCISE/4-3

What orbital has quantum numbers $\mathrm{n} = 5$, $\ell = 3$, $\mathrm{m} = -3$? (*Answer:* 5*f*)

TABLE 4-1

ORBITAL NAMES FOR DIFFERENT SETS OF QUANTUM NUMBERS

n	ℓ	m	*Name of Orbital*
1	0	0	1*s*
2	0	0	2*s*
2	1	−1	2*p*
2	1	0	2*p*
2	1	1	2*p*
3	0	0	3*s*
3	1	−1	3*p*
3	1	0	3*p*
3	1	1	3*p*
3	2	−2	3*d*
3	2	−1	3*d*
3	2	0	3*d*
3	2	1	3*d*
3	2	2	3*d*
4	0	0	4*s*
4	1	−1	4*p*
4	1	0	4*p*
4	1	1	4*p*
4	2	−2	4*d*
4	2	−1	4*d*
4	2	0	4*d*
4	2	1	4*d*
4	2	2	4*d*
4	3	−3	4*f*
4	3	−2	4*f*
4	3	−1	4*f*
4	3	0	4*f*
4	3	1	4*f*
4	3	2	4*f*
4	3	3	4*f*

The energy level diagram of the orbitals derived for the hydrogen atom is shown in Fig. 4–12. Notice that orbitals having the same principal quantum number have the same energy. That is, they are degenerate. For example, the 3*s*, the three 3*p*, and the five 3*d* orbitals are degenerate in a hydrogen atom.

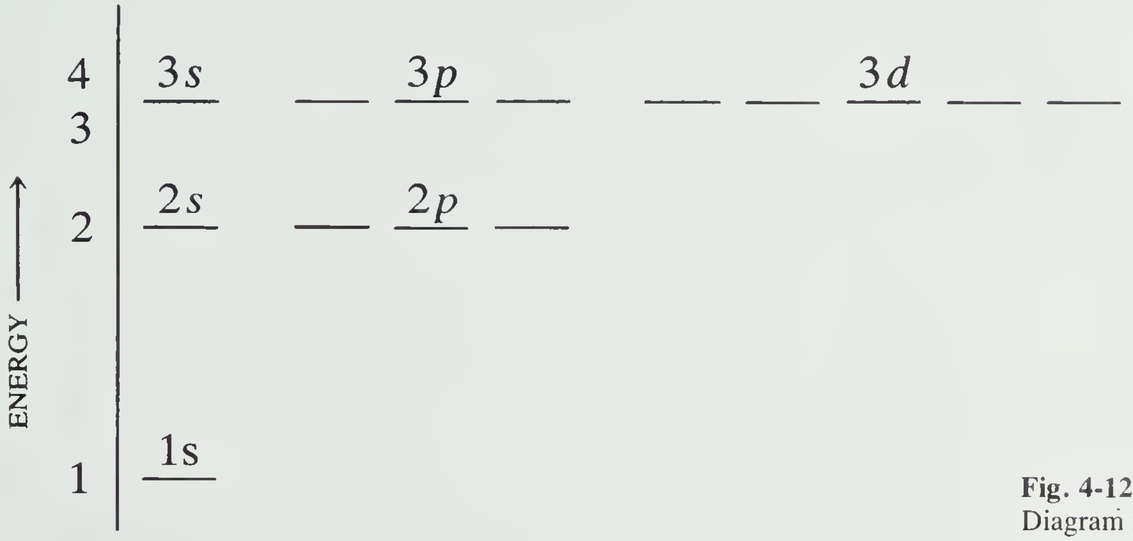


Fig. 4-12 The Energy Level Diagram for a Hydrogen Atom

There are higher energy levels containing more orbitals; however, the trend seems to be clear. A large number of orbitals can be derived mathematically for the hydrogen atom. This may seem to be a waste of time inasmuch as there is only one electron in the hydrogen atom. This electron can occupy only one orbital at a time. The other orbitals are empty. It must be remembered that in a large sample of hydrogen atoms most of the atoms would have their one electron in the lowest energy orbital, the 1*s*. However, some atoms could be in the excited state, and they would have electrons in the orbitals of the second, third, fourth, and higher energy levels.

The Bohr model was dropped because it was useful only for a one-electron system. Will this theory of orbitals work for a many-electron system? The theory will work as long as one is willing to learn some new rules and to modify the energy level diagram slightly.

The **Aufbau principle** states that in going from a hydrogen atom to a larger atom, one adds protons to the nucleus and electrons to orbitals having the same shape as those derived for the hydrogen atom. One starts at the orbitals having the

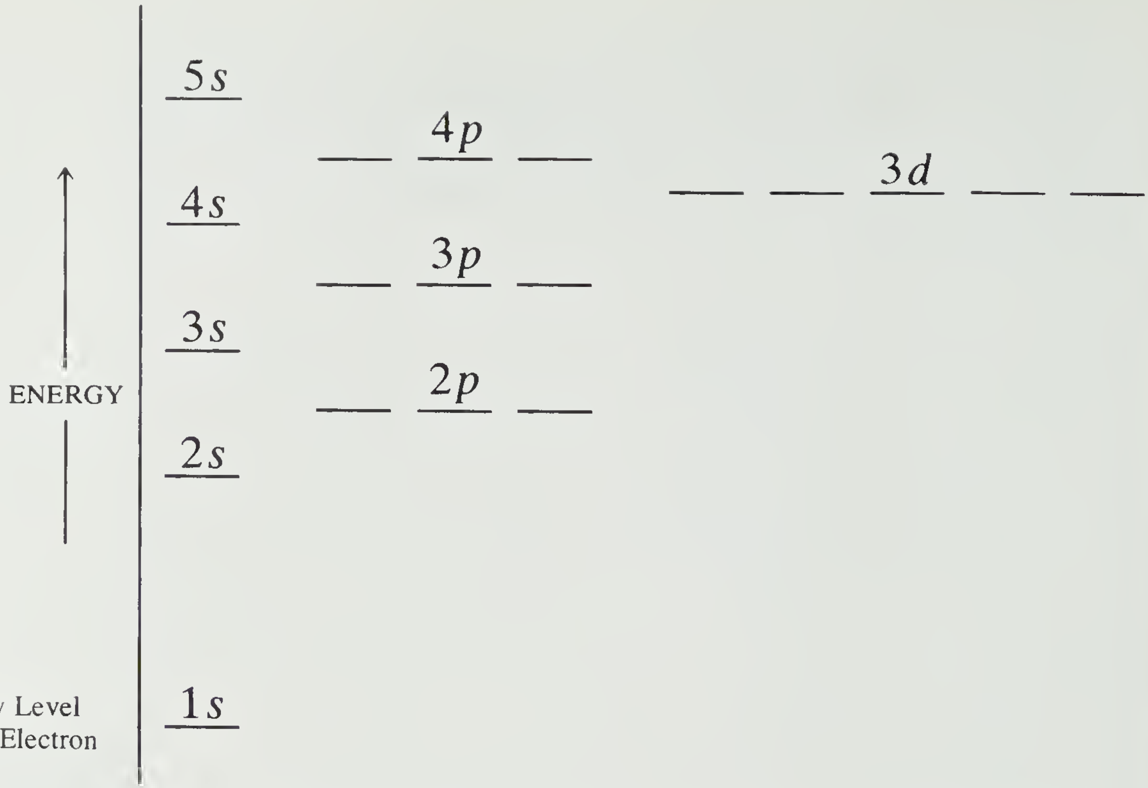


Fig. 4-13 The Energy Level Diagram for a Many-Electron Atom

lowest energy and fills them, in order of increasing energy, until one runs out of electrons. Stated more simply, electrons go into the lowest energy level available.

The **Pauli exclusion principle** states that an orbital can be empty, have one electron, or have two electrons. If two electrons are in the same orbital, they must have opposite spins. This introduces the final quantum number, s. The **spin quantum number,** s, can have only two values, +1/2 and −1/2. That is, an electron behaves as if it can spin clockwise or counterclockwise. The Pauli exclusion principle means that no two electrons in the same atom can have four identical values for the four quantum numbers.

The modified energy level diagram is shown in Fig. 4-13. This diagram shows that the second level is divided into two sublevels. That is, the 2*s* orbital is no longer degenerate with the three 2*p* orbitals. The first sublevel consists of the 2*s* orbital, and the second sublevel consists of the three 2*p* orbitals. In the same way, the third, fourth, and fifth energy levels are divided into sublevels of different energies. Also, the energy levels begin to overlap. For example, the fourth energy level begins before the third level is completed (i.e., the 4*s* sublevel is of lower energy than the 3*d* sublevel). The reasons for having to modify the original energy level dia-

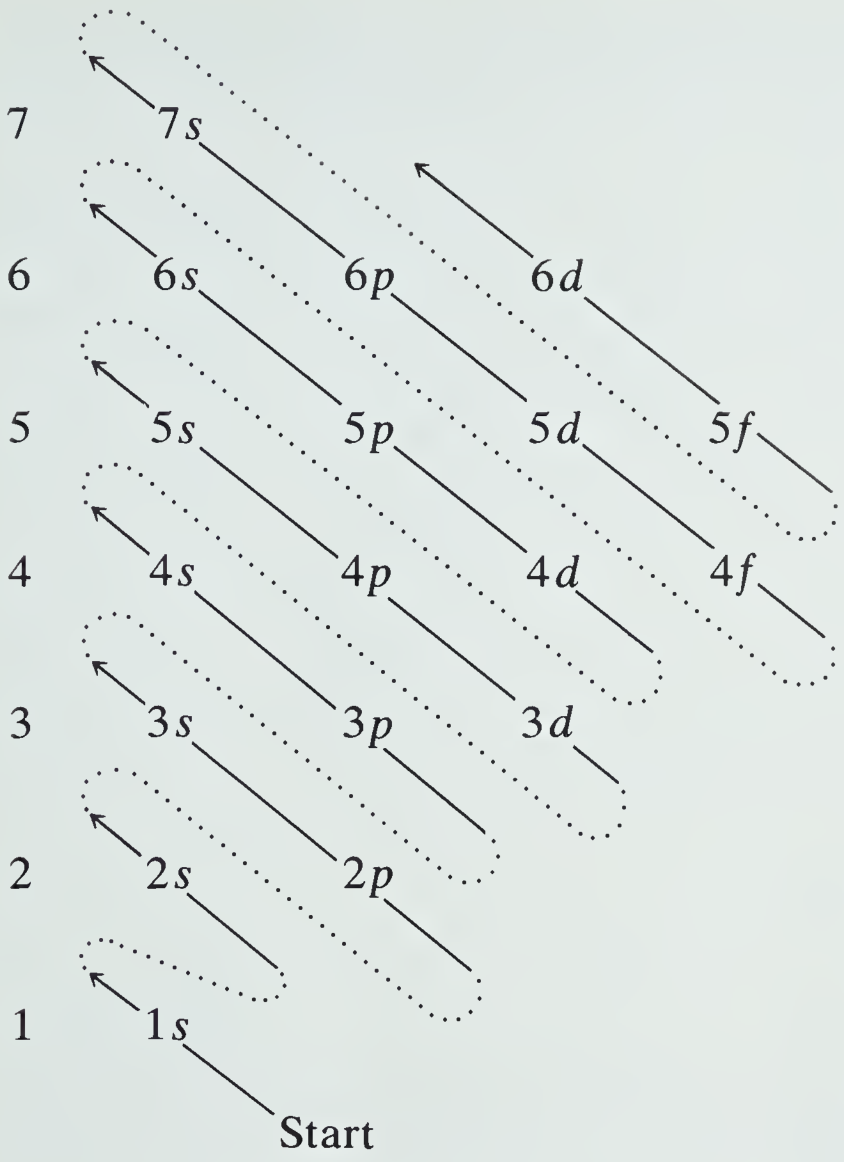


Fig. 4-14 Mnemonic for Filling Orbitals

gram, when describing a many-electron system, have been discussed by chemists; however, they are beyond the scope of an introductory course. The energies of the orbitals are approximately in the order: $1s < 2s < 2p < 3s < 3p < 4s \leqq 3d < 4p < 5s \leqq 4d < 5p < 6s \simeq 4f \simeq 5d < 6p$. It is possible to remember the order of filling by learning Fig. 4-14.

Finally, **Hund's rule** suggests that electrons in the same sublevel will not pair up until all the orbitals of the sublevel are at least half-filled (Fig. 4-15). The arrows represent electrons in an orbital. The spin direction is indicated by the direction of the arrow. Two paired electrons in an orbital are indicated by two arrows: one pointing up and one pointing down—meaning that they have opposite spins.

NUMBER OF ELECTRONS IN THE $2p$ SUBLEVEL	DISTRIBUTION		
	$2p_x$	$2p_y$	$2p_z$
1	↑		
2	↑	↑	
3	↑	↑	↑
4	↑↓	↑	↑
5	↑↓	↑↓	↑
6	↑↓	↑↓	↑↓

Fig. 4-15 Distribution of Electrons in the $2p$ Sublevel

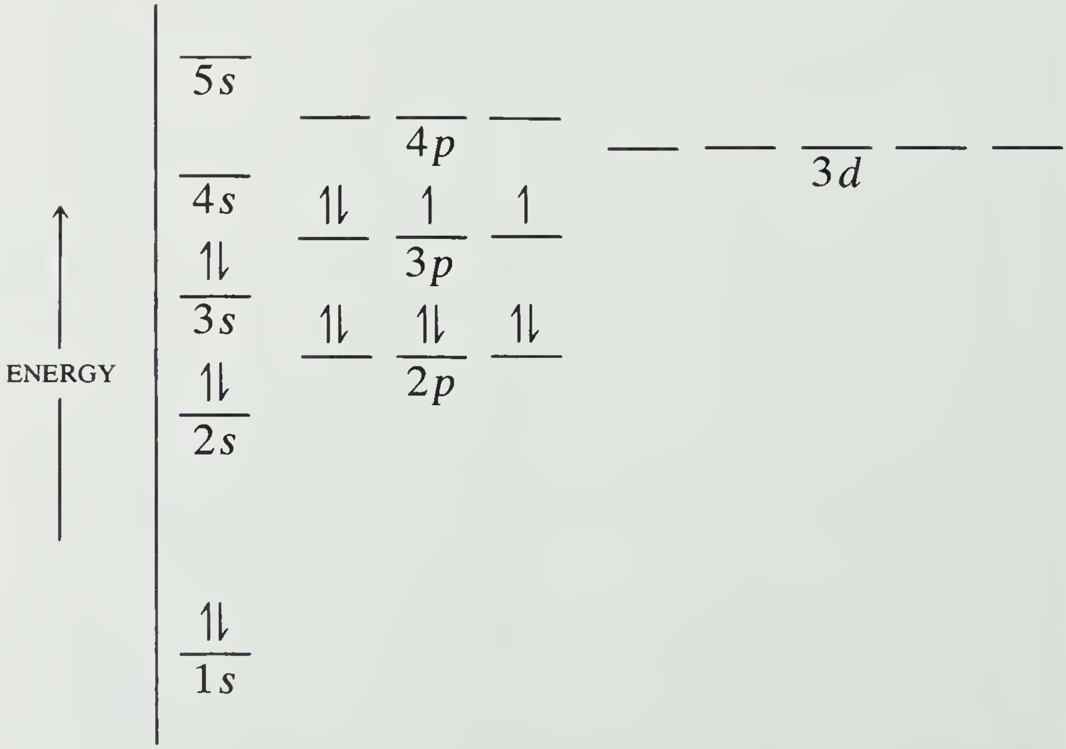
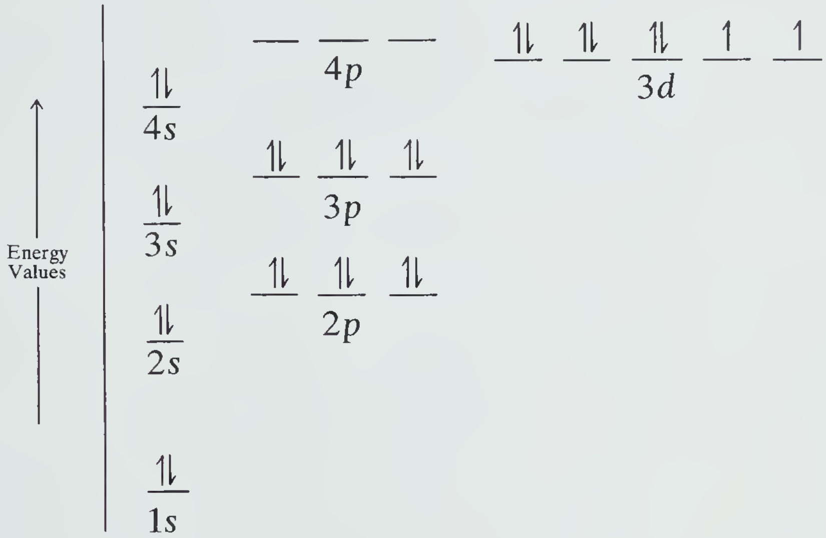


Fig. 4-16 The Energy Level Diagram for a Sulfur Atom

An example will show how these rules can be used to describe many-electron atoms. Consider the element sulfur. Sulfur has 16 protons and 16 electrons. It also has 16 neutrons, but the number of neutrons is of no concern to us at this point. Sixteen electrons can be placed into the energy level diagram as shown in Fig. 4-16.

SAMPLE PROBLEM/4-4

Draw an energy level diagram for element 28, nickel.



EXERCISE/4-4

Draw an energy level diagram for element 23, vanadium.

The distribution of electrons among the various orbitals of an atom is called its **electronic configuration.** The electronic configuration of sulfur is written as:

$$_{16}\text{S}\ \ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$$

The first and second energy levels are completely filled. However, the third energy level is only partly filled. The 3*s* orbitals and one of the 3*p* orbitals are filled. The other two 3*p* orbitals are half-filled. The 3*d* orbitals and all orbitals of the fourth, fifth, and higher levels are empty. Can you see that the electronic configuration of iron must be:

$$_{26}\text{Fe}\ \ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$$

SAMPLE PROBLEM/4-5

Predict the electronic configuration of element number 24, chromium.

When electrons are added according to the order given in Fig. 4-14, the predicted electronic configuration becomes:

$$\mathrm{Cr} \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$$

The actual electronic configuration of chromium deviates slightly from that predicted. It is found that chromium actually has the configuration:

$$\mathrm{Cr} \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$$

This deviation from the predicted behavior usually occurs in those elements which are close to filling or half-filling a sublevel. Hund's rule implies that half-filled sublevels would be relatively stable. Full sublevels, whether they are *s*, *p*, or *d*, also confer a measure of stability on an atom. When $3d$ sublevels are involved, with energies near those of the $4s$ sublevel, the stability effect is large enough to allow promotion of a $4s$ electron in chromium to the $3d$ sublevel. This gives a chromium atom a half-filled $3d$ sublevel containing five electrons.

EXERCISE/4-5

Predict the electronic configuration of element number 35, bromine. *Answer:*

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$$

or

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$$

The electronic configurations of the first 20 elements are given in Table 4-2.

The atomic theory that has been derived in this chapter is basic to our theory of compound formation. The next chapters will add the theories of molecular structure to the concepts of atomic structure.

TABLE 4-2

ELECTRONIC CONFIGURATIONS OF THE FIRST TWENTY ELEMENTS

Element	*Electronic Configuration*
H	$1s^1$
He	$1s^2$
Li	$1s^2\ 2s^1$
Be	$1s^2\ 2s^2$
B	$1s^2\ 2s^2\ 2p^1$
C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
Ne	$1s^2\ 2s^2\ 2p^6$
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
S	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Ar	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Ca	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

QUESTIONS

1. Contrast the Thomson model with the nuclear model of the atom.
2. Describe the experiment which caused the Thomson model to be replaced by the nuclear model of the atom.
3. How many neutrons are found in one atom of $^{60}_{27}\mathrm{Co}$? $^{90}_{38}\mathrm{Sr}$? $^{108}_{47}\mathrm{Ag}$? $^{207}_{82}\mathrm{Pb}$? $^{210}_{85}\mathrm{At}$? $^{238}_{92}\mathrm{U}$?

4. What fundamental particles are found in the nucleus of the atom?
5. What experimental evidence did Bohr have to support his belief that the energy of the electrons in a hydrogen atom is quantized?
6. When a hydrogen atom is excited, what happens to the electron in the atom?
7. Give two reasons why the Bohr model was eventually discarded.
8. What is one difference between the idea of a Bohr orbit and the idea of an orbital?
9. What are the quantum numbers n, ℓ, and m for each of the orbitals of the 5*p* sublevel? Of the 6*d* sublevel?
10. What orbital (1*s*, 2*s*, 2*p*, etc.) has quantum numbers (a) $n = 2$, $\ell = 1$, $m = 0$? (b) $n = 4$, $\ell = 2$, $m = -2$? (c) $n = 6$, $\ell = 3$, $m = 1$?
11. Use Hund's rule to place seven electrons in the orbitals of the 3*d* sublevel; in the orbitals of the 4*f* sublevel.
12. Draw the energy level diagram for element number 22 (titanium); number 25 (manganese); number 32 (germanium).
13. Write the electronic configurations for: ${}_{6}C$, ${}_{10}Ne$, ${}_{17}Cl$, ${}_{23}V$, ${}_{34}Se$.
14. Natural boron consists of 81.6% ${}^{11}_{5}B$ and 18.4% ${}^{10}_{5}B$. What is the average atomic mass of natural boron?
15. Natural potassium consists of 93.1% ${}^{39}_{19}K$ and 6.9% ${}^{41}_{19}K$. What is the average atomic mass of natural potassium? (*Answer:* 39.1 u)

QUESTIONS TO THINK ABOUT

16. Why can there be no *d* orbitals in the second ($n = 2$) energy level?
17. Suppose the spin quantum number had the values 0, +1/2, −1/2. How many electrons could one orbital hold? Why?
18. If the magnetic quantum number, m, took every integral value starting at 0 and going to $+\ell$, how many orbitals would have $n = 5$?
19. Suggest an atom (other than chromium), with atomic number smaller than 38, which might be expected to deviate from the predicted electronic configuration.

5

PERIODIC LAW

Dalton's atomic theory was such an effective stimulus in the search for elements that by the 1860s more than 60 elements were known. However, there was a problem. It was not possible to predict what elements were still undiscovered or to foretell their properties. In this chapter we shall see how, as time went on, various regularities were recognized in the properties of elements; how this led to the discovery of the periodic law and the development of the modern periodic table; and how the relationship between the properties of elements and their atomic structures finally became clear.

When you have finished reading this chapter you should be able to attain the following objectives:

1. State the Periodic Law.
2. Describe the general arrangement of Mendeleev's periodic table in terms of periods and families.
3. Explain why Mendeleev's periodic table represented an important advance in chemistry.
4. State the major difference between Mendeleev's periodic table and the modern periodic table.
5. Locate, in a modern periodic table, the representative elements, the transition metals, the lanthanides, and the actinides.
6. Locate, in a modern periodic table, the noble gases, the alkali metals, and the halogens.
7. Locate, in a modern periodic table, the metals, nonmetals, and metalloids.

8. Describe the arrangement of the modern periodic table in terms of energy levels.
9. Explain, in terms of electronic configurations, why elements in the same family have similar properties.
10. Write electron-dot symbols for the first 38 elements.
11. Explain the meaning of ionization potential and electron affinity.
12. Predict trends in atomic size, ionization potential, and electron affinity as one goes across a period or down a family in the periodic table.

5-1/PERIODIC LAW

Within twenty-five years after Dalton had proposed his atomic theory, enough elements had been discovered for some patterns of relationship to appear. In 1829, the German chemist Johann Döbereiner noticed similarities among certain elements. Similar elements seemed to appear in groups of three: sulfur, selenium, and tellurium; chlorine, bromine, and iodine; lithium, sodium, and potassium. He called them "triads."

In 1864 the English chemist John A. R. Newlands arranged the known elements in order of increasing atomic mass. He noticed that similar chemical and physical properties occurred after every eight elements. For example, atoms 2, 9, and 16 in his list (lithium, sodium, and potassium) resembled each other chemically. He was ridiculed for this suggestion. One prominent contemporary even asked if he had ever examined the elements according to the order of their initial letters. Nevertheless, it was Newlands who pointed out more clearly than anyone else had done previously the existence of the periodic recurrence of properties among the elements. But there was one flaw in his scheme. His proposed table had no gaps and therefore left no room for new elements.

Fig. 5-1 Dmitri Mendeleev (1834-1907) *(Photo courtesy of The Bettmann Archive)*

This flaw was corrected by two chemists working independently. The Russian chemist Dmitri Mendeleev (Fig. 5-1) and his German counterpart Lothar Meyer both discovered the periodic law in 1869. Mendeleev, however, is usually given priority because he published his ideas first. The **periodic law** states that when elements are arranged in order

TABLE 5-1

MENDELEEV'S PERIODIC TABLE

Row	*Group I*	*Group II*	*Group III*	*Group IV*	*Group V*	*Group VI*	*Group VII*	*Group VIII*
1	H = 1							
2	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 58.5 Ni = 59
5	Cu = 63	Zn = 65	Ga = 70	Ge = 72	As = 75	Se = 79	Br = 80	
6	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 96		Ru = 103 Rh = 104 Pd = 106
7	Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 120	Te = 125	I = 127	
8	Cs = 133	Ba = 137	La = 138	Ce = 140				
9								
10			Yb = 173		Ta = 182	W = 184		Os = 191 Ir = 193 Pt = 196
11	Au = 198	Hg = 200	Tl = 204	Pb = 206	Bi = 208			
12				Th = 232		U = 240		

of increasing atomic mass, elements with similar properties recur at regular intervals. Mendeleev prepared a periodic table to illustrate his arguments. A version of his table is given in Table 5-1.

In Mendeleev's table the elements were placed in horizontal rows or **periods**. Elements with similar properties were arranged in vertical groupings called **families**. The periodic occurrence of properties noticed by Newlands is reflected in the table. Chlorine, bromine, and iodine are all found in Group VII. The reactive metals lithium, sodium, and potassium are found in Group I; so are the coinage metals copper, silver, and gold.

Mendeleev's table contained several gaps. He predicted that new elements would be found to fill these gaps. The table made it possible to predict the properties of these yet undiscovered elements. The predictions were eventually confirmed and were remarkable in their accuracy.

Mendeleev's table has stood the test of time with few alterations required. The only major modification was the change required by the discovery of the first noble gas (argon) by Lord Rayleigh and Sir William Ramsay in 1894. After the discovery of electrons and protons and the development of the nuclear model of the atom, the Dutch physicist A. van den Broek suggested in 1911 that several minor inconsistencies would be removed if the table were arranged according to atomic number instead of atomic mass. The result is the modern periodic table which is shown at the back of the book. The revision required a change in the periodic law to its modern form: when the elements are arranged in order of increasing atomic number, elements with similar properties occur at regular intervals. Another way of stating the periodic law is: the physical and chemical properties of the elements are a periodic function of the atomic numbers.

5-2/THE MODERN PERIODIC TABLE

A *simplified* version of the modern periodic table, with the elements arranged in order of increasing atomic number, is shown in Fig. 5-2.

GROUP →

PERIOD ↓	I	II											III	IV	V	VI	VII	0
1	1																	2
2	3	4											5	6	7	8	9	10
3	11	12	← Transition Metals →										13	14	15	16	17	18
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
7	87	88	89	104	105	106												

6	58	59	60	61	62	63	64	65	66	67	68	69	70	71
7	90	91	92	93	94	95	96	97	98	99	100	101	102	103

Fig. 5-2 Arrangement of Elements in the Periodic Table According to Increasing Atomic Number

When the elements are arranged according to this scheme, elements with atomic numbers 2, 10, 18, 36, 54, and 86 are found in Group 0. These six elements—helium, neon, argon, krypton, xenon, and radon—are the least reactive of all the elements known. Since they are all gases at room temperature and pressure they are known as the **noble gas** family.

The elements with atomic numbers one greater than the noble gases—3, 11, 19, 37, 55, and 87—are lithium, sodium, potassium, rubidium, cesium, and francium. They all exhibit metallic properties and are highly reactive. For example, they all react vigorously with water to liberate hydrogen, and they all react with chlorine to form colorless salts which crystallize in cubic shapes and have similar formulas—LiCl, NaCl, KCl, RbCl, CsCl, FrCl. These chemically similar elements are called the **alkali metals** and are found in Group I of the periodic table.

The elements with atomic numbers 9, 17, 35, 53, and 85 are found in Group VII. They are fluorine, chlorine, bromine, iodine, and astatine. These elements all exhibit nonmetallic properties. They react with hydrogen to form compounds which dissolve in water to form acidic solutions. They react with the alkali metals to form salts with similar formulas and crystal shapes. These chemically similar elements are called the **halogen** family.

Hydrogen, with atomic number 1, is unique. It is usually included in Group I even though its chemical properties do not resemble those of the alkali metals. The fact is that hydrogen does not really fit anywhere in the table. There is no other element with properties like those of hydrogen.

The modern periodic table differs slightly from the arrangements used by Mendeleev and Meyer. The elements are arranged in order of increasing atomic number instead of increasing atomic mass. There are still horizontal rows or periods, but these periods have different lengths. The first period is short, consisting of only two elements. Periods 2 and 3 contain eight elements each. Periods 4 and 5 are long periods, each containing 18 elements. The sixth period is a very long period containing 32 elements, and the seventh period is incomplete. Elements having similar properties still appear in vertical columns called groups or families.

Groups I and II, on the left-hand side of the periodic table, and Groups III to VII, on the right-hand side, together constitute what are called the **representative elements**. The middle elements in the periodic table, between Groups II and III, are responsible for the extra length of the long periods and are called the **transition metals**. The very long periods, 6 and 7, are compressed in the table by removing 14 of their members and representing them separately below. These elements are called the **lanthanides** (rare-earth elements) and **actinides**, respectively.

The periodic table is useful for organizing chemical knowledge. The elements on the left of the zigzag line in the table are metals. Those on the right side are nonmetals. The most metallic elements are located in the lower left corner of the periodic table. The most nonmetallic (least metallic) elements are located in the upper right corner. There is a gradual transition from metallic to nonmetallic properties as one goes from left to right within a period. Since there is no sharp dividing line between metals and nonmetals, those elements near the zigzag line will exhibit properties of both metals and nonmetals. These elements are called metalloids (Section 3-7). Boron, aluminum, silicon, germanium, and arsenic fall into this category.

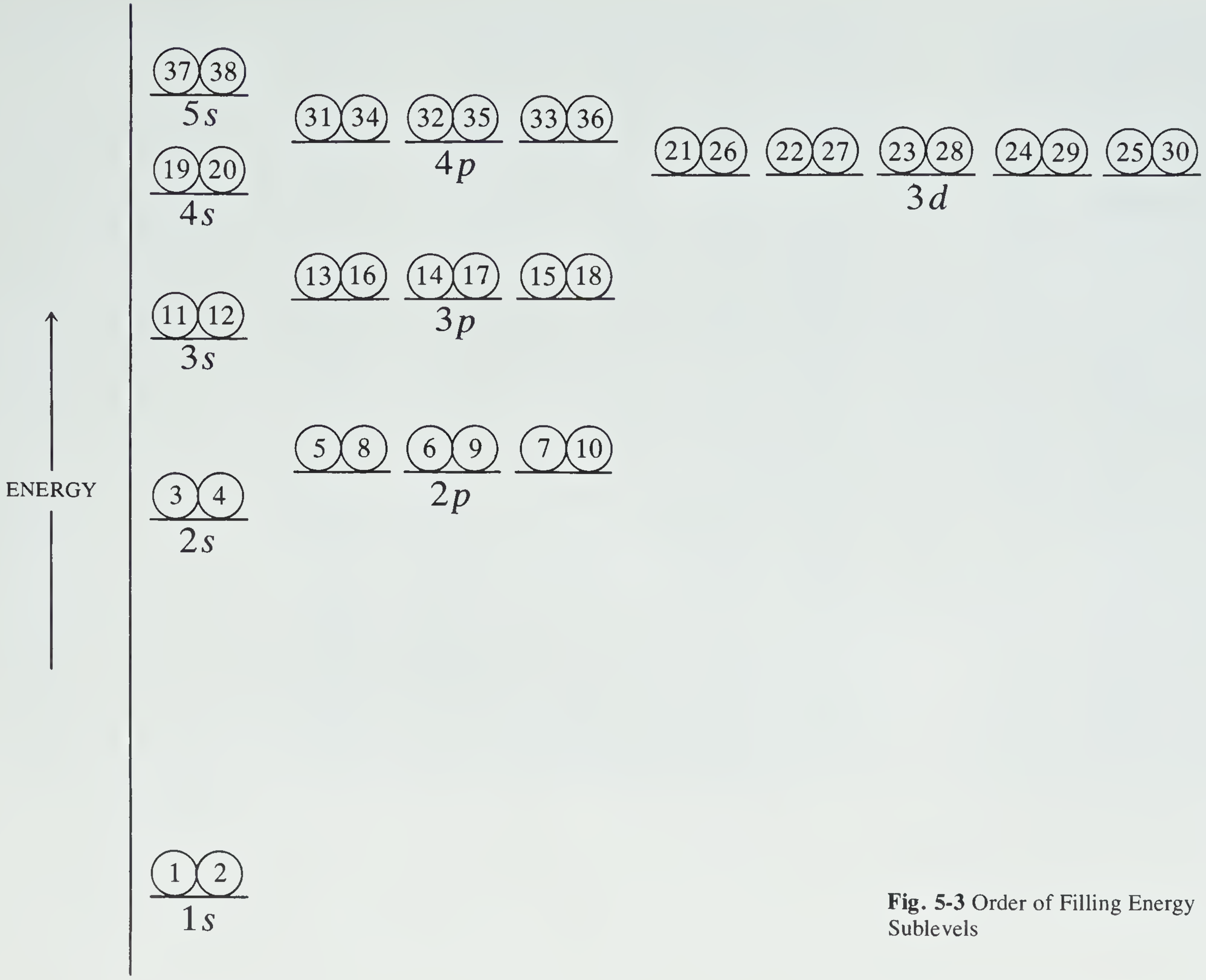


Fig. 5-3 Order of Filling Energy Sublevels

5-3/THE PERIODIC LAW AND ENERGY LEVELS

The energy level diagram for atom number 38, strontium, is shown in Fig. 5-3. It shows the order in which the 38 electrons of strontium are placed in the 19 orbitals of lowest energy. This diagram can also be used to give the electronic configuration of any element below number 38. For example, the energy level diagram for element 28, nickel, would contain only the first 28 electrons. The reader would make a mental note to omit electrons 29 to 38 from the diagram. Thus, the electronic configuration of nickel is:

$$_{28}\mathrm{Ni}\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$$

The energy sublevels are grouped into clusters of roughly similar energy by horizontal dotted lines. Thus the 2*s* and 2*p* sublevels are grouped together, as are the 3*s* and 3*p* sublevels. The next higher grouping, however, consists of 3*d*, 4*s*, and 4*p* sublevels, and they are in the relative order $s<d<p$. This suggests that for all atoms above atomic number 36, the energy sublevels in a given cluster will be filled in the order $s<d<p$. If two columns for the atoms with electronic configurations ending in s^1 and s^2 are placed at the left side of a piece of paper, if ten columns for the atoms that end in d^1 to d^{10} are placed in the middle, and if six columns for the atoms that end in p^1 to p^6 are placed at the right side of the paper, one can list the elements as their electrons fill up the energy level diagram:

s^1	s^2	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	p^1	p^2	p^3	p^4	p^5	p^6
1	2																
3	4											5	6	7	8	9	10
11	12											13	14	15	16	17	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
37	38																

A table very similar to the periodic table is obtained. This is not an accident. The periodic table was originally constructed to group elements according to their chemical properties. However, we have seen that it can also be constructed using energy level diagrams. Thus, chemical properties are apparently related to the electronic configurations of elements.

Consider elements 10, 18, and 36. Their electronic configurations are:

$_{10}\text{Ne}$ $1s^2\ 2s^2\ 2p^6$

$_{18}\text{Ar}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

$_{36}\text{Kr}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

All of these elements are noble gases. They all have filled outer s and p orbitals. It appears that whenever the outer s and p orbitals are filled with a total of *eight* electrons, the atom is chemically inert. Helium is also chemically inert because two electrons are sufficient to fill the first energy level. Thus, it is included in the noble gas family, not in Group II.

Consider elements 3, 11, 19, and 37:

$_{3}\text{Li}$ $1s^2\ 2s^1$

$_{11}\text{Na}$ $1s^2\ 2s^2\ 2p^6\ 3s^1$

$_{19}\text{K}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

$_{37}\text{Rb}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^1$

These elements all have electronic configurations ending in s^1. That is, their outer (or highest energy) orbitals are half-filled s orbitals. These elements all have similar properties.

Finally, consider elements 9, 17, and 35:

$_{9}\text{F}$ $1s^2\ 2s^2\ 2p^5$

$_{17}\text{Cl}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

$_{35}\text{Br}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

These elements are the halogens and experiments have shown that they all have similar chemical properties. Their electronic configurations all end in $s^2\ p^5$. That is, they have a total of *seven* electrons in their outer s and p orbitals.

SAMPLE PROBLEM/5-1

Consider elements 4, 12, 20, and 38. Show why they should all belong in the same family.

Their electronic configurations are:

Be $1s^2\ 2s^2$

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$

Ca $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

Sr $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$

The electronic configurations of these atoms all end in s^2, that is, these atoms all have two electrons in their outermost shells.

EXERCISE/5-1

Consider elements 5, 13, and 31. Show why they should belong in the same family.

In fact, the electronic configuration of any element in column I ends in s^1; for any element in column II it ends in s^2; for any element in column III it ends in $s^2\ p^1$; and so on. It appears that the important chemical properties of any element depend on the number of electrons in its outermost *s* and *p* orbitals.

The series of elements in which the *d* orbitals are being filled (elements 21 to 30) are all metals and have similar properties. Apparently, partially filled *d* orbitals do not contribute as much to the chemical properties of an element as partially filled *s* and *p* orbitals. It is important to remember that the outer *s* and *p* orbitals behave as a set of four orbitals. Even if the *s* orbital is filled, the *s* and *p* orbital set may still be only partially filled. For example, carbon ($1s^2\ 2s^2\ 2p^2$) has four electrons in the outer *s* and *p* orbitals, and although the *s* orbitals are filled, the *p* orbitals are only *partially* filled.

5-4/ELECTRON DOT SYMBOLS

The inner electrons of atoms are not usually involved in chemical reactions. It is the outermost *s* and *p* electrons which usually participate in chemical reactions. Since these outer electrons allow us to explain the combining power of atoms, they are called **valence electrons**. In an atom such as chlorine, with electronic configuration:

$${}_{17}\text{Cl} \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$$

the 1*s*, 2*s*, and 2*p* electrons are considered to be inner electrons. The 3*s* and 3*p* electrons (seven in all) are the valence electrons. A chlorine atom has seven valence electrons.

An iron atom has the electronic configuration:

$${}_{26}\text{Fe} \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$$

The valence electrons of iron are the two electrons in the 4*s* orbital. The six 3*d* electrons are considered *not* as valence electrons, but as *inner electrons* together with the other 18 electrons at lower energy levels. (When one of the 3*d* electrons *does* take part in chemical reactions, it is then considered as a third valence electron. Iron, therefore, has either two or three valence electrons, depending on the reaction taking place.)

Germanium has the electronic configuration:

$${}_{32}\text{Ge}\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^2$$

Germanium has four valence electrons, those in the 4*s* and 4*p* orbitals. The electrons in the 3*d* sublevel are included among the inner electrons. The two latter examples illustrate that the *valence electrons of an atom* are those in orbitals *with the highest principal quantum number.*

Since the valence electrons of an atom are so important in determining its chemical properties, chemists have developed a special symbol, the **electron dot symbol**, to represent an atom and its valence electrons. In an ordinary chemical symbol such as Cl, Fe, or Ge, the letters in the symbol represent the whole atom: nucleus, inner electrons, and valence electrons. In an electron dot symbol, however, the letters represent only the **kernel** of the atom, that is, the *nucleus* and the *inner electrons.* The *outer* or *valence electrons* are written explicitly as dots surrounding the kernel. Thus, the electron dot symbol for chlorine is $\cdot\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$. The Cl represents the nucleus and the ten inner electrons in the first two energy levels. The seven dots represent the seven valence electrons in the 3*s* and 3*p* orbitals. The positions of the dots have no relationship to the actual positions of the electrons. The main function of the dots is to remind us of the number of valence electrons belonging to the atom.

The electron dot symbol of germanium is $\cdot\dot{\mathrm{Ge}}:$; for iron it is Fe: *. Other electron dot symbols are H·, Na·, $\cdot\underset{\cdot}{\ddot{\mathrm{O}}}:$, $\dot{\mathrm{A}}\mathrm{l}:$, etc. The electron dot symbols of some representative elements are shown in Table 5-2. You will notice that the number of electron dots is the same as the number of the group to which the element belongs. The atoms of Group 0, however, have eight electron dots (helium, of course, has only two). This grouping of eight electrons is called an **octet**.

TABLE 5-2

ELECTRON DOT SYMBOLS OF SOME ELEMENTS

I	II	III	IV	V	VI	VII	0
H·							He:
Li·	Be:	$\dot{\mathrm{B}}:$	$\cdot\dot{\mathrm{C}}:$	$\cdot\underset{\cdot}{\dot{\mathrm{N}}}:$	$:\underset{\cdot}{\dot{\mathrm{O}}}:$	$\cdot\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$	$:\underset{\cdot\cdot}{\ddot{\mathrm{Ne}}}:$
Na·	Mg:	$\dot{\mathrm{A}}\mathrm{l}:$	$\cdot\dot{\mathrm{Si}}:$	$\cdot\underset{\cdot}{\dot{\mathrm{P}}}:$	$:\underset{\cdot}{\dot{\mathrm{S}}}:$	$\cdot\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$	$:\underset{\cdot\cdot}{\ddot{\mathrm{Ar}}}:$
K·	Ca:					$\cdot\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:$	$:\underset{\cdot\cdot}{\ddot{\mathrm{Kr}}}:$

SAMPLE PROBLEM/5-2

Write the electron dot symbols for rubidium and strontium.

Rubidium, in Group I, has one valence electron. Its electron dot symbol is therefore Rb·

---

* Iron may also react as $\dot{\mathrm{F}}\mathrm{e}:$; the third valence electron comes from the 3*d* sublevel.

Strontium, in Group II, has two valence electrons. Its electron dot symbol is therefore Sr:

EXERCISE/5-2

Write the electron dot symbols for indium and tin.

5-5/TRENDS IN THE PERIODIC TABLE—ATOMIC SIZE

The radii of atoms decrease as one moves from the left hand side of a period to the right hand side. This is due to the fact that as one goes from the left of a period to the right, electrons are all being placed in orbitals of the same energy level. The sizes of these orbitals would be predicted to be approximately equal. However, as one passes from the left to the right side of the period, protons are being added to the nucleus. As the nuclear charge increases, all the electrons are being pulled closer to the nucleus, and the size of the atom decreases.

SAMPLE PROBLEM/5-3

Of Si, Mg, and S, which element has the largest atomic radius? Why?

The atomic radius decreases as one moves from left to right in the periodic table. The atom with the largest atomic radius should be the farthest left in the periodic table. In this case that element is Mg.

EXERCISE/5-3

Of the elements Al, Na, and Cl, which one has the largest atomic radius? Why?

The atomic radii increase when one goes from the top of a group of the periodic table to the bottom of the same group. This is due to the fact that as one moves from the top of a group to the bottom, the extra electrons are going into energy levels that are further from the nucleus.

5-6/TRENDS IN THE PERIODIC TABLE—IONIZATION POTENTIAL

When a marble is aimed at a group of marbles inside a circle, the skillful player is able to cause one or more marbles to be knocked outside the circle. In the same way, an electron can be knocked out of an atom by being hit with a high-speed electron aimed at it from outside:

$$\mathrm{Li}\cdot \xrightarrow[\text{speed electron}]{\text{bombard with a high-}} \mathrm{Li}^{+} + e^{-}$$

The remaining positive particle is a lithium ion, and the process is called **ionization**. The symbol e^{-} represents a free electron.

The bombarding electron acquires its energy when it passes between two plates to which a voltage (or potential) is applied. The electron is attracted toward the positive plate at a speed which is proportional to the applied voltage, just as in a cathode ray tube. If the voltage is too low, the bombarding electron will not have enough energy to knock an electron out of the target atom. As the voltage is increased, however, a point will be reached at which ionization just begins. The minimum voltage which is just sufficient to remove one electron from an atom of an element is called the **ionization potential** of that element. The ionization potential of lithium is 5.4 V (volts). This means that if a bombarding electron is subjected to a potential of 5.4 V, it will have just enough energy to remove one electron from a lithium atom.

The most easily removed electron will be the one in the atom's highest-energy orbital. Since orbitals and energy levels are intimately related to the periodic table and periodicity of properties, we should expect to find that ionization potentials would vary in a periodic manner. This variation is quite apparent in Fig. 5-4. The exceptional stability of the noble gases is readily apparent. These gases have filled outer *s* and *p* orbitals, that is, they have achieved a completed octet of electrons. An atom with a completed octet is in a relatively stable state, and it is quite difficult to remove an electron from such an octet. Thus, the noble gases have very high ionization potentials.

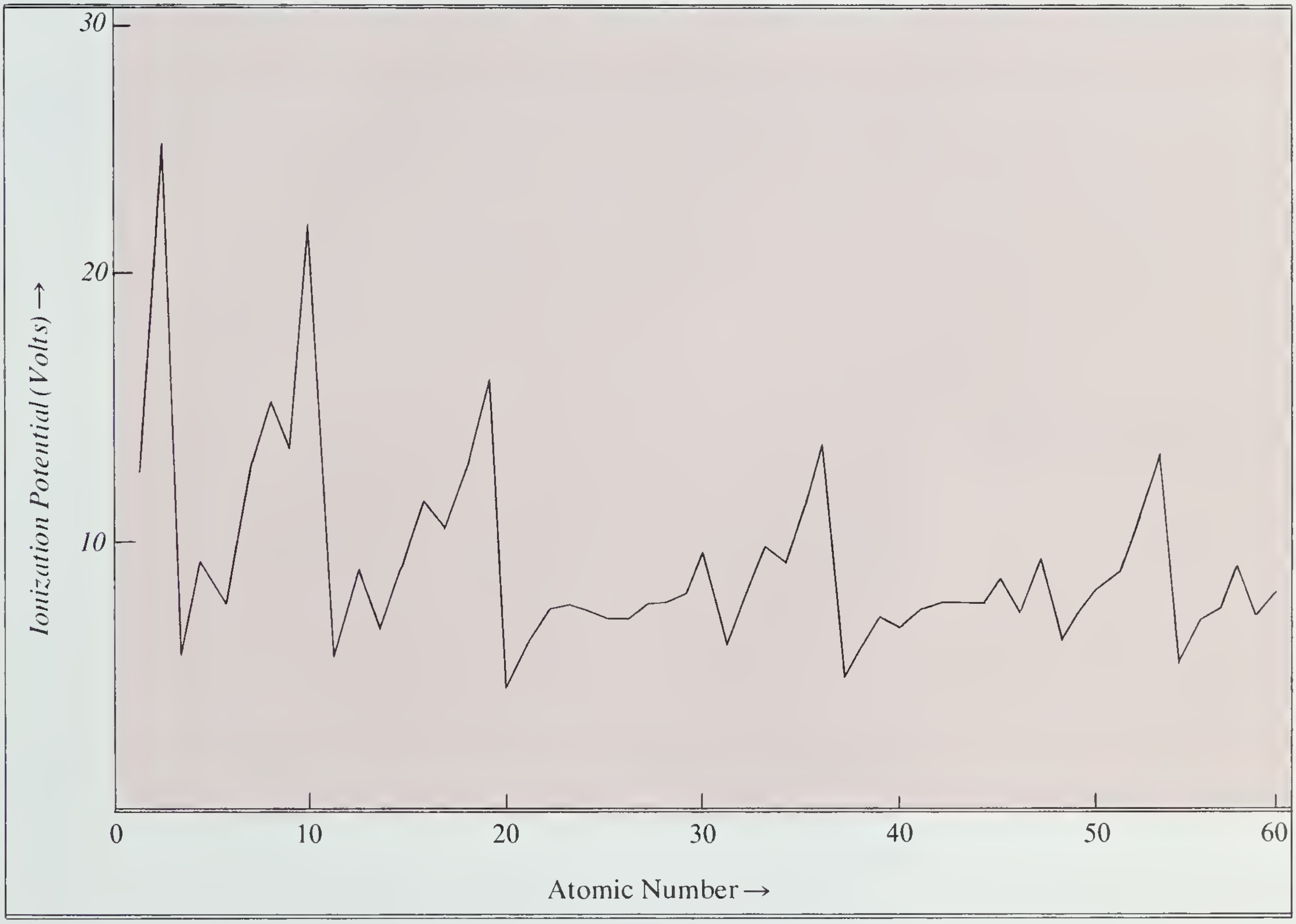


Fig. 5-4 Ionization Potential as a Function of Atomic Number

The alkali metals all have very low ionization potentials. They all readily lose their single valence electron in order to form a stable positive ion with a completed electron octet exposed.

The ionization potentials of the first 54 elements are arranged in the form of a periodic table in Fig. 5-5. The ionization potential increases as one goes from the left side to the right side of a period. This occurs because there are more

I	II											III	IV	V	VI	VII	0
13.6																	24.6
5.4	9.3											8.3	11.3	14.5	13.6	17.4	21.6
5.1	7.6	← Transition Metals →										6.0	8.1	11.0	10.4	13.0	15.8
4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	8.1	10.0	9.8	11.8	14.0
4.2	5.7	6.6	7.0	6.8	7.2	—	7.5	7.7	8.3	7.6	9.0	5.8	7.3	8.6	9.0	10.4	12.1

Fig. 5-5 Ionization Potentials (Volts) of the First 54 Elements

protons in the atoms of the right side of a period than there are in the atoms of the left side of the same period. That is, the positive nuclear charge increases as one moves from the left to the right of a period. This increased positive nuclear charge makes it more difficult to pull electrons from atoms on the right side of the periodic table. As a general rule, the atoms have a large ionization potential if they are on the right-hand side of the periodic table. They have a small ionization potential if they are on the left side of the periodic table.

Variations of the ionization potentials of the atoms in a group are predictable. The ionization potential decreases as one goes from the top of a group to the bottom. The outermost electrons of the small atoms of a group are closer to the nucleus and are more tightly held than the outer electrons of a larger atom in the group.

SAMPLE PROBLEM/5-4

Of the elements Ca, Be, and Mg, which has the highest ionization potential? Why?

The ionization potential decreases as one goes from the top to the bottom of a group. The atom with the highest ionization potential should be at the top of the group. In this case that element is Be.

EXERCISE/5-4

Of the elements B, Al, and Ga, which has the highest ionization potential? Why?

5-7/TRENDS IN THE PERIODIC TABLE—ELECTRON AFFINITY

Some atoms have a tendency to pick up additional electrons. They do so because this results in a lowering of energy of the system, i.e., the achievement of a more stable state for the added electrons. Energy will be given off since an added electron is moved into the positive field of the nucleus. **Electron affinity** is a measure of the energy given off when an electron is added to a neutral atom:

$$:\ddot{\underset{..}{X}}\cdot + 1\,e^- \rightarrow :\ddot{\underset{..}{X}}:^-$$

We can view the process of addition of an electron to a neutral atom to form a *negative ion* as the reverse of the removal of an electron from a negative ion to form a neutral atom. Since it is more difficult to remove an electron from a smaller ion (more energy is required because the electrons are closer to the nucleus) the electron affinity increases as the size of the atom decreases. That is, more energy is given off as a smaller atom accepts an additional electron to become an ion.

Electron affinity also depends on two additional and opposing factors: nuclear charge and the screening of the incoming electron from the nucleus by the electrons in the intervening orbitals. However, the effect of atomic size is the most important.

Because the size of atoms decreases from left to right across a period from Groups I to VII, the Group VII elements would be expected to have the highest electron affinities.

Within a group it appears that the elements at the top generally have a higher electron affinity than do the elements at the bottom. This is also to be expected since the smaller atoms are at the top of a group.

QUESTIONS

1. For each of the following triads, compare the average of the atomic masses of the first and third elements with the atomic mass of the second element: sulfur, selenium, and tellurium; chlorine, bromine, and iodine; lithium, sodium, and potassium. What regularity do you notice?
2. What would you predict for the atomic mass of the missing element in Group VII, Row 6, of Mendeleev's periodic table?
3. Find two adjacent elements in the modern periodic table which would appear in a different order when arranged in order of increasing atomic mass.
4. Write the electronic configurations for phosphorus and arsenic. Show why they both belong to the same family.
5. Why are the noble gases generally inert?
6. Why do partially filled *d* orbitals not contribute as much to the chemical properties of an element as partially filled *s* and *p* orbitals?
7. Write the electron dot symbols for: gallium; germanium; arsenic; selenium.
8. How many valence electrons do nitrogen, phosphorus, and arsenic have?
9. The elements whose electronic configurations end in $s^2\ p^2$ belong to which group in the periodic table?
10. What are elements that have some metallic and some nonmetallic properties called?
11. Which family of the periodic table contains the most metallic element? The most nonmetallic element?
12. Which group contains the elements which are hardest to ionize?
13. Which element should have the largest atomic radius and why: (a) B, Li, or F; (b) K, Li, or Na?
14. Which element loses an electron most readily and why: (a) B, Li, or F; (b) K, Li, or Na?

15. Which element has the largest electron affinity and why: (a) B, Li, or F; (b) Br, Cl, or I?
16. How many electrons would the following elements tend to gain or lose: Mg, Cl, N, Al, S, Ar? State whether the element gains or loses electrons.
17. In which energy level are the valence electrons of the following elements found: iodine, calcium, gallium, fluorine, francium?

QUESTION TO THINK ABOUT

18. You have landed on a strange planet and have been taken prisoner. You are told that your life will be spared if you are able to construct a periodic table for the natives. Their atomic theory is the same as ours except that their spin quantum numbers are $+1/2$, 0, and $-1/2$ and their magnetic quantum numbers take the values 0, 1, 2, . . . ℓ.
    (a) Construct an energy level diagram for the natives. This will differ from ours only because of the changes in the spin quantum numbers and the magnetic quantum numbers. Everything else, including the ordering of the orbitals and the naming of the orbitals, will be the same.
    (b) Construct a periodic table. Use atomic numbers instead of symbols and go as far as element number 35.
    (c) What are the atomic numbers of their first three noble gases?
    (d) What is the electronic configuration of their element number 24?
    (e) Which of the following elements should have similar chemical properties: 4, 7, 15, 16, 20, 27, 34, 35?
    (f) Which of the following elements should have the highest electron affinity: 13, 11, 27, 12?

6

CHEMICAL BONDING

Individual atoms possess the ability to bond to one another. A **molecule** is any electrically neutral collection of atoms that is held together tightly enough to be considered a single unit. **Chemical bonds** are the attractions between the atoms within a molecule.

Element No. 1, hydrogen, has been discussed as if it were normally found as individual atoms. In fact, a sample of hydrogen gas is actually made up of hydrogen molecules. Each hydrogen molecule consists of two hydrogen atoms bonded together. Thus, hydrogen gas consists of diatomic H_2 molecules. Other diatomic molecules are nitrogen (N_2), oxygen (O_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). Solid sulfur does not exist as individual atoms. It exists as molecules of sulfur, each containing eight sulfur atoms (S_8). Solid phosphorus exists as molecules of phosphorus, each containing four phosphorus atoms (P_4). Figure 6-1 shows models of some of these molecules.

Water vapor consists of molecules each containing two hydrogen atoms and one oxygen atom (H_2O). Methane gas consists of molecules. Each methane molecule contains one carbon atom and four hydrogen atoms (CH_4). Figure 6-2 shows models of water and methane.

The questions are: why do atoms bond together to form molecules, and why is there a limit to the number of each type

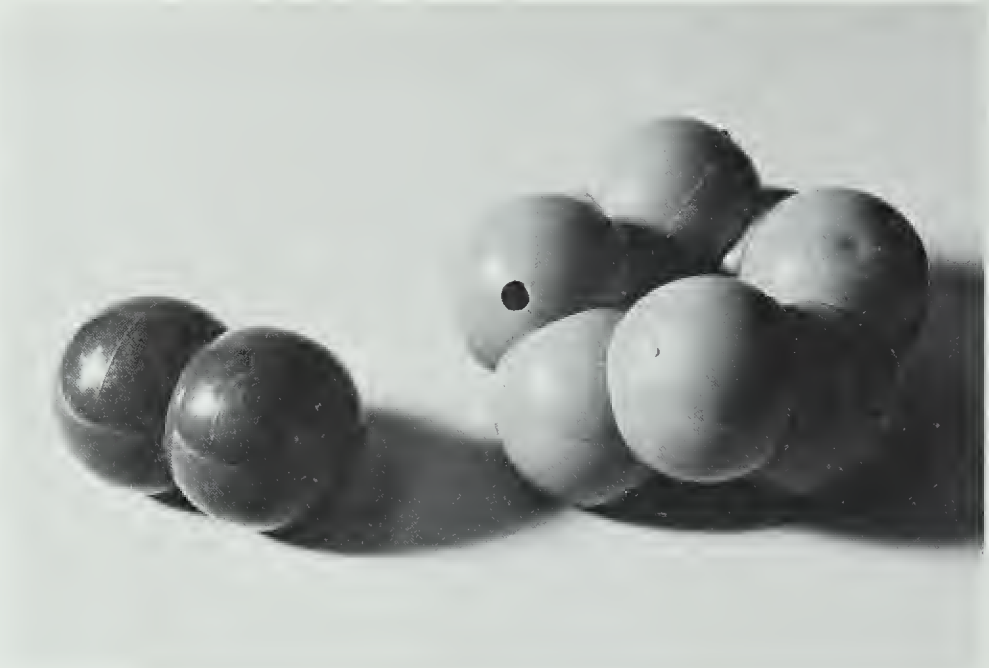


Fig. 6-1 Models of Chlorine (Cl_2) and Sulfur (S_8)

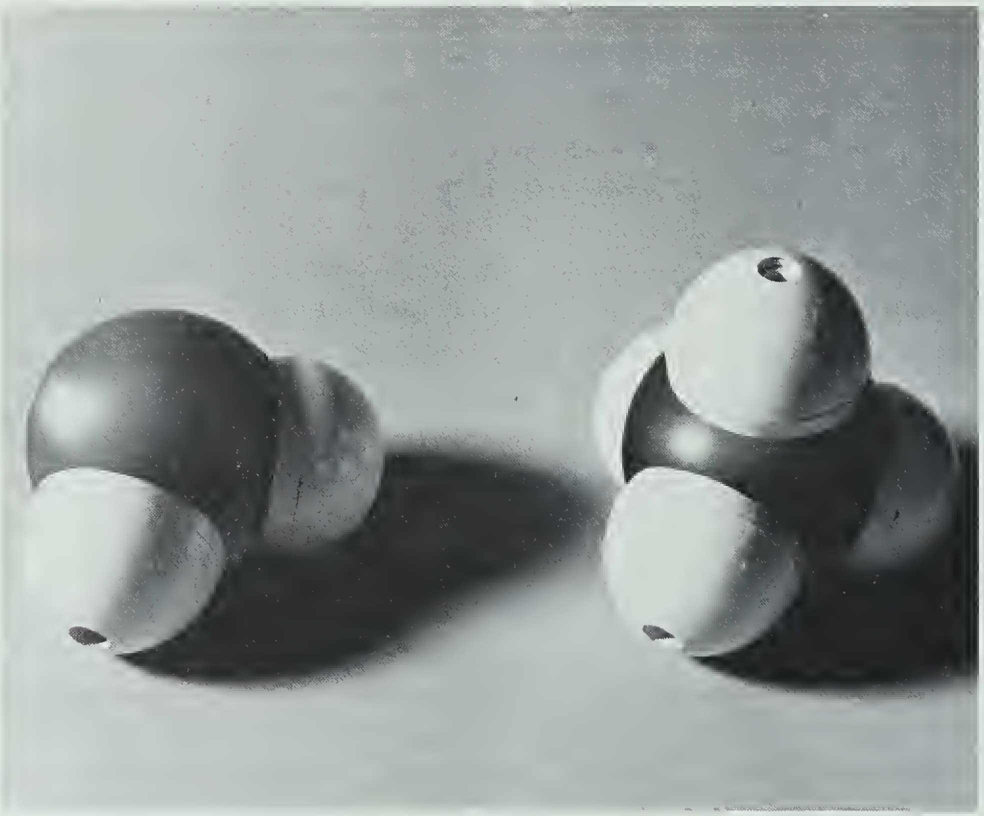


Fig. 6-2 Models of Water (H_2O) and Methane (CH_4)

of atom in a molecule? For example, why does a methane molecule have four hydrogen atoms but only one carbon atom?

By the time you have finished reading this chapter, you should be able to attain the following objectives:

1. Define and give an example of: molecule, chemical bond, ionic bond, covalent bond, polar covalent bond, and electronegativity.
2. Predict whether a given bond will be ionic or covalent.
3. Write equations, using electron dot symbols and formulas, for the formation of ionic and covalent compounds.
4. Draw orbital overlap pictures to represent formation of covalent bonds in simple molecules.
5. Draw orbital diagrams for simple covalent molecules.
6. Predict trends in electronegativity as one goes across a period or down a family within the periodic table.
7. Predict the positive and negative ends of a polar bond from a knowledge of the electronegativities of the atoms involved.
8. Describe the structure of a simple ionic crystal.
9. State and illustrate the octet rule.
10. Explain the meanings of single, double, and triple covalent bonding and give an example of each.

6-1/THE ROLE OF ELECTRONS IN BONDING

In a single atom, the electrons come under the influence of only one nucleus. The atom has a certain amount of potential energy associated with the distribution of its electrons in the orbitals. The atom is most stable when its electrons are in the orbitals of lowest possible energy. For example, the hydrogen atom is most stable when its electron is in the 1*s* (lowest energy) orbital. When two atoms come close together, the electrons of each atom come under the influence of the nucleus and the electrons of the other atom. If a bond is formed, the simultaneous attraction of electrons to two atomic nuclei must have produced a more stable (lower energy) state. The formation of a bond indicates that the molecule is more stable than the isolated atoms from which it is formed. If the formation of a bond between two atoms produces a molecule of lower energy, the extra energy is given off during bond formation.

A detailed description of the electrons in a molecule is difficult. There are two general methods of description. First, one can consider the entire molecule as a unit with each electron moving under the influence of all the nuclei and all the other electrons in the molecule. This approach suggests that every electron belongs to the molecule as a whole and can move anywhere throughout the molecule. Thus the orbitals are called *molecular orbitals* instead of atomic orbitals. Second, one can consider that the atoms in molecules behave as if they were isolated atoms except that one or more electrons in the outer *s* and *p* orbitals of one atom can move to the outer *s* and *p* orbitals of another atom. This description is called the *atomic orbital* or *valence bond* approach. It has its shortcomings, but its chief advantage is that it is easier to visualize than the molecular orbital approach. It will be used in the following sections.

6-2/IONIC BONDING

The most active metals are found in Groups I, II, and to a lesser extent III of the periodic table. These metals have low ionization potentials. That is, a relatively small amount of energy is required to cause them to lose electrons. The most active nonmetals are found in Groups VI and VII. These nonmetals have relatively large electron affinities. That is, they tend to gain electrons readily. When an active metal reacts with an active nonmetal, electron(s) are transferred from the metal to the nonmetal. The atoms of the nonmetal, having gained electrons, become negatively charged ions. The atoms of the metal, having lost electrons, become positively charged ions. These oppositely charged ions attract each other, and this attraction results in a type of bonding which is called **ionic bonding.**

A common example of ionic bonding is the reaction between sodium atoms ($1s^2\ 2s^2\ 2p^6\ 3s^1$) and chlorine atoms ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$). Suppose these two atoms collide. Sodium is a Group I element and it has one outer electron in the 3*s* orbital. If sodium gains some energy from the collision, the 3*s* electron leaves the sodium atom. A sodium ion is produced, and this ion has the same electronic configuration as the noble gas, neon:

$$\mathrm{Na}\cdot + \text{Energy} \rightarrow \mathrm{Na}^+ + 1\mathrm{e}^-$$

The electron which the sodium atom has lost is picked up by a chlorine atom and energy is produced:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + 1\mathrm{e}^- \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^- + \text{Energy}$$

The electron has entered a half-filled $3p$ orbital of a chlorine atom and a Cl^- ion ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) is produced. The Cl^- ion is called a *chloride ion* and it has the same electronic configuration as the noble gas, argon.

A positive and a negative ion are produced when the sodium atom collides with the chlorine atom. These ions attract one another because they have opposite charges. An ionic bond is formed and more energy is released:

$$\mathrm{Na}^+ + \mathrm{Cl}^- \rightarrow \mathrm{NaCl} + \text{Energy}$$

The energy released in the second and third steps is greater than the energy necessary for the first step. Thus the ionic bonding in sodium chloride results in a stable or lower energy state.

SAMPLE PROBLEM/6-1

Why does each lithium ion require one fluoride ion in the compound, lithium fluoride?

The electronic configurations are:

$$\begin{array}{ll} \mathrm{Li} & 1s^2\ 2s^1 \\ \mathrm{F} & 1s^2\ 2s^2\ 2p^5 \end{array}$$

Each lithium atom tends to lose its $2s$ electron, and each fluorine atom tends to add an electron to its half-filled $2p$ orbital:

$$\mathrm{Li}\cdot + \text{energy} \rightarrow \mathrm{Li}^+ + 1\mathrm{e}^-$$

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot + 1\mathrm{e}^- \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^- + \text{Energy}$$

$$\mathrm{Li}^+ + \mathrm{F}^- \rightarrow \mathrm{LiF} + \text{Energy}$$

EXERCISE/6-1

Why does each rubidium ion require one bromide ion in the compound, rubidium bromide?

When an ionic bond is formed by electron transfer between a metal and a nonmetal, there must be a balance of electrons gained and lost. After reaction the sodium ion and the chloride ion are left with completely filled outer *s* and *p* orbitals. When ionic bonds are formed, enough electrons are transferred for the ions produced to fill the outer *s* and *p* orbitals completely.

A Group II metal (such as calcium) has two outer electrons located in an *s* orbital. Calcium atoms can lose two electrons:

$$\mathrm{Ca{:}} + \text{Energy} \rightarrow \mathrm{Ca^{2+}} + 2\mathrm{e^-}$$

If calcium is reacting with chlorine, two chlorine atoms will be required to accept the two electrons from each calcium atom and two chloride ions will be formed:

$$2{:}\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot + 2\mathrm{e^-} \rightarrow 2{:}\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}{:}^- + \text{Energy}$$

The two chloride ions will be attracted to the calcium ion:

$$\mathrm{Ca^{2+}} + 2\mathrm{Cl^-} \rightarrow \mathrm{CaCl_2} + \text{Energy}$$

The subscript 2 indicates that there are two chloride ions ionically bonded to a calcium ion.

Calcium could react with an element from Group VI. Oxygen ($1s^2\ 2s^2\ 2p^4$) is a Group VI nonmetal. Oxygen atoms have six outer electrons. Oxygen would have to gain two electrons to achieve the same electronic configuration as the noble gas, neon:

$${:}\underset{\cdot}{\ddot{\mathrm{O}}}\cdot + 2\mathrm{e^-} \rightarrow {:}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{:}^{2-}$$

Thus one calcium atom could transfer two electrons to one oxygen atom and the ionic compound calcium oxide would be formed:

$$\mathrm{Ca^{2+}} + \mathrm{O^{2-}} \rightarrow \mathrm{CaO}$$

SAMPLE PROBLEM/6-2

Predict the formula of the ionic compound, beryllium oxide.

The electronic configurations are:

$$\begin{array}{ll} \text{Be} & 1s^2\ 2s^2 \\ \text{O} & 1s^2\ 2s^2\ 2p^4 \end{array}$$

Each beryllium atom can give up its two 2*s* electrons, and each oxygen atom adds two electrons:

$$\text{Be}: \rightarrow \text{Be}^{2+} + 2e^-$$

$$:\ddot{\underset{\cdot}{\text{O}}}\cdot + 2e^- \rightarrow :\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-}$$

Therefore one beryllium ion requires one oxide ion:

$$\text{Be}^{2+} + \text{O}^{2-} \rightarrow \text{BeO}$$

The formula is BeO.

EXERCISE/6-2

Predict the formula of magnesium sulfide.

Let us consider the example of the Group III metal, aluminum ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$), reacting with oxygen:

$$\underset{\cdot}{\text{A}}\text{l}: \rightarrow \text{Al}^{3+} + 3e^- \quad \text{and} \quad :\ddot{\underset{\cdot}{\text{O}}}\cdot + 2e^- \rightarrow :\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-}$$

$$\therefore \quad 2\ \underset{\cdot}{\text{A}}\text{l}: \rightarrow 2\ \text{Al}^{3+} + 6e^- \quad \text{and} \quad 3\ :\ddot{\underset{\cdot}{\text{O}}}\cdot + 6e^- \rightarrow 3\ :\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-}$$

$$2\ \text{Al}^{3+} + 3\ \text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3$$

Two aluminum atoms have lost 6 electrons and three oxygen atoms have received the 6 electrons. The formula Al_2O_3 indicates that there are three oxide ions for every two aluminum ions in aluminum oxide.

SAMPLE PROBLEM/6-3

When magnesium burns in air it reacts not only with oxygen to form magnesium oxide, but also with nitrogen to form magnesium nitride. What is a reasonable formula for magnesium nitride?

The electronic configurations are:

$$\begin{array}{ll} \mathrm{Mg} & 1s^2\ 2s^2\ 2p^6\ 3s^2 \\ \mathrm{N} & 1s^2\ 2s^2\ 2p^3 \end{array}$$

Each magnesium atom can lose two electrons, and each nitrogen atom can gain three electrons:

$$\mathrm{Mg}\colon \rightarrow \mathrm{Mg}^{2+} + 2\ \mathrm{e}^-$$

$$:\dot{\underset{\cdot}{\mathrm{N}}}\cdot + 3\ \mathrm{e}^- \rightarrow :\dot{\underset{\cdot\cdot}{\mathrm{N}}}:^{3-}$$

Three magnesium atoms will lose six electrons. These electrons can be accepted by two nitrogen atoms:

$$3\ \mathrm{Mg}^{2+} + 2\ \mathrm{N}^{3-} \rightarrow \mathrm{Mg_3N_2}$$

The formula is Mg_3N_2.

EXERCISE/6-3

What is a reasonable formula for lithium nitride? For gallium sulfide? (*Answers:* Li_3N; Ga_2S_3)

The atoms and the ions of an element have different chemical properties. Sodium is a soft, silvery-white metal and chlorine is a poisonous, greenish-yellow gas. However, sodium chloride (sodium ions and chloride ions) is white, solid, table salt and it is not poisonous except in large quantities.

In general, the ionic compounds which are formed when the elements of Groups I, II, or III react with the elements of Groups VI or VII resemble sodium chloride. They are usually white, brittle solids which melt at high temperatures. Their molten form or water solutions contain mobile positive and negative ions which conduct electricity.

6-3/COVALENT BONDING

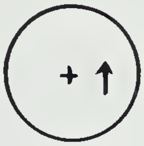
The transfer of electrons from one atom to another does not adequately represent all bond types. For example, when two hydrogen atoms collide, there is no reason for one hydrogen atom to give up its electron to the other hydrogen atom. We believe that there is no electron transfer in this case. The electrons are *shared* between the two hydrogen atoms, and the bond is a **covalent bond.**

Each hydrogen atom has one outer electron (H·). When two hydrogen atoms collide, an electron pair is shared equally between the two hydrogen nuclei:

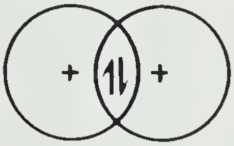
$$\mathrm{H\cdot} + \mathrm{\cdot H} \rightarrow \mathrm{H:H}$$

The representation H:H is an **electron dot formula** or **Lewis structure** and it is a simplification of a more complicated situation.

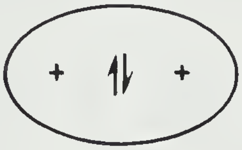
Let us take a second look at the formation of a bond between two hydrogen atoms. Each hydrogen atom has one electron in a 1*s* orbital:



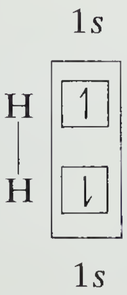
As two hydrogen atoms approach one another, it is possible for the two orbitals to overlap:



or simply



The pair of electrons is now simultaneously attracted to two nuclei and a covalent bond forms. This simultaneous attraction of the electron pair to two nuclei produces a more stable state, and a covalent bond is formed. A simple method of showing the orbitals that are involved in bonding is to represent only the outer *s* and *p* (i.e., valence) orbitals by small squares and their *electron populations* by arrows. A rectangle is drawn around orbitals that are involved in bonding. For the hydrogen molecule the orbital diagram is:

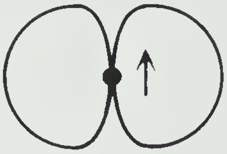


A single line drawn between two atoms (e.g., H—H) indicates that two electrons are shared between the two atoms. This is a **single covalent bond.**

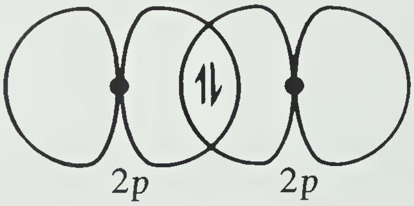
Suppose two fluorine atoms ($1s^2\ 2s^2\ 2p^5$) come together and form a bond. Each fluorine atom has seven electrons in its outer *s* and *p* orbitals. Therefore, each fluorine requires *one more* electron to achieve the electron configuration of the noble gas, neon. When the fluorine atoms collide, each tries to gain an eighth valence electron but neither fluorine atom can pull an electron from the other. They share a pair of electrons:

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

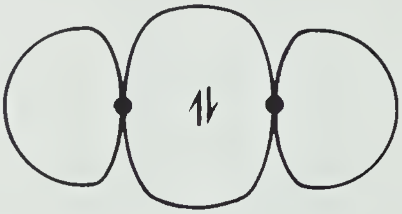
Each fluorine has a half-filled $2p$ orbital:



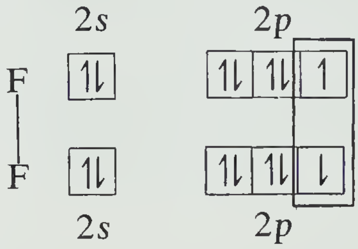
As the two fluorine atoms approach one another, it is possible for the two orbitals to overlap:



or simply



For the fluorine molecule, the orbital diagram is:



In the same way that two fluorine atoms form a single covalent bond, two chlorine atoms also form a single covalent bond. The electron dot formula for a chlorine molecule is $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$. The orbital diagram would be the same as the one shown for fluorine except that the orbitals involved are the $3s$ and $3p$, not the $2s$ and $2p$.

EXERCISE/6-4

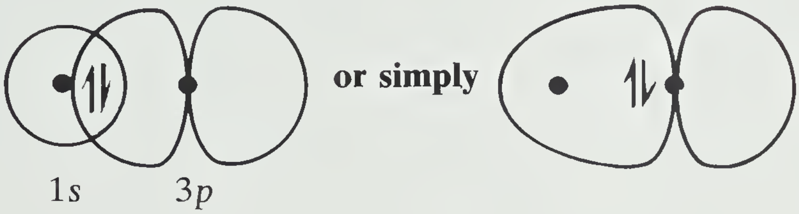
Describe the bonding which occurs in a molecule of iodine. Draw a molecular orbital overlap picture and an orbital diagram. What orbitals are involved in the bonding?

6-4/POLAR COVALENT BONDING AND ELECTRONEGATIVITY

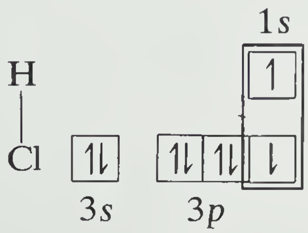
When a hydrogen atom and a chlorine atom collide, a *covalent bond* is formed:

$$\mathrm{H}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \rightarrow \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

The bonding orbitals involved are the 1*s* orbital of the hydrogen atom and a 3*p* orbital of the chlorine atom:

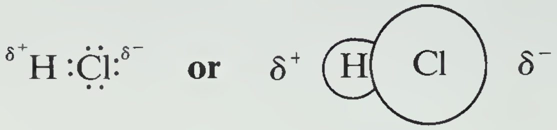


For the hydrogen chloride molecule, the orbital diagram is:



In the hydrogen chloride molecule, a pair of electrons is shared between two different types of atoms. Will the pair of electrons be shared equally? Will either the chlorine atom or the hydrogen atom have a stronger attraction for the shared pair of electrons?

Laboratory experiments have shown that the hydrogen chloride molecule is an *electrical dipole.* It has a slightly negative (δ^-) end and a slightly positive (δ^+) end. Further work has indicated that the chlorine end of the molecule is slightly negative and the hydrogen end of the molecule is slightly positive:



The molecule as a whole is electrically neutral. It has an equal number of protons and electrons. However, the electron pair is unequally shared. Apparently the chlorine atom has a greater attraction for the shared pair of electrons than does the hydrogen atom. The chlorine atom does not attract the shared pair strongly enough to gain complete possession of it. This is *not* an ionic bond. It is a covalent bond in which the unequal sharing of electrons has resulted in an electrical dipole. It is a **polar covalent bond.**

In a polar covalent bond, the shared pair spends more of its time near one of the atoms than it does with the second atom. This makes the former atom slightly negative, and the other atom becomes slightly positive. Generally, polar covalent bonding occurs when atoms of two different elements share a pair of electrons. Is it possible to predict which end of the molecule will be slightly negative and which end of the molecule will be slightly positive?

A quantitative measure of the electron-attracting ability of the atoms in a molecule is **electronegativity.** By measuring various properties such as ionization potentials and electron affinities of the atoms making up the molecule, how polar the molecule is, and the energy required to break the bond, it is possible to construct a table of electronegativities. Numerical values assigned for electronegativities of the various elements are included in the periodic table at the back of this book. These values were calculated by the American chemist Linus Pauling. The electronegativity values are such that the bigger the number is, the greater is the tendency of an atom to attract a shared pair of electrons to itself.

Fluorine has been assigned the highest electronegativity (4.0). Fluorine has a high ionization potential, and it has a high electron affinity. That is, it takes a relatively large amount of energy to force a fluorine atom to lose an electron, but a fluorine atom is ready to accept an electron in order to fill its outer *s* and *p* orbitals. These two factors both indicate that in any bond between fluorine and another element, it will be more difficult to transfer an electron from fluorine to the other element than it will be to transfer an electron from the other element to fluorine.

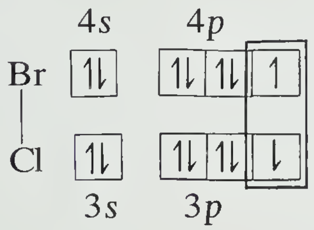
Cesium and francium both have the smallest electronegativity (0.7). They both have low ionization potentials and it is relatively easy to transfer an electron from cesium or francium to another element.

In general, the elements with the lowest ionization potentials have the lowest electronegativities and the elements with the highest ionization potentials have the highest electronegativities. Thus, the variation of electronegativity parallels the variation of ionization potentials. As one moves from left (metals) to right (nonmetals) across a period, the electronegativity increases. As one goes from top to bottom in a family or group, the electronegativity decreases.

Another example of a polar covalent bond is the bond between chlorine and bromine in the molecule, BrCl. Each of these atoms is in Group VII and each has seven valence electrons in its outer *s* and *p* orbitals. By sharing a pair of electrons each completes its outer *s* and *p* orbitals:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \rightarrow\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

The orbital diagram is:



The electronegativity of chlorine is 3.0 and it is 2.8 for bromine. A chlorine atom is more electronegative than a bromine atom. The shared pair of electrons spends more time near the chlorine nucleus, and the chlorine end of the molecule becomes negative with respect to the bromine end:

$$^{\delta+}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^{\delta-}$$

The shared pair will spend more time near the Cl because less energy is required to transfer an electron from Br to Cl than is required to transfer an electron from Cl to Br.

EXERCISE/6-5

Draw an orbital diagram and an electron dot formula for ICl. Is this a polar or a nonpolar molecule? If it is polar, which end of the molecule is the negative end?

6-5/THE BONDING CONTINUUM

There is no sharp distinction between ionic and covalent bonding. In a chemical bond between atoms M and X, the polarity of the bond depends on the natures of M and of X. If they each have the same ability to attract electrons, the bond will be covalent and nonpolar. If X can attract electrons better than M, the bond will be polar covalent. If X attracts electrons so strongly that one can say the electron pair spends essentially all of its time on X, the bond is ionic, and there is an M^+ ion and an X^- ion. In fact, an ionic bond is simply an *extreme case* of polar covalent bonding. In these extreme cases, chemists find it easier to think of the bond as being 100% ionic, but they keep in mind that a 100% ionic bond is not always entirely realistic.

Electronegativities help one to predict which bonds are ionic and which bonds are covalent. Two elements of very different electronegativities such as Na (0.9) and Cl (3.0) are expected to form ionic bonds. Two elements of slightly different electronegativities such as C (2.5) and H (2.1) are expected to form only slightly polar covalent bonds. The greater the difference in electronegativity, the more polar the bond becomes. If the difference in electronegativity between two bonding atoms exceeds 1.7, it is better to consider the bond to be ionic.

In any event, the transition between polar covalent bonding and ionic bonding is indefinite. It is better to think of a continuum with pure covalent (equal sharing) bonding at one end and ionic (electron transfer) bonding at the other end. In between is polar covalent bonding (Fig. 6-3).

One other point should be made in any comparison of ionic, polar covalent, and covalent bonding. The word *molecule* does not have much meaning in the case of ionic solids.

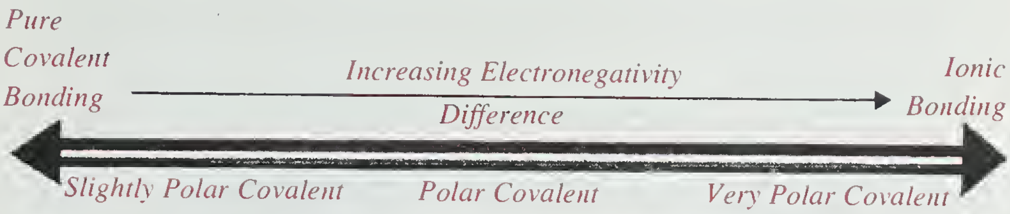


Fig. 6-3 The Bonding Continuum

Let us consider solid sodium chloride. Chlorine is so much more electronegative than sodium that sodium chloride is best considered to be ionic. When sodium reacts with chlorine, the sodium atom gives up its outer electron to the chlorine atom:

$$\text{Na}\cdot \rightarrow \text{Na}^+ + 1\text{e}^-$$

$$:\underset{\cdot\cdot}{\dot{\text{Cl}}}\cdot + 1\text{e}^- \rightarrow :\underset{\cdot\cdot}{\dot{\text{Cl}}}:^-$$

$$\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$$

In the gas phase, it is possible to get one positive sodium ion attracted to one negative chloride ion. However, solid sodium chloride is a cluster of ions (Fig. 6-4). Each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. It is impossible to say that a sodium ion is bonded to only one of the six surrounding chloride ions, and it is impossible to say that a chloride ion is bonded to only one of the six surrounding sodium ions. In fact, the formula NaCl merely tells the reader that for every positive sodium ion there is a chloride ion in the sodium chloride crystal. In the same way, the formula $CaCl_2$ indicates that in a crystal of ionic calcium chloride there are twice as many chloride ions as there are calcium ions.

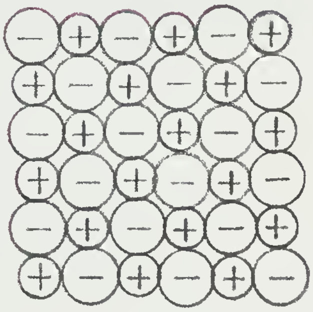


Fig. 6-4 One Layer of Solid Sodium Chloride

EXERCISE/6-6

Aluminum fluoride is probably an ionic compound. What is its formula? Describe a crystal of aluminum fluoride in terms of its ions.

Hydrogen chloride is an example of a polar covalent compound. The formula for hydrogen chloride is H—Cl and hydrogen chloride exists as molecules in the gas, liquid, or solid state. Each hydrogen chloride molecule consists of one

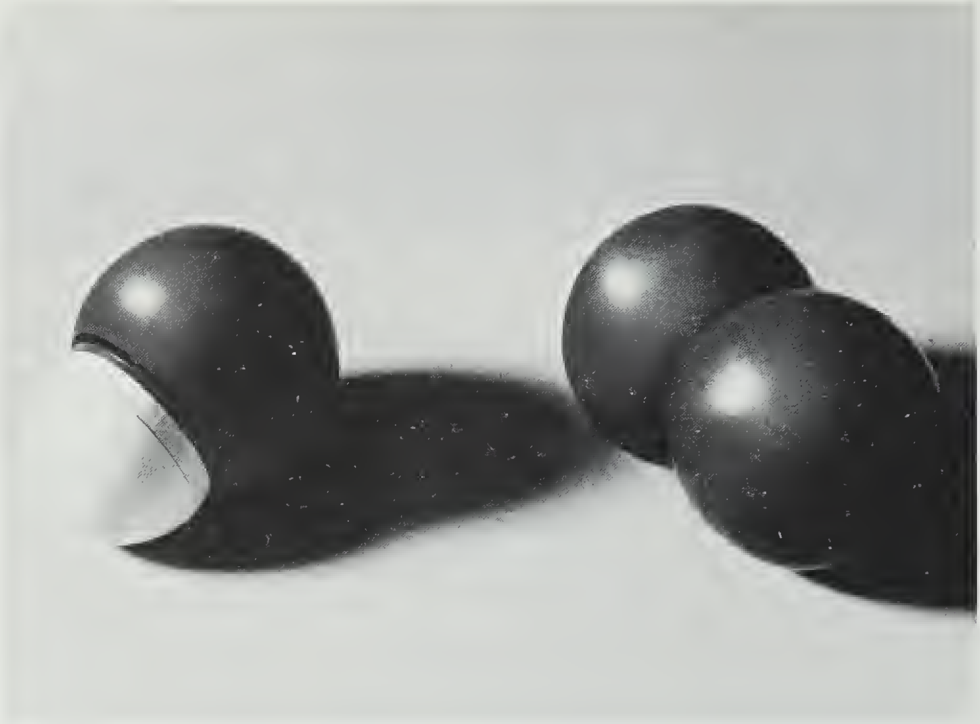


Fig. 6-5 Models of Hydrogen Chloride (HCl) and Chlorine (Cl_2)

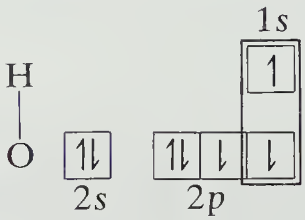
hydrogen atom bonded to a chlorine atom by a polar covalent bond (Fig. 6-5).

Chlorine (Cl_2) is a pure covalent substance. Each chlorine molecule consists of two chlorine atoms bonded together by a pure covalent bond. Chlorine exists as molecules in the gas, liquid, or solid state (Fig. 6-5).

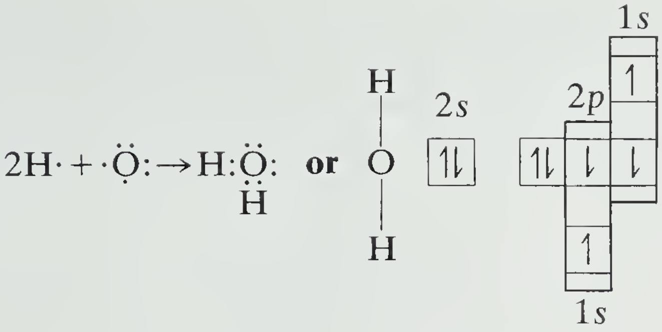
6-6/THE OCTET RULE

Suppose that oxygen ($1s^2\ 2s^2\ 2p^4$) were to form a bond with hydrogen:

$$H\cdot + \cdot\ddot{\underset{\cdot}{O}}: \rightarrow H:\ddot{\underset{\cdot}{O}}: \quad \textbf{or}$$

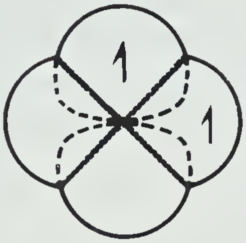


The oxygen still has one unpaired electron in a $2p$ orbital. This is closer to fluorine ($1s^2\ 2s^2\ 2p^5$) than it is to a noble gas electron configuration. The H—O molecule is reactive since the oxygen has the ability to form a second bond to another hydrogen atom:

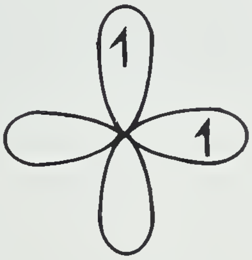


$$2\mathrm{H}\cdot + \cdot\ddot{\underset{\cdot}{\mathrm{O}}}: \rightarrow \mathrm{H}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\ddot{\mathrm{O}}}:$$

This compound formed by the reaction of hydrogen and oxygen is water, H_2O. The bonding orbitals of the oxygen are two of the 2*p* orbitals, and these 2*p* orbitals are at right angles to each other:*

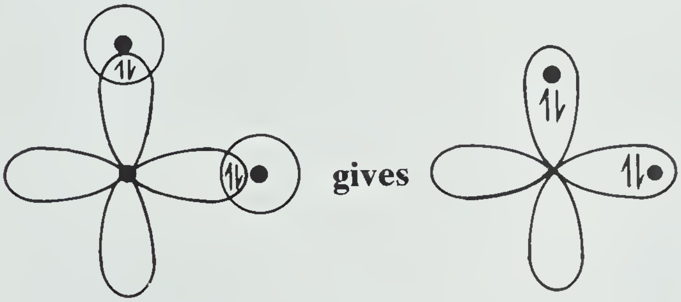


A

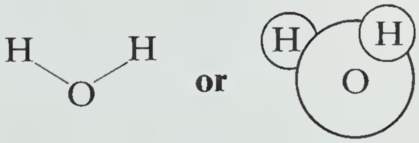


B

When the two hydrogen atoms bond to the oxygen atom, their 1*s* orbitals must overlap with the two 2*p* orbitals:



This study of the orbitals involved in bonding suggests that water will be a bent molecule:



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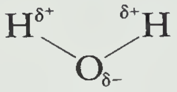
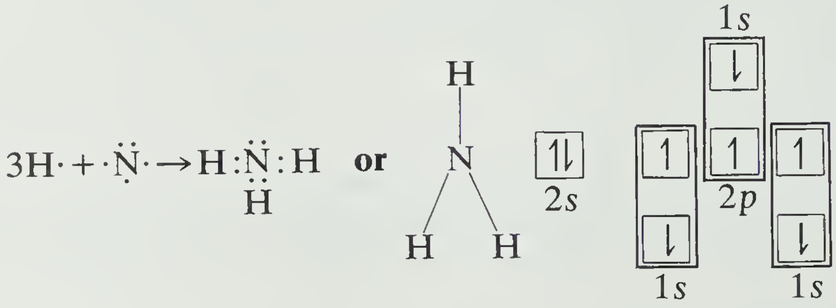
* Diagram A is a more nearly correct representation of the two *p* orbitals, since it shows that the orbitals intersect each other. However, it is frequently simplified as in Diagram B.

Since the electronegativity of the oxygen atom (3.5) is larger than the electronegativity of the hydrogen atoms (2.1), the bonding will be polar covalent. The oxygen end of the water molecule should be more negative than the hydrogen end:



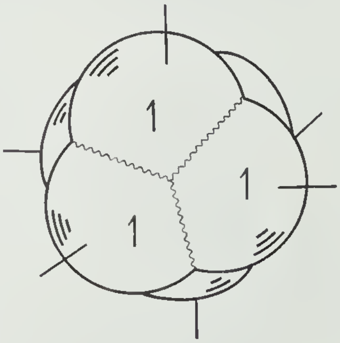
Experiments show that water is a polar molecule. Experiments also show that water is a bent molecule. The HOH bond angle is greater than 90° and this would be expected since the two hydrogen nuclei are likely to repel each other slightly.

Nitrogen ($1s^2\ 2s^2\ 2p^3$) has three unpaired electrons and we would expect a nitrogen atom to bond to three hydrogen atoms:

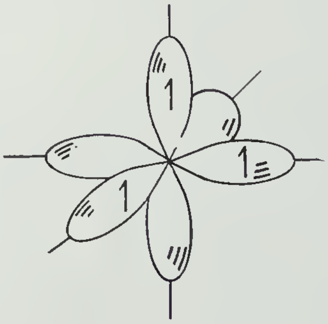


$$3\text{H}\cdot + \cdot\ddot{\text{N}}\cdot \rightarrow \text{H}:\underset{\text{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}}:\text{H}$$

The compound NH_3 is called ammonia. The bonding orbitals of the nitrogen are the three 2*p* orbitals and these orbitals are all at right angles to each other:*



A



B

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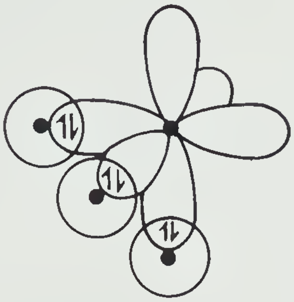
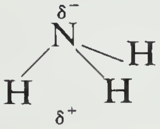
* Diagram A is a more nearly correct representation of the three *p* orbitals. However, since it is difficult to visualize, it is usually simplified as in Diagram B.

When the three hydrogen atoms bond to the nitrogen their 1*s* orbitals must overlap the three 2*p* orbitals:



This study of the orbitals involved in bonding suggests that ammonia is a pyramidal molecule (Fig. 6-6). Since the electronegativity of the nitrogen atom (3.0) is larger than the electronegativity of the hydrogen atoms (2.1), the bonding will be polar covalent. The nitrogen end of the molecule should be slightly more negative than the hydrogen end:



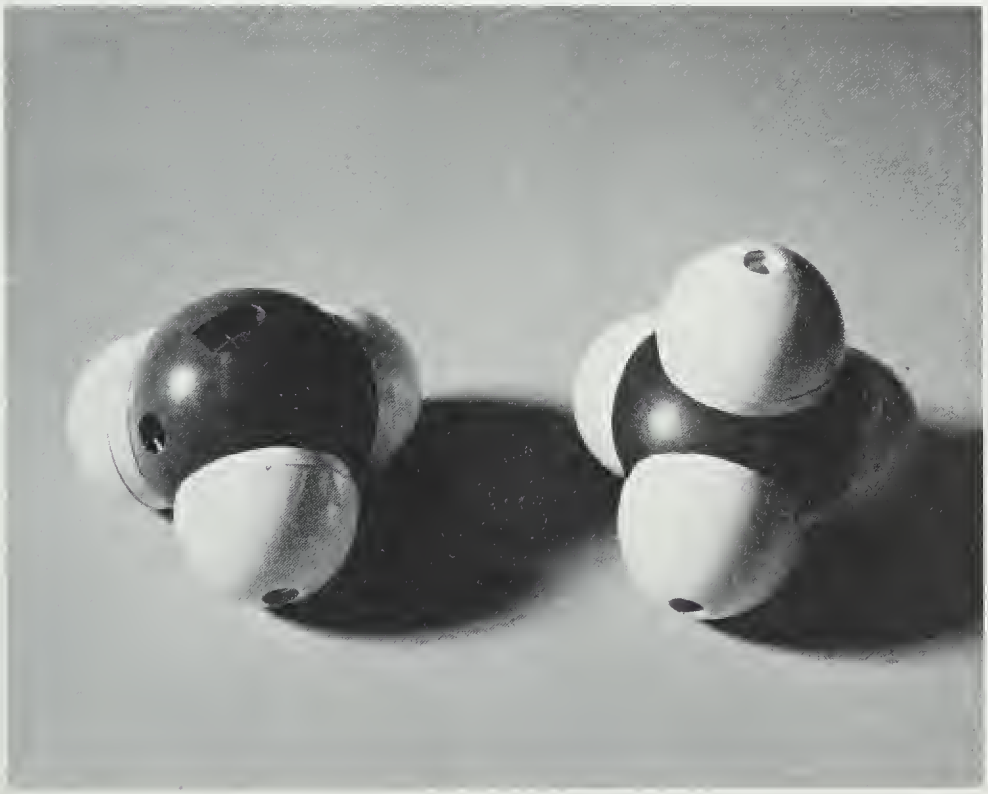
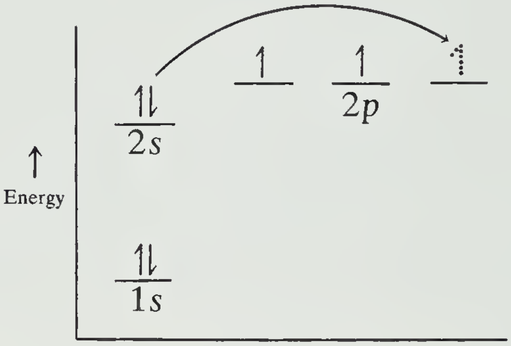


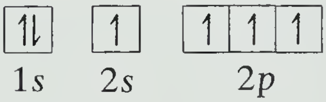
Fig. 6-6 Models of Ammonia (NH_3) and Methane (CH_4)

Experiments confirm these predictions. The study also predicts that the hydrogen-nitrogen-hydrogen bond angles in ammonia should be greater than 90° due to repulsions among the positive hydrogen nuclei. This has also been confirmed experimentally.

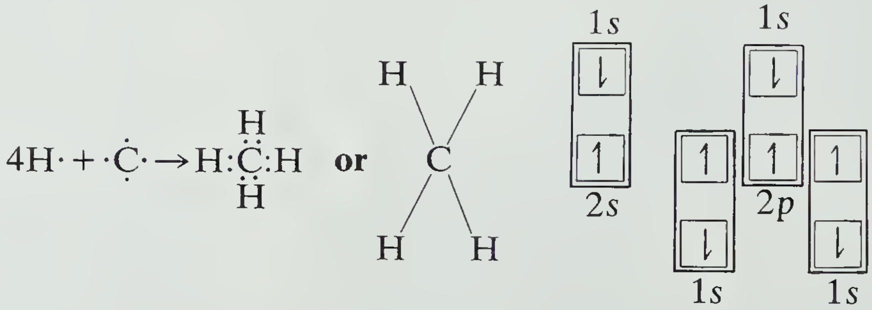
It has been demonstrated that carbon ($1s^2\ 2s^2\ 2p^2$) bonds with four hydrogen atoms to form the molecule CH_4 (methane). It seems that during bonding one of the $2s$ electrons is promoted to a vacant $2p$ orbital:



When the promotion is complete, carbon has four half-filled valence orbitals:



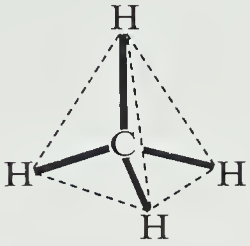
A carbon atom is then able to bond to four hydrogen atoms:



$$4\text{H}\cdot + \cdot\underset{\cdot}{\dot{\text{C}}}\cdot \rightarrow \text{H}:\overset{\text{H}}{\underset{\text{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}}}:\text{H}$$

The four shared pairs of electrons repel each other equally, and the methane molecule consists of a central carbon atom with four hydrogen atoms arranged symmetrically around it. All hydrogen-carbon-hydrogen bond angles are the same, and

C—H bonds point toward the corners of a regular tetrahedron. Methane is a tetrahedral molecule (Fig. 6-6):



Since the electronegativity of the carbon atom (2.5) is slightly larger than the electronegativity of the hydrogen atoms (2.1) the bonding will be slightly polar covalent. However, the carbon atom (δ^-) is in the center of the tetrahedral molecule so there is *no negative end* of the molecule. Since the positive hydrogen nuclei are symmetrically arranged about the central carbon atom, there is also *no positive end* of the molecule. The molecule as a whole is not polar even though each of the bonds in the molecule is slightly polar. Experiments confirm that methane is a nonpolar molecule. Experiments also show that the tetrahedral molecule carbon tetrachloride (CCl_4) is nonpolar since there is no definite positive end nor is there a definite negative end in the carbon tetrachloride molecule.

SAMPLE PROBLEM/6-4

The gas, silicon tetrafluoride, SiF_4, is formed by the action of hydrofluoric acid on glass. Describe as completely as possible a molecule of silicon tetrafluoride.

Silicon has the electronic configuration:

$$\text{Si} \quad 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$$

Each fluorine atom has a half-filled $2p$ orbital:

$$\text{F} \quad 1s^2\ 2s^2\ 2p^5$$

Prior to bonding, a $3s$ electron of silicon is promoted to the $3p$ level, resulting in four half-filled valence orbitals. The unpaired $2p$ electrons of fluorine can bond with the four unpaired electrons of silicon to form four carbon-fluorine bonds each pointed towards the corners of a regular tetrahedron.

Since fluorine atoms are more electronegative than silicon atoms, the silicon-fluorine bonds are polar, with their negative ends at the fluorine atoms. The molecule as a whole is nonpolar.

EXERCISE/6-7

Describe as completely as possible a molecule of germanium tetrabromide, $GeBr_4$.

The examples considered in this section have resulted in filled outer *s* and *p* orbitals for the oxygen, nitrogen, and carbon atoms. The **octet rule** is: when atoms combine, the bonds are formed in such a way that each atom is surrounded by an octet of electrons. There is no clear explanation for the outer shell's usually stopping at eight electrons. In fact, there are some cases where the outer shell does not reach eight electrons and there are other cases where the outer shell does not stop at eight electrons. However, for many compounds, the octet rule is a useful generalization, and the atoms involved in bonding tend to achieve the electron configuration of noble gases (s^2p^6 or 8 outer electrons).

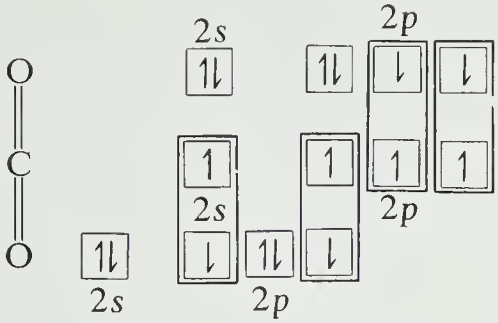
6-7/MULTIPLE BONDS

Carbon dioxide (CO_2) involves one carbon atom bonding to two oxygen atoms. If the carbon atom were to share a pair of electrons with each of the two oxygen atoms, none of the atoms in the molecule would have achieved the electronic configuration of a noble gas:

$$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot + 2\ \cdot\underset{\cdot}{\ddot{\mathrm{O}}}: \rightarrow :\underset{\cdot}{\ddot{\mathrm{O}}}:\underset{\cdot}{\dot{\mathrm{C}}}:\underset{\cdot}{\ddot{\mathrm{O}}}:$$

If two pairs of electrons are shared between the carbon atom and each of the two oxygen atoms, the three atoms in the molecule would each achieve the electronic configuration of the noble gas, neon:

$\dot{\underset{\cdot}{C}}\cdot + 2\cdot\dot{\underset{\cdot}{O}}: \rightarrow :\dot{O}: :C: :\dot{O}:$ **or**



When two pairs of electrons are shared between two atoms, the result is called **double covalent bonding.**

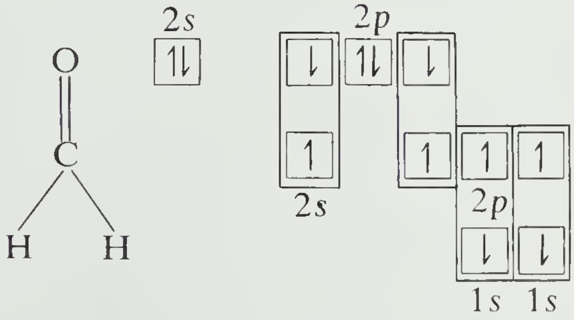
SAMPLE PROBLEM/6-5

Draw an electron dot formula and an orbital diagram for formaldehyde, CH_2O.

The only possible arrangement of electrons and atoms that obeys the octet rule is:

$$:\dot{C}\cdot + 2\,H\cdot + :\dot{\underset{\cdot}{O}}\cdot \rightarrow H:\underset{\underset{H}{\cdot\cdot}}{C}::\dot{\underset{\cdot}{O}}$$

The orbital diagram is:



EXERCISE/6-8

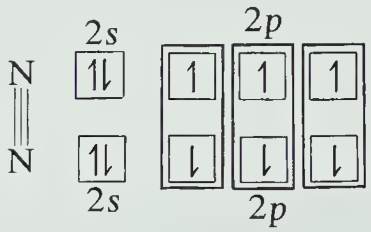
Draw an electron dot formula and an orbital diagram for carbon disulfide, CS_2.

The nitrogen molecule (N_2) is formed when two nitrogen atoms share electrons. If the two nitrogen atoms were to share a pair of electrons, neither of them would achieve the electronic configuration of a noble gas:

$$:\dot{\underset{\cdot}{N}}\cdot + \cdot\dot{\underset{\cdot}{N}}: \rightarrow :\dot{\underset{\cdot}{N}}:\dot{\underset{\cdot}{N}}:$$

However, if three pairs of electrons are shared between the two nitrogen atoms, each would achieve the electronic configuration of the noble gas, neon:

$:\underset{\cdot}{\dot{N}}\cdot + \cdot\underset{\cdot}{\dot{N}}: \rightarrow :N\vdots\vdots N:$ **or**

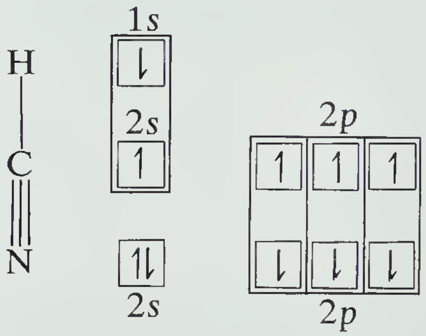


When three pairs of electrons are shared between two atoms, the result is called **triple covalent bonding.**

SAMPLE PROBLEM/6-6

Draw the electron dot formula and the orbital diagram for hydrogen cyanide, HCN.

$H\cdot + :\dot{C}\cdot + :\underset{\cdot}{N}\cdot \rightarrow H:C\vdots\vdots N:$



EXERCISE/6-9

Draw the electron dot formula and the molecular orbital diagram for the hypothetical molecule, phosphorus nitride, PN.

QUESTIONS

1. What is a molecule?
2. What types of elements are involved in ionic bonding?
3. Describe the three steps which occur when an ionic bond is formed in the case of potassium bromide (Refer to Sec. 6-2).
4. Why will each barium ion require two chloride ions in the compound barium chloride?
5. Why will each oxide ion require two potassium ions in the compound potassium oxide?
6. What is the main difference between an ionic bond and a covalent bond?
7. Assuming that the following elements combine to form ionic compounds, write the formulas of the compounds:
   (a) Sr and Cl (b) Rb and S
   (c) Al and S (d) Ca and N
8. Describe the bonding which occurs in the chlorine molecule. Which orbitals are involved in the bonding?
9. Draw the orbital diagram for a bromine molecule.
10. Draw the orbital diagram for the HClO molecule.
11. Draw the orbital diagram for a hydrogen sulfide molecule.
12. Draw electron dot formulas for PH_3, SiH_4, H_2Se, H_2O_2, I_2, and CCl_4.
13. Draw the electron dot formula for IBr. Is the bond between the iodine and the bromide polar? If it is, which end of the molecule is slightly negative?
14. Draw the electron dot formula and the orbital diagram for CH_3Cl and for Cl_2O.
15. A cesium atom has one electron in its outer shell and a selenium atom has six valence electrons. What is the formula for cesium selenide? What type of bonding is involved in cesium selenide? Describe a cesium selenide crystal.
16. A sulfur atom has six electrons in its outer shell and a hydrogen atom has one valence electron. What is the formula for hydrogen sulfide? Will the molecule be polar or nonpolar? Why? What orbitals are involved in bond formation in hydrogen sulfide?

17. Carbon tetrachloride is a nonpolar molecule which has four polar covalent bonds. Explain why this statement is also true with respect to carbon tetrabromide.
18. Which of the following would you predict to be extremely reactive: OBr, Br_2O, CH_3, CH_4?
19. Double covalent bonding occurs in the C_2H_4 molecule. Draw the electron dot formula and the orbital diagram for C_2H_4.
20. Triple covalent bonding occurs in the C_2H_2 molecule. Draw the electron dot formula and the orbital diagram for C_2H_2.
21. Using any of the following elements: F, H, Cl, Mg, K, and referring to an electronegativity table, make up compounds that demonstrate your understanding of ionic bonding, polar covalent bonding, and pure covalent bonding. Use electron dot formulas to show how electrons are shared or transferred.

QUESTIONS TO THINK ABOUT

22. Two different compounds with molecular formula C_2H_6O are known. Draw electron dot formulas for these two compounds.
23. Diamond consists of carbon atoms each of which is bonded in a three-dimensional network to four other carbon atoms. How does this explain the hardness of diamond?

7

CHEMICAL NOMENCLATURE AND FORMULA WRITING

In this chapter, we will concentrate on chemical formulas. Formula writing and naming compounds must be learned together because they go hand in hand. In order to write a formula, the *symbol* and the *oxidation number* of each element in the compound must be known. The sum of the positive oxidation numbers and the negative oxidation numbers of the elements in the compound must be zero. That is, in a neutral molecule, the sum of the oxidation numbers of atoms or ions with positive oxidation numbers must equal the sum of the oxidation numbers of atoms or ions with negative oxidation numbers.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Given oxidation number tables, write the formulas and names of common compounds.
2. Given the name of a substance, write its formula.
3. Given the formula of a substance, write its name.
4. State the meaning of a simple chemical equation.

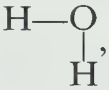
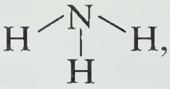
7-1/OXIDATION NUMBER

The *oxidation number* is used to keep track of the *positive* or *negative character* of atoms or ions. When electrons are removed or shifted away from an atom during a chemical reaction, the atom is given a more positive oxidation number.

When electrons are gained or shifted toward an atom during a reaction, the atom is given a more negative oxidation number. The actual numerical value of the oxidation number depends on the number of electrons shifted or transferred.

For simple ions, the oxidation number is equal to the charge on the ion. In NaF, the sodium ion has an oxidation number of +1 because it lost one electron. The fluoride ion has an oxidation number of −1 because it gained one electron. The elements of Group I of the periodic table have oxidation numbers of +1 since they all have one valence electron which they can lose. In compounds involving only two elements (binary compounds) the elements of Group VII of the periodic table usually have oxidation numbers of −1 since they all have seven valence electrons and can gain one more electron to complete a stable octet.

In compounds, the elements of Group II have oxidation numbers of +2 and the elements of Group III often have oxidation numbers of +3. In binary compounds, the elements of Group VI usually have oxidation numbers of −2 and the elements of Group V can have oxidation numbers of −3.

In covalent substances, the more electronegative element is assigned a negative oxidation number, and the less electronegative element is assigned a positive oxidation number. In HCl, the hydrogen atom has an oxidation number of +1 due to a shift (but not a transfer) of the valence electron of the hydrogen atom toward the more electronegative chlorine atom. The chlorine atom has an oxidation number of −1. In  $\begin{array}{l}\mathrm{H{-}O}\\ \quad\;|\\ \quad\,\mathrm{H}\end{array}$, the oxygen atom is more electronegative than the hydrogen atoms. The oxidation number of each hydrogen atom is +1 and the oxidation number of the oxygen atom is −2. In , the oxidation number of each hydrogen atom is +1 and the oxidation number of the nitrogen atom is −3.

Many elements have more than one oxidation number in their various compounds. Iron has an oxidation number of +2 in $FeCl_2$ and +3 in $FeCl_3$. Tin has oxidation numbers of +2 and +4 in $SnCl_2$ and $SnCl_4$, respectively.

We will not attempt to list every oxidation number of every element; however, the most common oxidation numbers of some of the most common elements are listed in Table 7-1.

TABLE 7-1

USUAL OXIDATION NUMBERS OF SOME COMMON ELEMENTS

Element	*Periodic Table Placement*	*Oxidation Number*
H		+1 (except −1 with metals)
Li	Group I	+1
Na	Group I	+1
K	Group I	+1
Ag	Transition metal	+1
Mg	Group II	+2
Ba	Group II	+2
Ca	Group II	+2
Ni	Transition metal	+2
Zn	Transition metal	+2
Pb	Group IV	+2
Al	Group III	+3
Cl	Group VII	−1 (with metals and many nonmetals)
Br	Group VII	−1 (with metals and many nonmetals)
I	Group VII	−1 (with metals and many nonmetals)
F	Group VII	−1
O	Group VI	−2 (except −1 in peroxides)
S	Group VI	−2 (also +4 and +6)
Hg	Transition metal	+1 and +2
Cu	Transition metal	+1 and +2
Fe	Transition metal	+2 and +3
Co	Transition metal	+2 and +3
Sn	Group IV	+2 and +4

7-2/WRITING FORMULAS FOR BINARY SUBSTANCES

Binary substances are compounds composed of only two elements. A table of oxidation numbers can be used to write the formulas of binary compounds. The sum of the positive oxidation numbers and the negative oxidation numbers of the elements in a compound must be zero.

SAMPLE PROBLEM/7-1

Write the formulas of the compounds of bromide ion (Br^-) with potassium ion (K^+), magnesium ion (Mg^{2+}), and aluminum ion (Al^{3+}).

Since potassium ion has an oxidation number of +1 and bromide ion has an oxidation number of −1, the formula of this compound is KBr.

$$\mathrm{KBr} \quad +1+(-1)=0$$

However, magnesium ion has an oxidation number of +2 and two bromide ions will be required since each has an oxidation number of −1. The formula of this compound is $MgBr_2$ and the subscript 2 indicates that there are two bromide ions for every magnesium ion in the compound.

$$\mathrm{MgBr_2} \quad +2+2(-1)=0$$

Finally, aluminum ion has an oxidation number of +3 and three bromide ions will be required for every aluminum ion. The formula of this compound is $AlBr_3$.

$$\mathrm{AlBr_3} \quad +3+3(-1)=0$$

EXERCISE/7-1

Write the formulas of the compounds of iodide ion (I^-) with K^+, Mg^{2+}, and Al^{3+}.

SAMPLE PROBLEM/7-2

Write the formulas of the compounds of sulfide ion (S^{2-}) with K^+, Mg^{2+}, and Al^{3+}.

Potassium ion has an oxidation number of +1 but sulfide ion has an oxidation number of −2. Thus, two potassium ions will be required to balance one sulfide ion. The formula of this compound is K_2S. The subscript 2 indicates that there are two potassium ions for every sulfide ion in the compound.

$$\mathrm{K_2S} \quad 2(+1)+(-2)=0$$

However, magnesium ion has an oxidation number (+2) which balances the oxidation number of the sulfide ion (−2). Magnesium sulfide is simply MgS.

$$\mathrm{MgS} \quad +2+(-2)=0$$

Finally, aluminum ion has an oxidation number of +3 and two aluminum ions have a combined oxidation number of +6. Sulfide ion has an oxidation number of −2 and three sulfide ions have a combined oxidation number of −6. In the case of aluminum sulfide, the simplest way to ensure that the sum of the positive oxidation numbers will equal the sum of the negative oxidation numbers is to use the formula Al_2S_3. There must be two aluminum ions for three sulfide ions.

$$\mathrm{Al_2S_3} \quad 2(+3)+3(-2)=0$$

EXERCISE/7-2

Write the formulas of the compounds of selenide ion (Se^{2-}) with K^+, Mg^{2+}, and Al^{3+}.

7-3/WRITING FORMULAS FOR SUBSTANCES COMPOSED OF MORE THAN TWO ELEMENTS

Some substances are composed of three elements (ternary compounds) or more than three elements. These substances often contain polyatomic ions called *radicals.* Some of the common radicals are listed in Table 7-2. As with simple ions, the oxidation number of a polyatomic ion is the same as its charge. Table 7-2 can be used with Table 7-1 to write the formulas of substances composed of more than two elements.

SAMPLE PROBLEM/7-3

Write the formulas of the compounds of: **(a)** NH_4^+ and Cl^-, **(b)** Na^+ and CO_3^{2-}, and **(c)** Ba^{2+} and SO_4^{2-}.

(a) Ammonium has an oxidation number of +1 and chloride ion has an oxidation number of −1. The formula of

TABLE 7-2

SOME COMMON RADICALS

Ammonium	NH_4^+	Hydrogen Carbonate	HCO_3^-
Acetate	$C_2H_3O_2^-$	Hydrogen Sulfate	HSO_4^-
Nitrate	NO_3^-	Carbonate	CO_3^{2-}
Nitrite	NO_2^-	Sulfate	SO_4^{2-}
Hydroxide	OH^-	Sulfite	SO_3^{2-}
Perchlorate	ClO_4^-	Thiosulfate	$S_2O_3^{2-}$
Chlorate	ClO_3^-	Peroxide	O_2^{2-}
Chlorite	ClO_2^-	Chromate	CrO_4^{2-}
Hypochlorite	ClO^-	Dichromate	$Cr_2O_7^{2-}$
Cyanide	CN^-	Oxalate	$C_2O_4^{2-}$
Cyanate	CNO^-	Phosphate	PO_4^{3-}
Thiocyanate	CNS^-	Phosphite	PO_3^{3-}
Permanganate	MnO_4^-		

this compound is NH_4Cl.

$$NH_4Cl \quad +1+(-1)=0$$

(b) Sodium ion has an oxidation number of +1, but carbonate ion has an oxidation number of −2. Thus there must be two sodium ions for every carbonate ion and this is indicated by a subscript 2 following the Na. The formula is Na_2CO_3.

$$Na_2CO_3 \quad 2(+1)+(-2)=0$$

(c) Barium ion has an oxidation number of +2 and sulfate ion has an oxidation number of −2. The formula of this compound is $BaSO_4$.

$$BaSO_4 \quad +2+(-2)=0$$

EXERCISE/7-3

Write the formulas of the compounds of: **(a)** NH_4^+ and NO_3^-, **(b)** Ag^+ and PO_4^{3-}, and **(c)** Al^{3+} and PO_4^{3-}.

In writing the formulas of compounds which include more than one unit of a given radical, the formula of that radical is enclosed in parentheses and the number of units of the radical is indicated with a subscript. Sample Problem 7-4 illustrates this point.

SAMPLE PROBLEM/7-4

Write the formulas of the compounds of: **(a)** Ca^{2+} and NO_3^-, **(b)** NH_4^+ and PO_4^{3-}, and **(c)** Al^{3+} and SO_4^{2-}.

(a) Two nitrate ions (each with oxidation number of −1) are required for each calcium ion (+2). Thus the formula for nitrate ion is enclosed in parentheses and a subscript 2 is used. The formula is $Ca(NO_3)_2$.

$$Ca(NO_3)_2 \quad +2+2(-1)=0$$

$Ca(NO_3)_2$ may be read "Ca onto NO_3 taken twice." The word *onto* implies that more than one unit of a radical follows. The word *taken* implies that more than one unit of a radical has preceded. In practice, chemists often shorten the reading to "Ca, NO_3 taken twice."

(b) Three ammonium ions (each +1) are required for each phosphate ion (−3). The formula for ammonium ion is enclosed in parentheses and a subscript 3 is used. The formula is $(NH_4)_3PO_4$. It is read "NH_4 taken three times PO_4."

$$(NH_4)_3PO_4 \quad 3(+1)+(-3)=0$$

(c) Two aluminum ions (each +3) are required for three sulfate ions (each −2). The formula for sulfate ion is enclosed in parentheses and a subscript 3 is used. Furthermore, a subscript 2 follows the aluminum. The formula is $Al_2(SO_4)_3$. It is read "Al two onto SO_4 taken three times," or "Al two, SO_4 taken three times."

$$Al_2(SO_4)_3 \quad 2(+3)+3(-2)=0$$

EXERCISE/7-4

Write the formulas of the compounds of: **(a)** Al^{3+} and NO_3^-, **(b)** NH_4^+ and SO_3^{2-}, and **(c)** Al^{3+} and SO_3^{2-}.

7-4/NAMING BINARY SUBSTANCES

(*a*) *Hydrogen and Another Element*

Compounds of hydrogen and a metal are named by writing the name of the metal followed by the word *hydride*. Thus, NaH is sodium hydride.

The Group IV element carbon forms many compounds with hydrogen. These are called *hydrocarbons* and they are discussed in Chapter 13.

Nonsystematic or trivial names are normally used for compounds containing hydrogen and a Group V element. For example, NH_3 is called ammonia and AsH_3 is called arsine.

Compounds of hydrogen and a nonmetal from Groups VI and VII are named by writing the word hydrogen followed by the stem of the name of the nonmetal to which the ending "-ide" has been added. Thus, HCl is hydrogen chloride and H_2S is hydrogen sulfide. Of course, H_2O has the trivial name water. As we shall see in Chapter 8, solutions of these compounds dissolved in water are acids. They are named by using the prefix "hydro-," the stem of the name of the nonmetal, and the ending "-ic," followed by the word "acid." Thus, a solution of HCl dissolved in water is called hydrochloric acid, a solution of HBr in water is called hydrobromic acid, and a solution of H_2S in water is called hydrosulfuric acid.

(*b*) *Metal and Nonmetal*

A compound of a metal and a nonmetal is named by writing the name of the metal followed by its oxidation number, followed by the stem of the name of the nonmetal to which the ending "-ide" has been added. The oxidation number is written as a Roman numeral and is enclosed in parentheses. This is called the Stock system for the name of the metal. If, however, a metal has only one possible oxidation number (Groups I and II and some other metals), the Roman numeral is normally omitted (Table 7-3).

In the older naming system, if a metal had two oxidation numbers, this was indicated by using the ending "-ous" for the lower oxidation number and "-ic" for the higher oxidation number. Furthermore, these endings were frequently added to the stem of the Latin name of the element. Thus, iron(II) was ferrous and iron(III) was ferric. Tin(II) was stannous and

TABLE 7-3

NAMES OF SOME COMPOUNDS COMPOSED OF A METAL AND A NONMETAL

Formula	*Name*	*Older Name*
NaCl	Sodium Chloride	
CaO	Calcium Oxide	
FeS	Iron(II) Sulfide	Ferrous Sulfide
$FeBr_3$	Iron(III) Bromide	Ferric Bromide
$SnCl_2$	Tin(II) Chloride	Stannous Chloride
$SnCl_4$	Tin(IV) Chloride	Stannic Chloride

tin(IV) was stannic. Similarly, mercury(I) was mercurous and mercury(II) was mercuric.

(*c*) *Two Nonmetals*

Compounds of two nonmetals are named by writing the name of each nonmetal preceded by a prefix which indicates the number of atoms of the nonmetal. The prefixes are mono-(1), di-(2), tri-(3), tetra-(4), penta-(5), hexa-(6), hepta-(7), and octa-(8). Normally the prefix "mono-" is omitted from the name of the first of the two nonmetals. The stem of the name of the more electronegative element has the ending "-ide." Thus CO is carbon monoxide, CO_2 is carbon dioxide, NO_2 is nitrogen dioxide, N_2O_5 is dinitrogen pentoxide, and CCl_4 is carbon tetrachloride.

However, the Stock system can also be used. Thus, NO_2 can be called nitrogen(IV) oxide and N_2O_5 can be called nitrogen(V) oxide.

7-5/NAMING SUBSTANCES COMPOSED OF MORE THAN TWO ELEMENTS

(*a*) *Acids*

A compound composed of hydrogen and a negative radical from Table 7-2 is named by writing the word *hydrogen* followed by the name of the radical. Thus, H_2SO_4 is hydrogen sulfate, HNO_2 is hydrogen nitrite, and H_3PO_4 is hydrogen phosphate. However, the solutions made by dissolving these compounds in water (aqueous solutions) are acids. The ending "-ate" as in hydrogen sulfate and hydrogen phosphate becomes "-ic" as in sulfuric acid and phosphoric acid. The ending "-ite" as in hydrogen nitrite becomes "-ous" as in nitrous acid (Table 7-4).

TABLE 7-4

NAMING TYPICAL ACIDS

Formula	*Aqueous Solution*
$HC_2H_3O_2$	Acetic Acid
HNO_3	Nitric Acid
HNO_2	Nitrous Acid
$HClO_4$	Perchloric Acid
$HClO_3$	Chloric Acid
$HClO_2$	Chlorous Acid
$HClO$	Hypochlorous Acid
$HMnO_4$	Permanganic Acid
H_2CO_3	Carbonic Acid
H_2SO_4	Sulfuric Acid
H_2SO_3	Sulfurous Acid
$H_2C_2O_4$	Oxalic Acid
H_3PO_4	Phosphoric Acid
H_3PO_3	Phosphorous Acid

(*b*) *Other Substances*

Substances formed from the combination of metals and negative radicals can be named by using the Stock system for the metal and following this with the name of the radical. If the negative radical is hydroxide, the substance is a base. Typical bases include NaOH (sodium hydroxide), KOH (potassium hydroxide), and $Ca(OH)_2$ (calcium hydroxide). Otherwise the substance is a salt (Table 7-5).

TABLE 7-5

NAMING TYPICAL SALTS

Formula	*Name*
$LiC_2H_3O_2$	Lithium Acetate
$Ba(NO_3)_2$	Barium Nitrate
$Fe(NO_2)_2$	Iron(II) Nitrite
$Fe(ClO_4)_3$	Iron(III) Perchlorate
$NaClO_3$	Sodium Chlorate
$Ca(ClO_2)_2$	Calcium Chlorite
$KClO$	Potassium Hypochlorite
$KMnO_4$	Potassium Permanganate
Na_2CO_3	Sodium Carbonate
$KHCO_3$	Potassium Hydrogen Carbonate
$Al_2(SO_4)_3$	Aluminum Sulfate
$NaHSO_4$	Sodium Hydrogen Sulfate
$K_2C_2O_4$	Potassium Oxalate
$AlPO_4$	Aluminum Phosphate
$AlPO_3$	Aluminum Phosphite

EXERCISE/7-5

Draw a large table similar to Table 7-6. Fill in each blank with the formula and name of the compound that results when the positive ion at the left is combined with the negative ion at the top.

EXERCISE/7-6

Give formulas for the following compounds: hydrogen bromide, hydriodic acid, carbon tetrabromide, sulfur trioxide, potassium oxalate, iron(III) nitrate, iron(III) sulfite, cobalt(II) chlorate, cobalt(II) oxalate, tin(IV) nitrite, and tin(IV) sulfite.

TABLE 7-6

NAMES AND FORMULAS OF COMPOUNDS

	OH^-	F^-	$C_2H_3O_2^-$	O^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$	PO_3^{3-}	
H^+								
Na^+								
NH_4^+								
Ag^+								
Cu^{2+}								
Ca^{2+}								
Ni^{2+}								
Zn^{2+}								
Hg^{2+}								
Al^{3+}								

7-6/INTRODUCTION TO CHEMICAL EQUATIONS

The chemical equation is a shorthand method for describing a chemical change. The symbols and formulas are used to indicate the substances involved in the change. In order to balance an equation, one must know what substances react and what substances are formed, and one must know the formulas of all substances in the reaction.

When water is decomposed, hydrogen and oxygen are formed:

$$H_2O \rightarrow H_2 + O_2$$

The formula for the reactant is on the left, and the formulas for the products are on the right. The arrow is read as "yields" and the plus sign is read as "and." When a plus sign appears on the left side, it implies "reacts with."

The above equation does not obey the Law of Conservation of Mass. Two atoms of oxygen in the O_2 molecule could not be formed from one water molecule containing only one oxygen atom. The proper coefficients (numbers) must be placed in front of each formula:

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

The equation is read, "two water molecules yield two hydrogen molecules and one oxygen molecule." Remember that subscripts in a correct formula cannot be changed in order to make an equation balance. Substances have a definite atomic composition.

The symbol for heat is Δ.

$$2\,KClO_3 \xrightarrow{\Delta} 2\,KCl + 3\,O_2(g)$$

The (g) indicates that a gas (in this case, oxygen) is given off in a reaction. The above equation is read, "two potassium chlorate formula units yield (when heated) two potassium chloride formula units and three gaseous oxygen molecules." As was stated in Chapter 6, the word *molecule* does not have much meaning in the case of ionic solids such as potassium chlorate and potassium chloride. Therefore, we referred to oxygen molecules but potassium chlorate and potassium chloride *formula units.*

An (ℓ) indicates a pure liquid, (s) indicates a solid, and (aq) indicates an aqueous solution (i.e., a substance dissolved in water). For example, an aqueous solution of silver nitrate reacts with an aqueous solution of sodium chloride to yield solid silver chloride and an aqueous solution of sodium nitrate. This information can be conveyed by the chemical equation:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

SAMPLE PROBLEM/7–5

What is meant by the following chemical equation?

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2(g)$$

This equation means that one formula unit of calcium carbonate yields (when heated) one calcium oxide formula unit and one gaseous carbon dioxide molecule.

EXERCISE/7-7

If CH_4 is methane, what is meant by the following chemical equation?

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

QUESTIONS

1. What is the formula for lithium sulfide? Potassium iodide? Magnesium bromide? Magnesium sulfide? Aluminum sulfide? Aluminum chloride?
2. What is the formula for iron(III) chloride? Iron(II) oxide? Cobalt(II) bromide? Tin(IV) chloride?
3. What is the formula for magnesium hydroxide? Iron(III) carbonate? Carbon tetrabromide? Diphosphorus pentasulfide? Nitrogen(V) sulfide?
4. What is the formula for permanganic acid? Oxalic acid? Ammonium chromate? Sodium perchlorate? Potassium thiosulfate? Aluminum sulfite?
5. Name each of the following compounds: LiH, NH_3, FeS, $SnBr_4$, Hg_2Cl_2, N_2S_5, N_2O, and Al_2O_3.
6. Name each of the following compounds: $(NH_4)_2Cr_2O_7$, $Cu(NO_3)_2$, $Ba(HCO_3)_2$, CaC_2O_4, $Pb(C_2H_3O_2)_2$, and $Al_2(S_2O_3)_3$.
7. Write the name of the aqueous solution of each of the following: H_2SO_4, HCl, HNO_3, $HC_2H_3O_2$, H_3PO_4, and $HClO_4$.

8. What do the following equations mean?

   (a) $CaO(s) + H_2O(\ell) \rightarrow Ca(OH)_2(s)$
   (b) $C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g)$ (C_3H_8 is propane)
   (c) $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
   (d) $Na_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2\,NaCl(aq)$

QUESTIONS TO THINK ABOUT

9. What is the total number of atoms in one molecule of $HC_2H_3O_2$?
10. What is the total number of atoms represented by the formula $Ca(HCO_3)_2$?
11. What is the oxidation number of the metal in each of the following compounds: $SrCl_2$, YbI_3, $TlCNO$, V_2O_5, and $Y(OH)_3$?
12. What is the oxidation number of the radical in each of the following compounds: Na_2MoO_4, $Mg(IO_3)_2$, $CaSiO_3$, $Al(C_2H_5O)_3$, and $Li_2B_4O_7$?

8

SOLUTIONS

In this chapter we begin with an explanation of solutions and the solution process. We then discuss various types of solutions and the factors that affect solubility. We go on to consider solutions of electrolytes and extend the discussion to include various aspects of the chemistry of acids and bases, finishing with a brief description of the concept of pH.

When you have completed studying this chapter, you should be able to attain the following objectives:

1. Define and give examples of: solution, solvent, solute, electrolyte, and nonelectrolyte.
2. Name five types of solution and give an example of each.
3. Describe the processes occurring during the solution of a nonelectrolyte.
4. Define a saturated solution and describe the equilibrium processes occurring in a saturated solution.
5. Describe the effect of temperature on solubility.
6. State the postulates of the modern theory of electrolytes.
7. Describe the processes occurring during the solution of an electrolyte.
8. Explain the effects of molecular polarity on the solubility of a particular solute in a particular solvent.

9. Distinguish between dissociation and ionization and give an example of each.
10. Define and give examples of: acid, base, strong acid, weak acid, strong base, weak base, conjugate acid, conjugate base, neutralization, salt.
11. Write equations for acid-base reactions according to the Brønsted-Lowry theory and identify the conjugate acid and base pairs in each.
12. Write ionic equations for the neutralization reactions of strong acids and bases.
13. Explain the meaning and use of the pH scale.

8-1/INTRODUCTION

When a lump of sugar is placed in a cup of tea, the sugar disappears, but it remains unchanged. We know that the sugar is unchanged when it mixes with the water of the tea because we can still taste it. This is an example of a solution. The sugar has dissolved in the hot water of the tea.

A **solution** is a homogeneous (the same throughout) mixture of two or more substances. The composition of a solution can vary within certain limits. One can dissolve one lump, two lumps, or three lumps of sugar in a cup of tea, but one cannot dissolve a box of sugar cubes in one cup of tea. When the sugar dissolves in the tea, the sugar molecules are distributed randomly and evenly throughout the cup of tea. Once the tea has been stirred, the uniform sweetness of the tea tells us that the solution is homogeneous.

In some ways, the tea example is confusing. Tea itself is a solution of many substances dissolved in water. Therefore, let us think of sugar dissolved in pure water. Two words that we should consider are solvent and solute. Generally we refer to the substance that is present in larger quantity as the **solvent**. The **solute** is the substance present in smaller amount. In our example, water is the solvent and sugar is the solute. The sugar dissolves in the water. However, we are allowed to interchange the terms whenever it is convenient. In solutions where one substance is a liquid and the other substance is a gas or a solid, the liquid is usually called the solvent.

8-2/TYPES OF SOLUTION

Liquid solutions are made by dissolving solids, liquids, or gases in liquids. Sugar in water is an example of a solution of a solid dissolved in a liquid (Fig. 8-1). Salt water is another example of a common type of solution. Water is the solvent in a great many solutions. Solutions made by dissolving substances in water are called *aqueous solutions*. Much of our discussion of solutions will deal with aqueous solutions. Other aqueous solutions include alcohol dissolved in water (liquid in a liquid) and carbon dioxide dissolved in water (gas in a liquid).

A solution of alcohol in water is an example of a liquid dissolved in another liquid. Alcohol and water mix in any proportion. They are said to be miscible (easily mixed) in all proportions. However, some combinations of liquids do not mix to any great extent. Gasoline floats on top of water, but it will not dissolve very well in the water. Gasoline and water are practically immiscible.

Gaseous solutions are made by dissolving a gas in another gas (Fig. 8-2). All gases mix in all proportions to produce homogeneous solutions. Air itself is a solution of oxygen and many other gases dissolved in nitrogen.

A solid solution is formed when one solid substance is mixed with another solid substance to produce a homogeneous mixture (Fig. 8-3). Many alloys are solid solutions. For example, brass is a solid solution in which zinc atoms have been mixed homogeneously into the solid crystal of copper atoms.

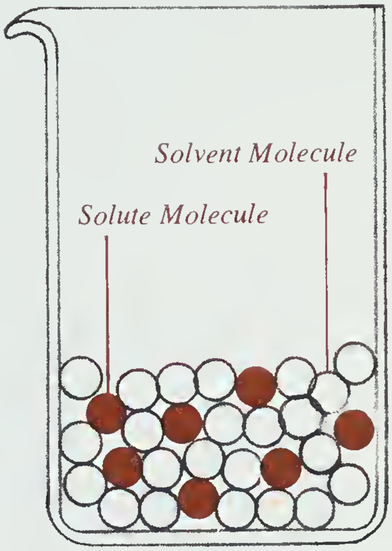


Fig. 8-1 A Liquid Solution

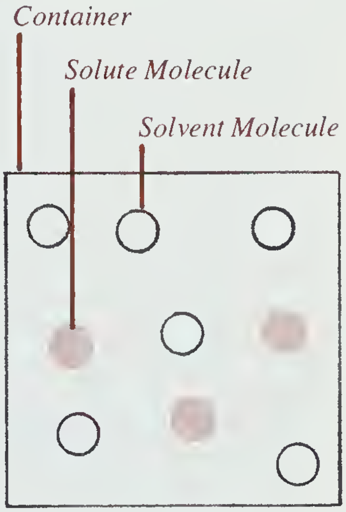


Fig. 8-2 A Gaseous Solution

8-3/THE SOLUTION PROCESS

Consider the dissolving of sugar crystals in water. Once the sugar crystals are placed in the water, sugar molecules from the surface of the crystals become dislodged and move into spaces between the water molecules. This process is called **dissolving**. As the sugar molecules leave the surface of the sugar crystals, the crystals become smaller and the amount of sugar dissolved in the water becomes larger.

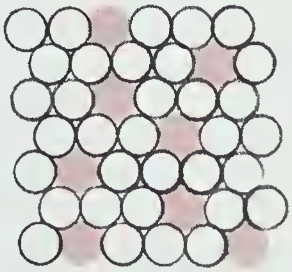


Fig. 8-3 A Solid Solution

However, an opposing process soon begins. Sugar molecules contain polar oxygen-hydrogen bonds, as do water molecules. The positive ends of these bonds (the hydrogen atoms) in a sugar molecule are attracted to the negative ends (the oxygen atoms) in other molecules. Similarly, the negative ends of these bonds in a sugar molecule are attracted to the positive ends in other molecules. Thus when sugar molecules in the solution collide with undissolved sugar crystals, they are attracted to and stick to the surface of the crystals. This process is called **precipitation**. As more and more sugar molecules dissolve, more and more sugar molecules precipitate. Finally a state of balance or **equilibrium** occurs. If the speed at which sugar molecules dissolve equals the speed at which sugar molecules precipitate, solution equilibrium is reached. This is called a state of **dynamic equilibrium** because two opposing processes (dissolving and precipitating) occur at equal speeds. At this point the solution is said to be *saturated* with sugar (Fig. 8-4).

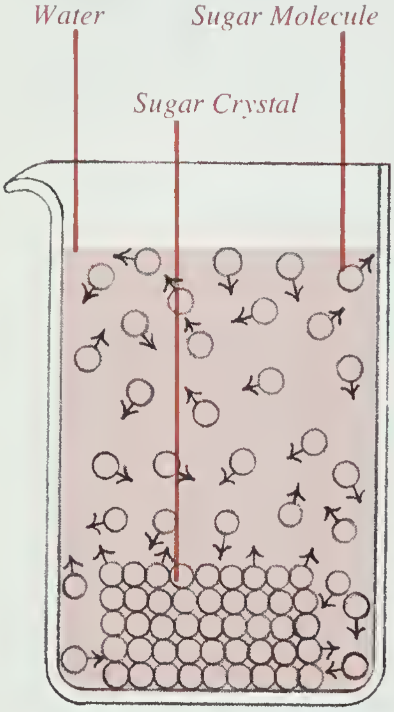


Fig. 8-4 A Saturated Solution

A simple model can help us to understand a dynamic equilibrium. Suppose two rooms are connected by an open door. Ten students are in each room. Each student is told that he can go from one room to the other as long as a student in the other room will take his place. At all times there are ten students in each room but they are not always the same students. Some students are going from one room to the other, and other students are going in the opposite direction. In the same way, in a saturated solution, some sugar molecules are dissolving while other sugar molecules are precipitating. However, there is always the same amount of sugar in the solution.

A **saturated solution** contains the maximum amount of solute that can remain dissolved in a given amount of solvent. The speed at which the solute molecules dissolve equals the speed at which the solute molecules precipitate. A solution equilibrium is reached. Usually, a solution is saturated if undissolved solute remains visible no matter how hard the solution is stirred.

If the solution is *unsaturated*, all of the solute molecules will be in solution. There will be no solution equilibrium because there will be no opposing processes of dissolving and precipitating.

8-4/FACTORS AFFECTING SOLUBILITY

(*a*) *Pressure*

Of the various types of solutions, only gases dissolved in liquids (or solids) are affected very much by pressure. In the soft drink industry, carbon dioxide is dissolved in a water-based syrup. The carbon dioxide is more soluble if it is forced into the water under pressure. Henry's Law states that the solubility of gases in liquids is directly proportional to the pressure of the gas above the liquid.

Figure 8-5 shows that under higher pressure the gas molecules are more likely to come in contact with and dissolve in the liquid layer.

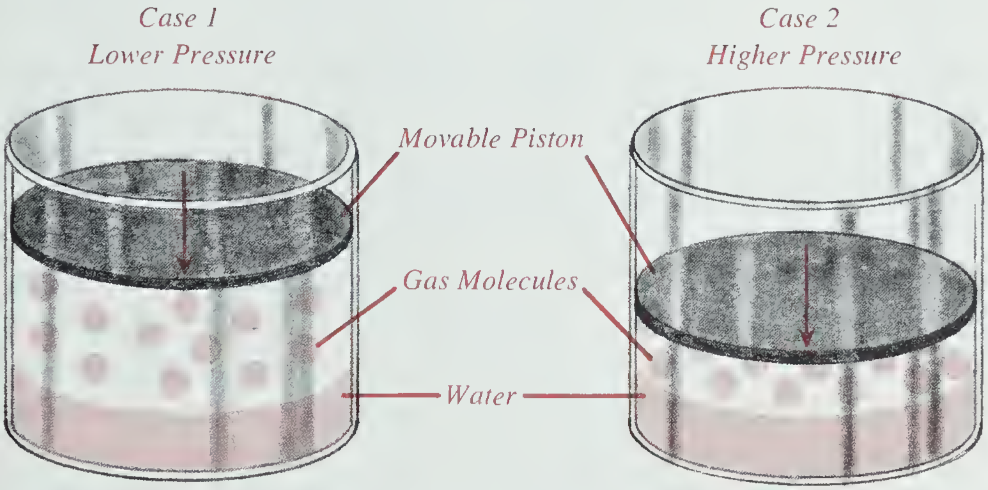


Fig. 8-5 Henry's Law

(*b*) *Temperature*

In the case of gases dissolved in liquids, rising temperatures cause the gas molecules to leave the liquid. Thus, the solubility of gases in liquids decreases as the temperature of the solution is increased.

However, energy is usually required to cause solid molecules to leave a crystal and mix with the solvent. Thus, unless there is some other opposing factor, solids are usually more soluble in warmer than in cooler liquids. The heat energy is used to enable the solute molecules to break away from the crystals.

Less energy is required to cause mixing of liquids in liquids, and the solubility of a liquid in a liquid seldom depends on the temperature of the system.

8-5/ELECTROLYTES AND NONELECTROLYTES

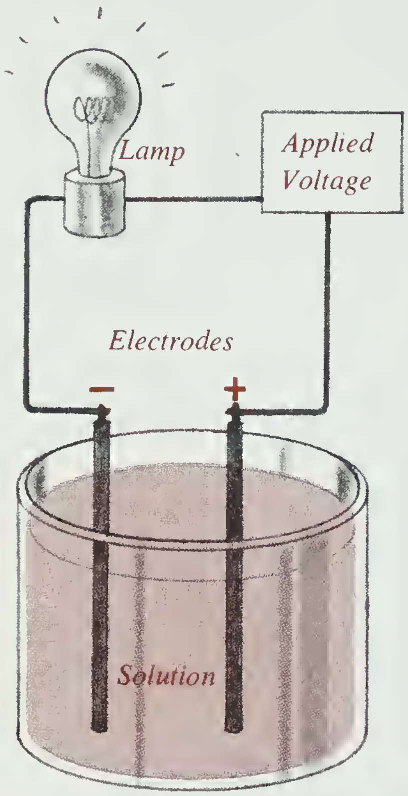


Fig. 8-6 Apparatus for Determining the Conductivity of a Solution

An electric current will pass through some solutions. The solutes in these solutions are called **electrolytes**. However, an electric current will not pass through other solutions, and the solutes in these solutions are called **nonelectrolytes**. Sugar is a nonelectrolyte, but sodium chloride is an electrolyte.

The ability of a solution to conduct electricity can be determined with the simple apparatus shown in Fig. 8-6. A pair of electrodes, in series with a light bulb, is connected to a source of electricity. No current can flow through the circuit as long as the electrodes are separated. However, when the two electrodes are joined by a substance which will conduct electricity, such as a copper wire or a solution of an electrolyte, a current will flow and the light bulb will glow.

Pure water is essentially a nonconductor of electricity. When many covalently bonded substances such as sugar are dissolved in water, the solutions do not conduct electricity. However, ionic substances such as sodium chloride, when dissolved in water, form solutions that do conduct electricity.

In order for a solution to conduct electricity, charged particles must exist in the solution. In fact, up to a certain limit, the more charged particles there are the better the solution will conduct electricity. It is the movement of the charged particles that allows the current to pass through a solution of an electrolyte.

The English scientist Michael Faraday assumed that the formation of these charged particles in the solution was caused by the presence of the charged electrodes of the conductivity apparatus. However, further experiments, especially the important work of the Swedish chemist Svante Arrhenius, led to the development of the modern theory of electrolytes:

(1) Electrolytes in solution exist in the form of ions.
(2) An ion is an atom or group of atoms which has an electric charge.
(3) In electrolyte solutions, the total positive ionic charge must equal the total negative ionic charge.

In the case of a nonelectrolyte, such as sugar dissolved in water, *no* ions are present. When sugar molecules dissolve in water, they become surrounded by a layer of water molecules, but their structure is unchanged and they remain uncharged.

When charged electrodes are placed in a solution containing hydrated sugar molecules (sugar molecules surrounded by a layer of water molecules), the neutral sugar molecules do not migrate towards one electrode or the other. Thus, a nonelectrolyte will *not* conduct electricity in solution.

8-6/DISSOLVING IONIC SUBSTANCES

Sodium chloride is a typical ionic compound. Sodium is in Group I. A sodium atom has one outer electron which it can lose. Chlorine is in Group VII of the periodic table. A chlorine atom has seven outer electrons and can gain one electron to complete its octet:

$$\mathrm{Na}\cdot \rightarrow \mathrm{Na}^{+} + 1e^{-}$$

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + 1e^{-} \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:^{-}$$

When crystals of sodium chloride form, the positive sodium ions are attracted to the negative chloride ions because unlike charges attract. One layer of a sodium chloride crystal is shown in Fig. 8-7.

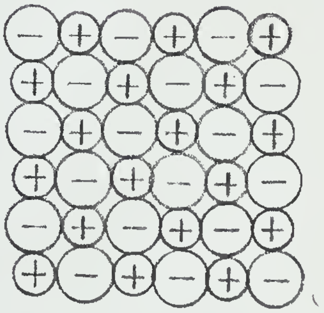
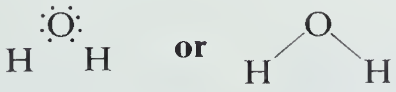


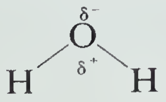
Fig. 8-7 One Layer of a Sodium Chloride Crystal

A solution of sodium chloride in water conducts electricity and therefore must contain ions. The question is, what process is able to overcome the attraction between the sodium ions and the chloride ions? Why do the sodium ions separate from the chloride ions as they dissolve?

To answer this question, we must look at the structure of the water molecule. Water is a bent molecule in which the two oxygen-to-hydrogen bonds are covalent bonds:



Because oxygen is a more electronegative element than hydrogen, the oxygen atom attracts the two shared pairs of electrons more effectively than do the two hydrogen atoms. The oxygen end of the molecule is slightly negative and the hydrogen end of the molecule is slightly positive:



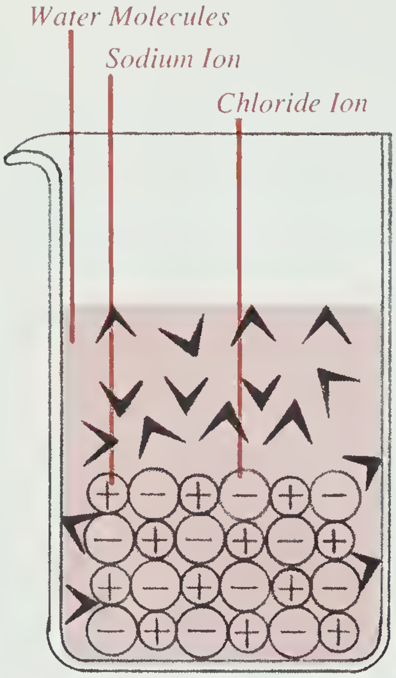


Fig. 8-8 A Crystal of NaCl in a Beaker of Water

Thus, water is a polar molecule which can be represented schematically as:

When a crystal of sodium chloride is placed in water, the negative oxygen ends of the water molecules are attracted to the positive sodium ions, and the positive hydrogen ends of the water molecules are attracted to the negative chloride ions as illustrated in Fig. 8-8.

The water-surrounded sodium ions move off into the solution. They are called hydrated or aqueous sodium ions $Na^+(aq)$. The water-surrounded chloride ions, called hydrated or aqueous chloride ions $Cl^-(aq)$, also move into solution as shown in Fig. 8-9.

This process is represented by the equation:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

The (aq) is our method of showing that each ion is surrounded by a number of water molecules. However, we have not indicated how many water molecules are involved. This is a useful device since different ions will be surrounded by different numbers of water molecules. The process in which ions separate from each other and from the crystal is called **dissociation**. It is the layer of water molecules around each ion which diminishes the attraction of the sodium ions for the chloride ions. Ions are already present in the sodium chloride crystal. In solution, the ions have separated or dissociated.

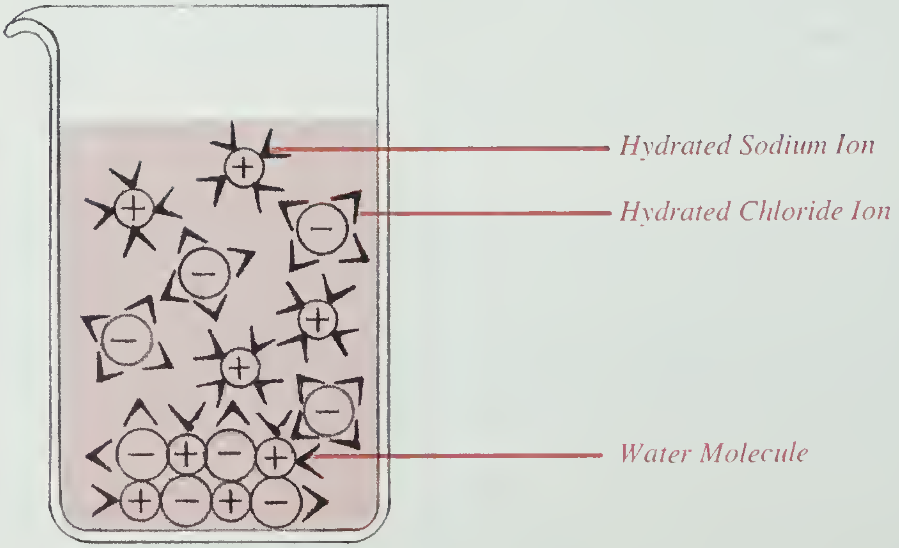


Fig. 8-9 A Schematic Representation of the Dissolving of NaCl

Other ionic substances dissociate in water much as sodium chloride does. However, some ionic substances dissolve more readily in water than does sodium chloride and some dissolve less readily in water:

$$Na_2SO_4(s) \rightarrow 2\ Na^+(aq) + SO_4^{2-}(aq)$$

$$(NH_4)_3PO_4(s) \rightarrow 3\ NH_4^+(aq) + PO_4^{3-}(aq)$$

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

8-7/LIKE DISSOLVES LIKE

Carbon tetrachloride is a nonpolar molecule. When a crystal of sodium chloride is placed in a beaker of carbon tetrachloride, the carbon tetrachloride molecules are not appreciably attracted to the positive sodium ions or to the negative chloride ions. There is no force acting to separate these ions and pull them into solution; therefore the sodium chloride is not as soluble in nonpolar carbon tetrachloride as it is in polar water.

Why is gasoline not as soluble in polar water as it is in nonpolar carbon tetrachloride? In water, all of the polar water molecules are attracted to one another. Thus, the attractive forces between the water molecules have to be overcome before gasoline molecules can move between the water molecules. Since the water molecules have no attraction for those of the gasoline, they tend not to separate from one another to make room for the gasoline. On the other hand, carbon tetrachloride molecules are not polar and are not strongly attracted to one another. They are also not strongly attracted to the molecules of the gasoline. However, there is no great force to be overcome in order to get the carbon tetrachloride molecules to separate from one another to make room for the gasoline. Thus nonpolar gasoline dissolves much more readily in nonpolar carbon tetrachloride than it does in polar water.

Polar or ionic substances are more soluble in polar solvents than in nonpolar solvents. Nonpolar substances are more soluble in nonpolar solvents than in polar solvents. Thus, "like dissolves like."

8-8/IONIZATION—FORMING IONS FROM MOLECULES

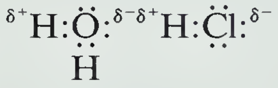
Certain covalent molecules ionize when they dissolve in water. A good example is the hydrogen chloride molecule (HCl). Normally hydrogen chloride is a gas; however, it can be liquefied and solidified by cooling. Whether it is a gas, solid, or liquid, hydrogen chloride will not conduct electricity. Hydrogen chloride is a nonelectrolyte.

When hydrogen chloride molecules are dissolved in water, the solution (called hydrochloric acid) will conduct electricity. Ions are present. The hydrogen chloride molecules must have reacted with the water molecules.

Hydrogen chloride, like water, is a polar substance:

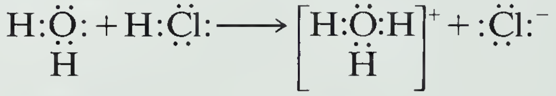
$$^{\delta+}\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^{\delta-}$$

The chlorine end of the molecule is slightly negative and the hydrogen end of the molecule is slightly positive. One would expect that a hydrogen chloride molecule would be attracted to a water molecule:



$$^{\delta+}\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\ddot{\mathrm{O}}}}:^{\delta-\,\delta+}\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^{\delta-}$$

During a collision between a hydrogen chloride molecule and a water molecule, a hydrogen ion (i.e., a proton—H^+) is transferred from the hydrogen chloride to the water:



$$\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\ddot{\mathrm{O}}}}: + \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}: \longrightarrow \left[\mathrm{H}:\underset{\mathrm{H}}{\underset{\cdot\cdot}{\ddot{\mathrm{O}}}}:\mathrm{H}\right]^{+} + :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^{-}$$

$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

When the hydrogen ion leaves the HCl molecule, it leaves its electron behind forming a chloride ion.

The H_3O^+ is called the **hydronium ion**. Both the hydronium ion and the chloride ion are surrounded by a layer of water molecules (they are hydrated):

$$H_2O + HCl \rightarrow H_3O^+(aq) + Cl^-(aq)$$

This process is called **ionization**. Ionization involves the formation of ions from molecules. Notice that the term dissociation was used in reference to the dissolving of an ionic substance like sodium chloride. Sodium chloride crystals consist of positive sodium ions and negative chloride ions. During the dissolving process, sodium ions and also chloride ions separate or dissociate from the crystal. However, in the case of hydrogen chloride, HCl molecules *react* with H_2O molecules to form ions—that is, they *ionize*.

8-9/ACIDS AND BASES

One molecule which we normally consider to be a nonelectrolyte is actually a weak electrolyte. It ionizes slightly and conducts electricity to a slight extent. That molecule is water. On collision of two water molecules, it is possible for a hydrogen ion of one molecule to transfer to the second water molecule:

$$H_2O + H_2O \rightarrow H_3O^+(aq) + OH^-(aq)$$

A hydronium ion (H_3O^+) and a hydroxide ion (OH^-) are formed. Both ions are hydrated.

This is an ionization process, but only about one out of every 300 million water molecules is involved in the ionization process. The ionization of water may appear to be an unimportant process since such a small proportion of the water molecules actually ionize. However, the ability to ionize is one of water's most important properties. The quantities of hydronium ions and hydroxide ions present can, for example, have a great effect on many of the metabolic reactions in living cells.

In pure water, the number of hydronium ions must equal the number of hydroxide ions since they are both formed together during the ionization process. Whenever the quantity of hydronium ions equals the quantity of hydroxide ions in any aqueous solution, the solution is neutral. It is possible to add substances to water which will increase either the quantity of hydronium ions or the quantity of hydroxide ions.

We have already seen that hydrogen chloride dissolves in water and ionizes to form hydronium ions and chloride ions. When hydrogen chloride dissolves in water it increases the number of hydronium ions present in the water, and it is called an acid—hydrochloric acid. Any substance which increases the number of hydronium ions present in an aqueous solution is called an **acid**.

Hydrochloric acid is called a **strong acid** because it ionizes extremely well. Essentially 100 percent of the hydrogen chloride molecules ionize to form hydronium ions and chloride ions when the hydrogen chloride dissolves in water. Nitric acid is another example of a strong acid having one ionizable hydrogen atom which can be transferred to a water molecule:

$$HNO_3 + H_2O \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Not all acids ionize very well. Acetic acid is called a **weak acid** because it ionizes poorly when it is dissolved in water:

$$HC_2H_3O_2 + H_2O \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

The majority of the acetic acid molecules dissolve as molecules, just as sugar dissolves as molecules. Only a small percentage of the acetic acid molecules actually ionize. Weak acids ionize slightly when they are dissolved in water.

Sulfuric acid is an acid which can transfer two hydrogen ions to two water molecules. The first hydrogen ion leaves the sulfuric acid molecule easily. Therefore sulfuric acid is a strong acid:

$$H_2SO_4 + H_2O \rightarrow H_3O^+(aq) + HSO_4^-(aq)$$

The second hydrogen ion can also leave the HSO_4^- ion, but it does not leave as readily as the first hydrogen ion:

$$HSO_4^- + H_2O \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$

This is definitely a *two-step* process; however, it is often written as one step:

$$H_2SO_4 + 2\ H_2O \rightarrow 2\ H_3O^+(aq) + SO_4^{2-}(aq)$$

As a group, acids have certain properties in common. They have a sour taste, they turn litmus paper red, and they react with some metals to generate hydrogen gas.

It is possible to add substances to water which will increase the quantity of hydroxide ions. These substances are called **bases**. Typical bases are sodium hydroxide and potassium hydroxide:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

A few of the properties of bases are: they feel slippery, they have a bitter taste, and they turn litmus paper blue.

In this section we have defined acids and bases in aqueous solutions: acids increase the quantity of hydronium ions in water and bases increase the quantity of hydroxide ions. According to this definition, carbon dioxide acts as a weak acid since, as it dissolves in water, some of the carbon dioxide molecules react to cause an increase in the amount of hydronium ions present in the water:

$$CO_2 + 2\ H_2O \rightarrow H_3O^+(aq) + HCO_3^-(aq)$$

Also, ammonia acts as a weak base since, as it dissolves in water, some of the ammonia molecules ionize to cause an increase in the hydroxide ion concentration:

$$NH_3 + H_2O \rightarrow NH_4^+(aq) + OH^-(aq)$$

8-10/BRØNSTED-LOWRY THEORY OF ACIDS AND BASES

A more general definition of acids and bases is given by the Brønsted-Lowry Theory: an acid is a *proton* (i.e., H^+ ion) *donor* and a base is a *proton acceptor.* This definition is not limited to solutions where water is the solvent. It applies also to other systems. For example, gaseous hydrogen chloride donates a proton to gaseous ammonia to form an ammonium ion (NH_4^+) and a chloride ion (Cl^-). These ions immediately combine to form solid ammonium chloride:

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

The hydrogen chloride acts as an acid and the ammonia acts as a base.

When acetic acid dissolves in water an acetic acid molecule donates a proton to a water molecule:

$$HC_2H_3O_2 + H_2O \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

The acetic acid is an acid. The water is a base. In this reaction hydronium ions and acetate ions are formed. The H_3O^+ ion can donate a proton to a base. It is called the conjugate acid of H_2O. The $C_2H_3O_2^-$ ion can accept a proton from an acid. It is called the conjugate base of acetic acid.

The following series of equations will illustrate the use of the Brønsted-Lowry Theory:

$$\underset{\textit{Acid}}{HCl} + \underset{\textit{Base}}{H_2O} \rightarrow \underset{\textit{Conjugate Acid}}{H_3O^+(aq)} + \underset{\textit{Conjugate Base}}{Cl^-(aq)}$$

$$\underset{\textit{Acid}}{HNO_3} + \underset{\textit{Base}}{H_2O} \rightarrow \underset{\textit{Conjugate Acid}}{H_3O^+(aq)} + \underset{\textit{Conjugate Base}}{NO_3^-(aq)}$$

$$\underset{\textit{Acid}}{H_2O} + \underset{\textit{Base}}{NH_3} \rightarrow \underset{\textit{Conjugate Acid}}{NH_4^+(aq)} + \underset{\textit{Conjugate Base}}{OH^-(aq)}$$

$$\underset{\textit{Acid}}{H_2O} + \underset{\textit{Base}}{H_2O} \rightarrow \underset{\textit{Conjugate Acid}}{H_3O^+(aq)} + \underset{\textit{Conjugate Base}}{OH^-(aq)}$$

8-11/NEUTRALIZATION AND SALTS

Water ionizes only slightly into hydronium ions and hydroxide ions. When hydronium ions and hydroxide ions are brought together from separate solutions, their natural tendency is to react to form water molecules. This process is called **neutralization**.

Hydrochloric acid is a solution containing hydronium ions and chloride ions [$HCl + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$]. Sodium hydroxide solution contains sodium ions and hydroxide ions [$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$]. When these two solutions are mixed, the hydronium ions combine with the hydroxide ions to form water molecules:

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow 2\,H_2O + Na^+(aq) + Cl^-(aq)$$

Notice that hydrated sodium ions and hydrated chloride ions occur both as reactants and as products in this equation. This means that they do not take part in the reaction at all. As many sodium ions are present at the start of the reaction as at the end. Similarly, as many chloride ions are present at the start of the reaction as at the end. Since they do not participate directly in the reaction, they are called "spectator" ions and can be cancelled from each side of the equation:

$$H_3O^+(aq) + \cancel{Cl^-(aq)} + \cancel{Na^+(aq)} + OH^-(aq) \rightarrow 2\,H_2O + \cancel{Na^+(aq)} + \cancel{Cl^-(aq)}$$

The actual neutralization process is therefore:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O$$

This net ionic equation describes the neutralization of any strong acid by a strong base.

The sodium ions and chloride ions are left in the water. However, if the water is removed by evaporation, solid sodium chloride is formed:

$$Na^+(aq) + Cl^-(aq) \rightarrow NaCl(s)$$

Sodium chloride is a member of a class of substances called salts. **Salts** consist of a positive ion of a base combined with the negative ion of an acid. An acid and a base neutralize one another to form water and ions which can combine to form a salt.

Another example of neutralization is the reaction of potassium hydroxide with nitric acid. Potassium hydroxide reacts with nitric acid to form water. Potassium ions and nitrate ions remain dissolved in the water:

$$K^+(aq) + OH^-(aq) + H_3O^+(aq) + NO_3^-(aq) \rightarrow 2\ H_2O + K^+(aq) + NO_3^-(aq)$$

If the water is removed by evaporation, the salt, potassium nitrate, is collected as a solid:

$$K^+(aq) + NO_3^-(aq) \rightarrow KNO_3(s)$$

This process is an example of an acid-base neutralization forming water and a salt. Even though ions are involved, it is often convenient to write the equation as:

$$KOH + HNO_3 \rightarrow H_2O + KNO_3$$

SAMPLE PROBLEM/8-1

Write the net ionic equation corresponding to the neutralization of aluminum hydroxide by sulfuric acid represented by the equation:

$$2\ Al(OH)_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6\ H_2O$$

In ionic form this becomes:

$$2\ Al^{3+}(aq) + 6\ OH^-(aq) + 6\ H_3O^+(aq) + 3\ SO_4^{2-}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ SO_4^{2-}(aq) + 12\ H_2O$$

Cancel and remove spectator ions to give:

$$6\ OH^-(aq) + 6\ H_3O^+(aq) \rightarrow 12\ H_2O$$

Divide all coefficients by the highest common factor (in this case, 6) to give the net ionic equation:

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2\ H_2O$$

This net ionic equation is identical to that for the neutralization of hydrochloric acid with sodium hydroxide.

EXERCISE/8-1

Write the net ionic equations corresponding to the following neutralization reactions:

$$Al(OH)_3 + 3\ HCl \rightarrow AlCl_3 + 3\ H_2O$$

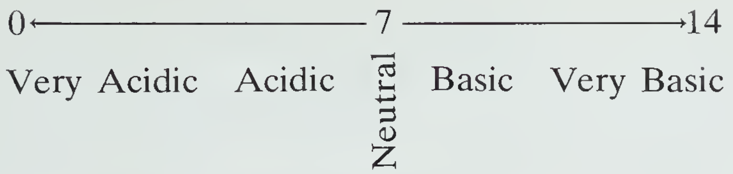
$$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2\ H_2O$$

8-12/THE pH SCALE

One term that has become widely used is pH. The pH of a solution is related to the quantity of hydronium ions in a given amount of solution. Advertisers refer to the pH of grooming products, biologists refer to the pH of lake water, oceanographers refer to the pH of seawater, and chemists refer to the pH of a solution.

The pH scale is defined in such a way that the numerical pH value becomes lower as a solution becomes more acidic. For example, there would be more H_3O^+ ions in one litre of a solution of pH 3 than there would be in one litre of a solution of pH 4.

In a neutral solution the quantity of H_3O^+ ions equals the quantity of OH^- ions and the pH is 7. When the quantity of H_3O^+ ions exceeds the quantity of OH^- ions, the solution is acidic and the pH is less than 7. On the other hand, if the quantity of OH^- ions exceeds the quantity of H_3O^+ ions, the solution is basic and the pH is greater than 7. The following diagram shows how one can qualitatively use the pH scale to assess the acidity or basicity of a solution:



The pH's of some common substances are:

Gastric Fluid	1.7
Lemon Juice	2.6
Wine	3.7
Tomatoes	4.5
Coffee	5.1
Milk	6.5
Blood	7.4
Seawater	7.8

QUESTIONS

1. Define the following terms: (a) solution, (b) miscible, (c) saturated solution, (d) electrolyte, (e) ion.
2. Describe the concept of dynamic equilibrium as it applies to a saturated solution.
3. Why is there more dissolved nitrogen than dissolved oxygen in any pond, lake, river, etc.?
4. Why will a nonelectrolyte not conduct electricity when it is dissolved in water?
5. The ionic substance, potassium bromide, is an electrolyte. Describe the dissolving of KBr in water to produce a solution which conducts electricity. What is the role of the water molecules in this process?
6. What is meant by the equation:

$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)?$$

7. Why does a nonpolar solute not dissolve very well in a polar solvent?
8. Why does an ionic substance not dissolve very well in a nonpolar solvent?
9. Distinguish between ionization and dissociation. Why do we say that HCl ionizes in water but NaCl dissociates in water?

10. What is an acid? What does an acid do to the quantity of $H_3O^+(aq)$ in a volume of water?
11. Distinguish between a strong acid and a weak acid. Give an example of each.
12. In the following equations select the reactant which acts as a base:

(a) $C_2H_3O_2^-(aq) + H_2O \rightarrow HC_2H_3O_2 + OH^-(aq)$

(b) $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3 + H_2O$

(c) $HSO_4^-(aq) + H_2O \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$

13. Write the net ionic equation corresponding to the neutralization of phosphoric acid by potassium hydroxide. The molecular equation is:

$$H_3PO_4 + 3\ KOH \rightarrow K_3PO_4 + 3\ H_2O$$

What is the salt produced?

14. Write the net ionic equation corresponding to the neutralization of aluminum hydroxide by nitric acid. The molecular equation is:

$$Al(OH)_3 + 3\ HNO_3 \rightarrow Al(NO_3)_3 + 3\ H_2O$$

What is the salt produced?

15. How does the pH scale enable one to assess the basicity or acidity of a solution?

QUESTIONS TO THINK ABOUT

16. What are the equilibrium processes occurring in an aqueous solution of acetic acid?
17. Originally Arrhenius believed that there must be the same number of positive and negative ions in a solution. However, the modern theory of electrolytes states that the total positive ionic charge must equal the total negative ionic charge. Is there a difference between these two statements? If so, why did Arrhenius' original theory have to be modified?
18. Why was carbon tetrachloride used in the dry cleaning industry? Why is it no longer used in this industry?
19. What is the Lewis theory of acids and bases? What advantage has this theory over the Brønsted-Lowry theory?

9

CHEMICAL REACTIONS

Many chemical reactions are known. In this chapter we classify them into four major categories and balance equations for simple examples of each type. Reactions involving the transfer of electrons from one substance to another are discussed in some detail and illustrated by a description of the chemistry of the halogen family. The discussion includes descriptions of the operation of both electrolytic cells (devices which use electrical energy to produce chemical changes) and electrochemical cells (devices which convert the energy associated with chemical change into electrical energy).

When you have completed studying this chapter, you should be able to attain the following objectives:

1. Explain the four types of chemical reaction and write equations for examples of each.
2. Classify a given reaction into one of the four categories, given the chemical equation for the reaction.
3. Balance simple chemical equations by inspection.
4. Define oxidation, reduction, oxidizing agent, reducing agent and give an example of each. (2)
5. Given a list of chemical equations:
   (a) Identify those which involve transfer of electrons.
   (b) Identify the oxidizing and reducing agents.

   (c) State which atoms are oxidized and reduced.
   (d) Diagram the gain and loss of electrons.
6. Give a general description of an electrochemical cell and its operation.
7. Give a general description of the electrolytic cell and its operation.
8. Describe the electrolytic preparations of fluorine and chlorine.

9-1/TYPES OF REACTIONS

It is not easy to classify all chemical reactions precisely. Nevertheless, most reactions can be classified under one of the following four major categories:

Addition reactions, or direct combinations, are reactions in which atoms and molecules join together directly to produce larger molecules. Equations for addition reactions are usually of the type:

$$A + B \rightarrow AB$$

Some examples of addition reactions are:

(a) Formation of sulfur dioxide by combustion of sulfur:

$$S + O_2 \rightarrow SO_2$$

(b) Reaction of zinc and sulfur to form zinc sulfide:

$$Zn + S \rightarrow ZnS$$

(c) Formation of calcium hydroxide when calcium oxide reacts with water:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Decomposition reactions are just the opposite of addition reactions. Equations for decomposition reactions are usually of the type:

$$AB \rightarrow A + B$$

Some examples are:

(a) Decomposition of carbonic acid:

$$H_2CO_3 \rightarrow H_2O + CO_2$$

(b) Formation of oxygen by heating mercury(II) oxide:

$$2\,HgO \xrightarrow{\Delta} 2\,Hg + O_2$$

(c) Preparation of oxygen by heating potassium perchlorate:

$$KClO_4 \xrightarrow{\Delta} KCl + 2\,O_2$$

Displacement or **substitution** reactions involve a change of partners. In these reactions one atom or group of atoms in a molecule is replaced by another atom or group of atoms. The general equation is usually written as:

$$AB + C \rightarrow AC + B$$

Some examples are:

(a) Zinc metal and copper sulfate react to form copper metal and zinc sulfate:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

(b) Magnesium reacts with hydrogen chloride to liberate hydrogen:

$$Mg + 2\,HCl \rightarrow MgCl_2 + H_2$$

(c) Chlorine liberates bromine from calcium bromide:

$$Cl_2 + CaBr_2 \rightarrow Br_2 + CaCl_2$$

Double decomposition or **metathetic** reactions involve a joint exchange of partners, according to the general equation:

$$AB + CD \rightarrow BC + AD$$

Some examples are:

(a) Neutralization of sodium hydroxide with hydrochloric acid:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

(b) Formation of hydrogen sulfide by the action of hydrochloric acid on iron(II) sulfide:

$$FeS + 2\,HCl \rightarrow H_2S + FeCl_2$$

(c) Precipitation of barium sulfate when solutions of barium chloride and ammonium sulfate are mixed:

$$BaCl_2 + (NH_4)_2SO_4 \rightarrow BaSO_4 + 2\,NH_4Cl$$

9-2/BALANCING CHEMICAL EQUATIONS

In Section 7-6 you learned the basic principles involved in writing a chemical equation: the Law of Conservation of Mass must be obeyed. That is, there must be as many atoms of each type on the left-hand side as on the right-hand side when the equation is balanced.

Before an equation can be balanced, the formulas of all the reactants and products must first be known. Only then can a start be made at placing the proper coefficients in front of each formula in order to balance the numbers of atoms on each side of the equation. Usually the procedure that works best is:

(a) Balance all atoms other than oxygen and hydrogen.
(b) Balance oxygen.
(c) Balance hydrogen.

Let us put the principles into operation by balancing the following equations:

(a) $SF_4 + H_2O \rightarrow SO_2 + HF$
(b) $Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$
(c) $Ca(OH)_2 + H_3PO_4 \rightarrow Ca_3(PO_4)_2 + H_2O$

Equation (a) $SF_4 + H_2O \rightarrow SO_2 + HF$

Step 1. Balance atoms other than oxygen and hydrogen. Since sulfur is balanced at the moment, we shall start by balancing fluorine. With four fluorine atoms on the left, there must be four fluorine atoms, or 4 HF, on the right:

$$\underline{1}\ SF_4 + H_2O \rightarrow SO_2 + \underline{4}\ HF$$

We shall temporarily underline the coefficients to remind ourselves that they are temporarily fixed and should not be changed unless absolutely necessary. The "1" in front of the SF_4 is not absolutely necessary, but it is a convenience during the balancing process.

Step 2. Balance sulfur. Now that we have fixed one sulfur atom on the left, we need one sulfur atom, or 1 SO_2, on the right:

$$\underline{1}\ SF_4 + H_2O \rightarrow \underline{1}\ SO_2 + \underline{4}\ HF$$

Step 3. Balance oxygen. With two oxygen atoms fixed on the right, we therefore need two oxygen atoms, or 2 H_2O, on the left:

$$\underline{1}\ SF_4+\underline{2}\ H_2O \rightarrow \underline{1}\ SO_2+\underline{4}\ HF$$

Step 4. Balance hydrogen. Since all coefficients are fixed, hydrogen should be balanced. A check shows four hydrogen atoms (2 H_2O) on the left and four hydrogen atoms (4 HF) on the right. The balanced equation is therefore:

$$SF_4+2\ H_2O \rightarrow SO_2+4\ HF$$

Notice that coefficients of 1 are omitted from the balanced equation. If there is no coefficient in front of a formula, the coefficient is assumed to be 1.

Equation (b) $Al+H_2SO_4 \rightarrow Al_2(SO_4)_3+H_2$

Step 1. Balance atoms other than oxygen and hydrogen. Since aluminum appears first in the equation, start with aluminum:

$$\underline{2}\ Al+H_2SO_4 \rightarrow \underline{1}\ Al_2(SO_4)_3+H_2$$

Step 2. Balance sulfur:

$$\underline{2}\ Al+\underline{3}\ H_2SO_4 \rightarrow \underline{1}\ Al_2(SO_4)_3+H_2$$

Step 3. Balance oxygen. Oxygen is already balanced with 12 atoms on each side of the equation.

Step 4. Balance hydrogen:

$$\underline{2}\ Al+\underline{3}\ H_2SO_4 \rightarrow \underline{1}\ Al_2(SO_4)_3+\underline{3}\ H_2$$

All atoms are now balanced. The final equation is:

$$2\ Al+3\ H_2SO_4 \rightarrow Al_2(SO_4)_3+3\ H_2$$

Equation (c) $Ca(OH)_2+H_3PO_4 \rightarrow Ca_3(PO_4)_2+H_2O$

Step 1. Balance atoms other than oxygen and hydrogen. Start with calcium:

$$\underline{3}\ Ca(OH)_2+H_3PO_4 \rightarrow \underline{1}\ Ca_3(PO_4)_2+H_2O$$

Step 2. Balance phosphorus:

$$\underline{3}\ Ca(OH)_2+\underline{2}\ H_3PO_4 \rightarrow \underline{1}\ Ca_3(PO_4)_2+H_2O$$

Step 3. Balance oxygen. There are $6+8=14$ oxygen atoms on the left and only eight [in the $Ca_3(PO_4)_2$] have been fixed on the right. The six remaining oxygen atoms must be present as 6 H_2O:

$$\underline{3}\ Ca(OH)_2+\underline{2}\ H_3PO_4 \rightarrow \underline{1}\ Ca_3(PO_4)_2+\underline{6}\ H_2O$$

Step 4. Balance hydrogen. Hydrogen atoms are already balanced with six atoms on each side. The balanced equation is therefore:

$$3\ Ca(OH)_2 + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ H_2O$$

SAMPLE PROBLEM/9-1

Write balanced equations to represent:

(a) The combustion of acetylene gas, C_2H_2, to form carbon dioxide and water.

(b) The removal of carbon dioxide from the air in a spacecraft by its reaction with sodium hydroxide according to the unbalanced equation:

$$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O$$

(c) The preparation of carbon dioxide gas by the action of sulfuric acid on sodium hydrogen carbonate according to the unbalanced equation:

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

(a) The unbalanced equation is:

$$C_2H_2 + O_2 \rightarrow CO_2 + H_2O$$

Balance C: $\underline{1}\ C_2H_2 + O_2 \rightarrow \underline{2}\ CO_2 + H_2O$

Balance O: We can not balance oxygen at this point because we have not yet fixed the number of oxygen atoms on either side. In balancing carbon atoms, however, we have fixed the number of hydrogen atoms on the left.

Balance H: $\underline{1}\ C_2H_2 + O_2 \rightarrow \underline{2}\ CO_2 + \underline{1}\ H_2O$

Now balance O: $\underline{1}\ C_2H_2 + \underline{5/2}\ O_2 \rightarrow \underline{2}\ CO_2 + \underline{1}\ H_2O$

Multiply both sides by 2 to get rid of fractions.

$$\underline{2}\ C_2H_2 + \underline{5}\ O_2 \rightarrow \underline{4}\ CO_2 + \underline{2}\ H_2O$$

The balanced equation is:

$$2\ C_2H_2 + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$$

This problem illustrates the fact that it is perfectly permissible to have fractional coefficients during the balancing process. Both sides of the equation must be multiplied by an appropriate factor to get the final balanced equation with whole number coefficients.

(b) $$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O$$

Balance C: Already balanced.

Balance Na: $\underline{1}\ CO_2 + \underline{2}\ NaOH \rightarrow \underline{1}\ Na_2CO_3 + H_2O$

Balance O: $\underline{1}\ CO_2 + \underline{2}\ NaOH \rightarrow \underline{1}\ Na_2CO_3 + \underline{1}\ H_2O$

Balance H: H is now balanced with two atoms on each side.

The balanced equation is:

$$CO_2 + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

(c) $$NaHCO_3 + H_2SO_4 \rightarrow CO_2 + Na_2SO_4 + H_2O$$

Balance Na:

$$\underline{2}\ NaHCO_3 + H_2SO_4 \rightarrow CO_2 + \underline{1}\ Na_2SO_4 + H_2O$$

Balance C:

$$\underline{2}\ NaHCO_3 + H_2SO_4 \rightarrow \underline{2}\ CO_2 + \underline{1}\ Na_2SO_4 + H_2O$$

Balance S:

$$\underline{2}\ NaHCO_3 + \underline{1}\ H_2SO_4 \rightarrow \underline{2}\ CO_2 + \underline{1}\ Na_2SO_4 + H_2O$$

Balance O:

$$\underline{2}\ NaHCO_3 + \underline{1}\ H_2SO_4 \rightarrow \underline{2}\ CO_2 + \underline{1}\ Na_2SO_4 + \underline{2}\ H_2O$$

Balance H: Balanced.

The balanced equation is:

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

EXERCISE/9-1

Write balanced equations to represent:

(a) The combustion of methane, CH_4, to form carbon dioxide and water vapor.

(b) The combustion of the rocket fuel, B_5H_9, which burns to form B_2O_3 and water vapor.

(c) The formation of ammonium sulfate particles in the upper atmosphere according to the unbalanced equation:

$$NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$$

9-3/REACTIONS INVOLVING ELECTRON TRANSFER

Chemical reactions can be classified into two major types according to another criterion:

(1) Reactions which do not involve transfer of electrons from one atom to another.

(2) Reactions which do involve transfer of electrons from one atom to another.

Double decomposition reactions do not generally involve electron transfers. Addition, decomposition, and displacement reactions frequently involve transfer of electrons between atoms.

The following reactions, for example, all involve electron transfers:

$$2\,Mg + O_2 \rightarrow 2\,MgO \quad \text{(addition)}$$

$$2\,HgO \rightarrow 2\,Hg + O_2 \quad \text{(decomposition)}$$

$$2\,Na + 2\,H_2O \rightarrow 2\,NaOH + H_2 \quad \text{(displacement)}$$

$$Cl_2 + 2\,NaBr \rightarrow Br_2 + 2\,NaCl \quad \text{(displacement)}$$

How do we know that electrons are being transferred between atoms? We calculate the oxidation numbers of the atoms involved (Section 7-1). When an atom loses electrons during a reaction, its oxidation number becomes more positive. When an atom gains electrons, its oxidation number becomes less positive (more negative).

SAMPLE PROBLEM/9-2

In which of the following reactions is electron transfer involved?

(a) $H_2 + Br_2 \rightarrow 2\,HBr$

(b) $2\,Na_3PO_4 + 3\,BaCl_2 \rightarrow Ba_3(PO_4)_2 + 6\,NaCl$

(c) $Zn + 2\,HCl \rightarrow ZnCl_2 + H_2$

(a) The oxidation numbers are indicated above each atom in the equation:

$$\overset{0}{H_2} + \overset{0}{Br_2} \rightarrow 2\,\overset{+1}{H}\overset{-1}{Br}$$

Both H and Br change oxidation state, so electron transfer must be involved.

(b) The oxidation numbers are indicated above each atom or radical:

$$2\,\overset{+1}{Na_3}\overbrace{PO_4}^{-3} + 3\,\overset{+2}{Ba}\overset{-1}{Cl_2} \rightarrow \overset{+2}{Ba_3}\overbrace{(PO_4)}^{-3}{}_2 + 6\,\overset{+1}{Na}\overset{-1}{Cl}$$

No atoms change oxidation state, so electron transfer is not involved. This is a double decomposition reaction.

(c) $$\overset{0}{Zn} + 2\,\overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2} + \overset{0}{H_2}$$

Both Zn and H change oxidation state, so electron transfer is involved.

EXERCISE/9-2

In which of the following reactions is electron transfer involved?

(a) $P_4 + 5\,O_2 \rightarrow P_4O_{10}$

(b) $Ba + 2\,H_2O \rightarrow Ba(OH)_2 + H_2$

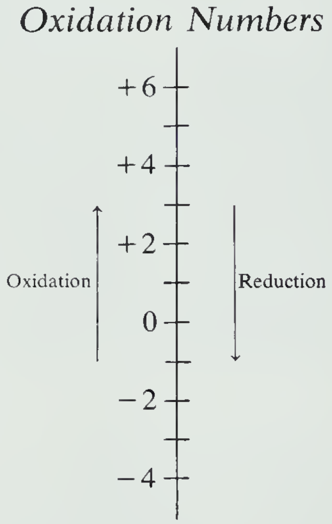
(c) $(NH_4)_2SO_4 + Pb(NO_3)_2 \rightarrow 2\,NH_4NO_3 + PbSO_4$

The loss of electrons from an atom, with a consequent increase in oxidation number, is called **oxidation.** The substance which loses the electrons is said to be **oxidized,** and the substance which removes them is called the **oxidizing agent.**

The gain of electrons by an atom, with a consequent decrease in oxidation number, is called **reduction.** The substance which gains the electrons is said to be **reduced,** and the substance which supplies them is called the **reducing agent.**

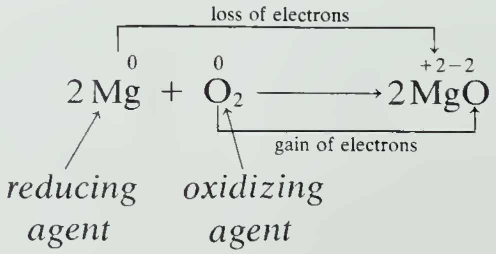
Oxidation and reduction always occur together. If one atom is oxidized during a chemical reaction, some other atom must be reduced. If an atom loses electrons, they must be accepted by another atom. Hence reactions which involve electron transfer are usually called **oxidation-reduction** reactions or simply **redox** reactions.

The definitions of oxidation and reduction are frequently remembered by the sentence, "LEO the lion says GER." The capitalized letters stand for "Loss of Electrons is Oxidation; Gain of Electrons is Reduction." Their relationship to oxidation numbers may be remembered by a simple diagram:


Oxidation Numbers

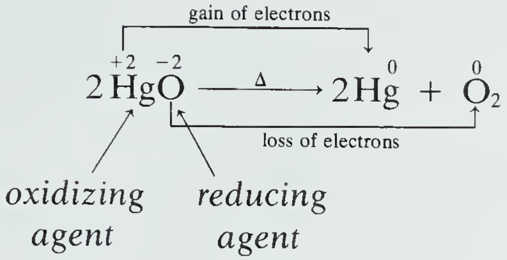
If the oxidation number of an atom goes up on the scale, the atom is oxidized. If the oxidation number goes down the scale, the atom is reduced.

In the reaction between magnesium and oxygen, the oxidation number of magnesium increases from 0 to +2. Magnesium, with only two valence electrons, tends to donate them to some other atom in order to achieve a stable octet. In losing these electrons, the magnesium atoms are oxidized. Each oxygen atom, having six valence electrons, will accept the two electrons to achieve an octet, and is reduced in the process. The oxidation number of oxygen is decreased from 0 to −2. These statements can be summarized as:



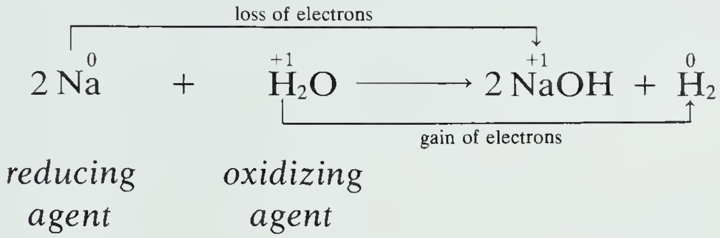
$$2\overset{0}{Mg} + \overset{0}{O_2} \longrightarrow 2\overset{+2-2}{MgO}$$

When mercury(II) oxide is decomposed to oxygen and mercury, the oxide ions transfer electrons to the mercury(II) ions:



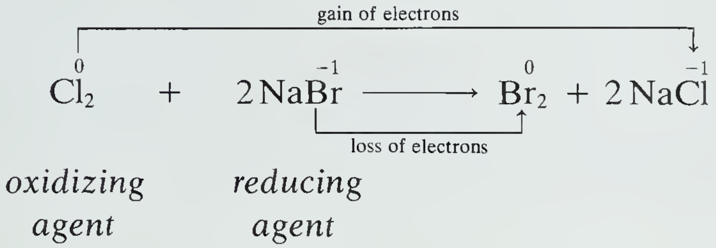
$$2\,\overset{+2}{\mathrm{Hg}}\overset{-2}{\mathrm{O}} \xrightarrow{\Delta} 2\,\overset{0}{\mathrm{Hg}} + \overset{0}{\mathrm{O}_2}$$

When sodium reacts with water to form hydrogen and sodium hydroxide, sodium atoms transfer electrons to hydrogen atoms:



$$2\,\overset{0}{\mathrm{Na}} + \overset{+1}{\mathrm{H}_2}\mathrm{O} \longrightarrow 2\,\overset{+1}{\mathrm{Na}}\mathrm{OH} + \overset{0}{\mathrm{H}_2}$$

Finally, the reaction between chlorine and sodium bromide can be summarized as:



$$\overset{0}{\mathrm{Cl}_2} + 2\,\mathrm{Na}\overset{-1}{\mathrm{Br}} \longrightarrow \overset{0}{\mathrm{Br}_2} + 2\,\mathrm{Na}\overset{-1}{\mathrm{Cl}}$$

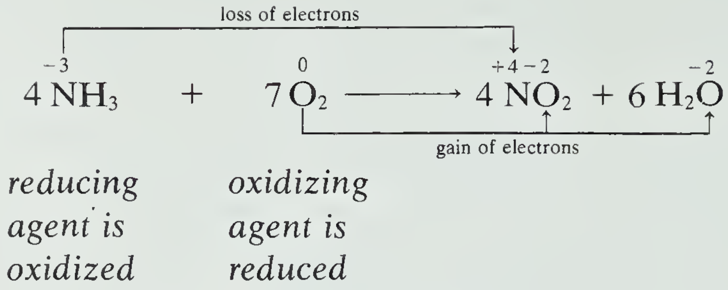
SAMPLE PROBLEM/9-3

In each of the following redox reactions, indicate the oxidizing agent, the reducing agent, the substance oxidized, the substance reduced, and diagram the gain and loss of electrons in each reaction.

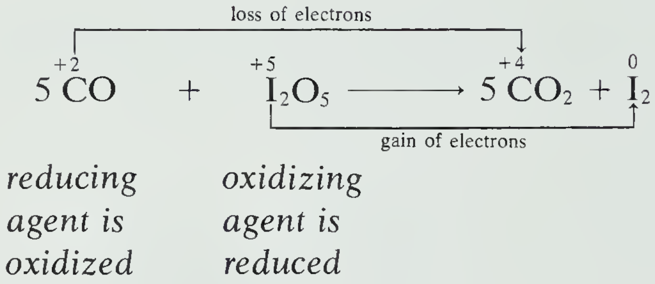
(a) $4\,NH_3 + 7\,O_2 \rightarrow 4\,NO_2 + 6\,H_2O$

(b) $5\,CO + I_2O_5 \rightarrow 5\,CO_2 + I_2$

(a)



(b)



EXERCISE/9-3

In each of the following redox reactions, indicate the oxidizing agent, the reducing agent, the substance oxidized, the substance reduced, and diagram the gain and loss of electrons in each reaction.

(a) $Ni + HgCl_2 \rightarrow Hg + NiCl_2$

(b) $Mg + 2\,HCl \rightarrow MgCl_2 + H_2$

9-4/ELECTRICITY FROM OXIDATION-REDUCTION REACTIONS

Consider what happens when a piece of zinc metal is immersed in a solution of copper sulfate:

$$CuSO_4 \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

The copper sulfate solution consists of hydrated sulfate ions and blue hydrated copper ions. Very quickly the zinc metal becomes coated with metallic copper. As time goes on the zinc strip gradually dissolves, flakes of metallic copper accumulate at the bottom of the container, and the blue color of the solution gradually fades away.

A reaction has occurred between the zinc atoms and the copper ions:

$$Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$$

The sulfate ions are spectator ions and serve simply to balance the positive charge of the metal ions. Each zinc atom has lost two electrons to form a zinc ion, and each copper ion has gained two electrons to form a copper atom:

$$\text{Oxidation:} \quad Zn \rightarrow Zn^{2+} + 2e^-$$

$$\text{Reduction:} \quad Cu^{2+} + 2e^- \rightarrow Cu$$

The copper ions have accepted electrons from the zinc atoms at the surface of the strip immersed in the copper sulfate solution. It is not possible to detect a flow of electrons because the electrons are transferred directly from the zinc atoms to the copper ions.

EXERCISE/9-4

When a copper wire is immersed in a colorless solution of silver nitrate, the solution gradually turns blue and silver crystals begin to grow on the wire. Explain what is happening in terms of oxidation, reduction, and transfer of electrons.

The reaction between zinc and copper sulfate occurs spontaneously. If the zinc atoms and copper ions could be kept separate from each other, the electrons could be forced to flow through an external wire. Since a flow of electrons constitutes an electric current, we would then have an **electrochemical cell:** a device for converting chemical energy into electrical energy.

A simple device which separates the reactants consists of a container divided into two compartments by a porous barrier (Fig. 9-1). One compartment contains a zinc strip immersed in a solution of zinc sulfate; the other contains a copper strip immersed in a solution of copper sulfate. These metal strips, which are immersed in the solutions, are called **electrodes.**

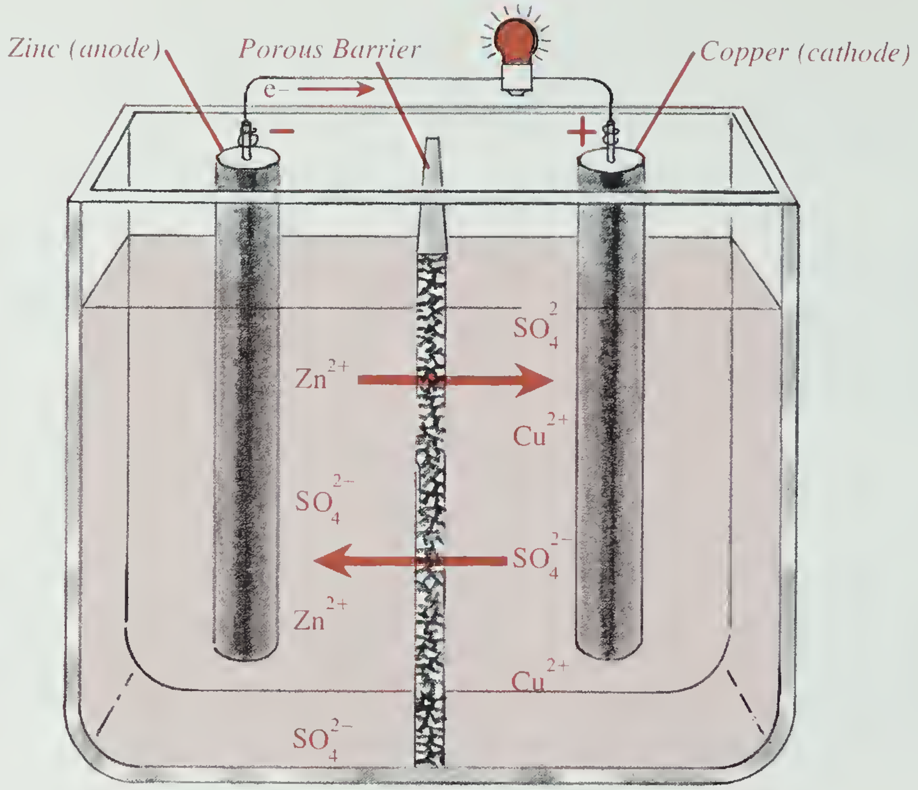


Fig. 9-1 An Electrochemical Cell

At the zinc electrode, zinc atoms tend to go into solution as zinc ions, leaving their electrons behind on the metal. When a wire is connected between the two electrodes, the electrons, which repel each other, can travel through the wire to the copper electrode. At that point copper ions in the other compartment can remove electrons from the surface of the copper electrode and become reduced to copper atoms. Again the reaction has occurred between the zinc atoms and the copper ions:

$$Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$$

However, this time it is possible to detect the flow of electrons because the electrons are transferred from the zinc atoms to the copper ions via a wire. This flow of electrons (electric current) through the wire constitutes the **external circuit** and can be used to light a bulb or do other useful work.

We should also realize that as surplus zinc ions are formed in one compartment, sulfate ions will tend to diffuse through the porous barrier into that compartment from the other side. The sulfate ions do this in order to balance out the excess positive charge created as zinc ions are produced. As copper ions are removed by reduction in the other compartment, zinc ions will tend to diffuse *in* from the opposite side of the porous barrier to replace the positive charge that has been removed. This migration of ions in opposite directions through the porous barrier constitutes what is known as the **internal circuit.**

In any electrochemical cell, oxidation takes place at the **anode.** In this cell, the zinc electrode is the anode. Anions (negative ions) migrate toward the anode. In this case, sulfate ions migrate toward the zinc electrode. Reduction takes place at the **cathode.** In this cell, the copper electrode is the cathode. Cations (positive ions) migrate toward the cathode. In this case, zinc ions migrate toward the copper electrode.

Many useful types of cells have been developed to make use of indirect electron transfer. Among these are lead storage batteries, dry cells, nickel-cadmium cells, and fuel cells.

EXERCISE/9-5

Draw a diagram of a cell that can be used to obtain electrical energy from the spontaneous reaction:

$$Cu(s) + 2\ AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\ Ag(s)$$

Label the anode and the cathode, and indicate the direction of flow of electrons in the external circuit and of ions in the internal circuit. Write the equations for the reactions occurring at each electrode.

9-5/OXIDATION-REDUCTION REACTIONS FROM ELECTRICITY

In 1800 William Nicholson and Sir Antony Carlyle connected platinum wires to the terminals of a battery and immersed the ends of the wire in a container of water. They found that hydrogen was evolved at one wire and oxygen was evolved at the other wire, thus demonstrating that an electric current could be used to produce a chemical reaction. The use of an electric current to produce a chemical change is called **electrolysis.** As in the case of an electrochemical cell, the conductors immersed in the liquid are called electrodes and the liquid itself is called an electrolyte.

A device which uses electrical energy to bring about a chemical change is called an **electrolytic cell.** The electric current can be provided by an automobile battery, a dry cell, or any other suitable source such as a direct current (DC) generator. Wires lead from the positive and negative terminals of the source to two electrodes immersed in an electrolyte containing positive and negative ions (Fig. 9-2).

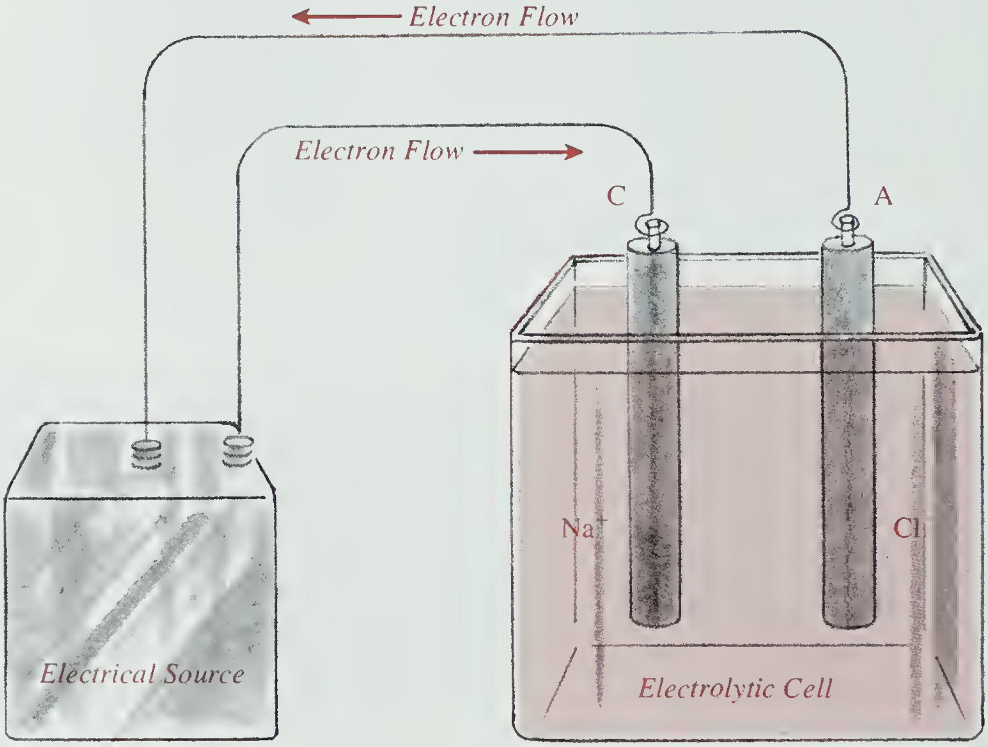


Fig. 9-2 An Electrolytic Cell

Consider a cell containing molten sodium chloride. Electrons flow from the negative electrode of the source to electrode C. Electrode C becomes negatively charged, and positive sodium ions migrate toward it. Each sodium ion gains one electron from electrode C, becoming a sodium atom:

$$\text{Reduction:} \quad Na^+ + e^- \rightarrow Na\cdot$$

This gain of electrons by sodium ions constitutes a reduction, and the electrode (C) at which reduction occurs is the cathode.

Meanwhile, electrons are removed from electrode A by the positive terminal of the electrical source. Electrode A acquires a positive charge, and the negative Cl^- ions migrate toward it. Each Cl^- ion gives up one electron to electrode A, becoming a chlorine atom:

$$\text{Oxidation:}\quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:^{-} \rightarrow\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot + 1e^{-}$$

Two chlorine atoms combine to form a chlorine molecule:

$$2\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot \rightarrow \mathrm{Cl_2}$$

The overall reaction at electrode A is:

$$2\ \mathrm{Cl^-} \rightarrow \mathrm{Cl_2} + 2e^-$$

This loss of electrons by chloride ions constitutes an oxidation, and the electrode (A) at which oxidation occurs is the anode.

The equation representing the sum of the anode and cathode reactions is:

$$2\ \mathrm{Na^+} + 2e^- \rightarrow 2\ \mathrm{Na}$$

$$\underline{2\ \mathrm{Cl^-} \rightarrow \mathrm{Cl_2} + 2e^-}$$

$$2\ \mathrm{Na^+} + 2\ \mathrm{Cl^-} \rightarrow 2\ \mathrm{Na} + \mathrm{Cl_2}$$

$$\textbf{or}\quad 2\ \mathrm{NaCl} \xrightarrow{\text{electrolysis}} 2\ \mathrm{Na} + \mathrm{Cl_2}$$

Thus an electric current has succeeded in decomposing a substance into simpler components.

The current in the external circuit consists of the flow of electrons through the wires. Within the electrolytic cell the current (internal circuit) is carried by ions migrating to and from the two electrodes. Positive ions (cations) migrate to the cathode and negative ions (anions) migrate to the anode.

SAMPLE PROBLEM/9-4

Describe the construction and operation of an electrolytic cell which uses molten copper(II) chloride as an electrolyte.

It would consist of two electrodes dipped into the molten copper(II) chloride and connected to an electrical source. At the electrode connected to the negative terminal of the source (the cathode) the reaction is:

$$\text{Reduction:}\quad Cu^{2+} + 2e^- \rightarrow Cu$$

Thus copper metal would be deposited on the cathode. At the anode the reaction is:

$$\text{Oxidation:}\quad 2\,Cl^- \rightarrow Cl_2 + 2e^-$$

Chlorine gas is liberated at the anode. The overall reaction is:

$$Cu^{2+} + 2\,Cl^- \xrightarrow{\text{electrolysis}} Cu + Cl_2$$

Electrons travel from the anode to the cathode in the external circuit. In the internal circuit Cu^{2+} ions migrate to the cathode, and Cl^- ions move toward the anode.

EXERCISE/9-6

Describe schematically an electrolytic cell which uses molten aluminum bromide as the electrolyte. Write equations for the reactions which occur at the electrodes and for the overall reaction. Indicate the motion of particles in the external and internal circuits.

Let us now consider the chemistry of the elements of Group VII, the halogens. We shall see how oxidation and reduction are involved in their chemical reactions, and find that electrolysis is used to separate these elements from their compounds.

9-6/PROPERTIES OF THE HALOGENS

The elements fluorine, chlorine, bromine, iodine, and astatine are found in Group VII of the periodic table. They are known as the **halogens,** from two Greek words meaning "salt former." The name arises from the fact that with metals such as sodium, potassium, calcium, and magnesium, they form salts, similar to ordinary table salt. These salts are among the most abundant soluble salts found in nature (especially in seawater).

The halogens are considered as a family because they all have similar electronic configurations, with a total of seven electrons in their valence shells. Thus one atom of any halogen can add one electron to form an ion with a single negative charge:

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Br}}}\cdot \quad + \quad e^- \quad \rightarrow \quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Br}}}:^-$$

bromine atom	*electron*	*bromide ion*

This negative ion can then pair up with a positive ion such as a potassium ion, K^+, by electrostatic attraction, to form a typical salt such as potassium bromide, KBr.

Some properties of the halogens are summarized in Table 9-1. The specific values are not as noteworthy as the regular variation in a given property as one goes from the top to the bottom of the periodic table within the halogen family.

TABLE 9-1

PROPERTIES OF THE ELEMENTS

Element	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
Formula	F_2	Cl_2	Br_2	I_2
Appearance at room temperature	pale yellow gas	yellow-green gas	red-brown liquid	purple-black solid
Melting point (°C)	−223	−102	−7	114
Boiling point (°C)	−187	−34.1	59	183
Atomic radius (nm)*	0.072	0.099	0.114	0.133
Ionization potential (V)	17.34	12.95	11.80	10.6
Electronic structure	2, 7	2, 8, 7	2, 8, 18, 7	2, 8, 18, 18, 7

* nm = nanometre (10^{-9} m)

The atomic radius increases as one proceeds from fluorine to iodine because successive energy levels are being filled in the atoms concerned. Fluorine has the highest ionization potential, that is, it holds on most tightly to its electrons. This is consistent with its small atomic radius and the earlier argument that the outermost electrons of the smaller atoms of a family, being closer to the nucleus, are more tightly held than the outer electrons of a larger atom in the family.

9-7/PREPARATION OF THE HALOGENS

Each member of the halogen family requires only one electron to complete its valence shell. The tendency to acquire this additional electron is so strong that the halogens are not normally found in nature in the free state. They are usually found as the halide ions, F^-, Cl^-, Br^-, I^- combined with metal ions.

The halogens may be prepared by passing an electric current through a molten halide (electrolysis). For fluorine this is the only method available. Since fluorine is the most electronegative of all the elements, no other substance is capable of oxidizing (removing the electrons from) fluoride ions to form fluorine atoms.

Fluorine is named after fluorite, CaF_2, a fluorine-containing mineral which flows readily without having to be heated strongly. Fluorine was first prepared by the French chemist Henri Moissan in 1887. He faced formidable problems because fluorine is so reactive that as soon as it is formed it immediately attacks the walls of the container, the electrodes, the solvent, and anything else in the vicinity. The element is now prepared commercially by electrolysis. Two major problems arise. First, the high reactivity of fluorine makes it difficult to find suitable materials from which to construct the electrodes and the cell. Second, molten fluorides are poor conductors of electricity. However, hydrogen fluoride and potassium fluoride combine to form a compound with formula $KF \cdot 2\,HF$. This compound is a good conductor, and since it melts at 70°C it can be kept in a molten state by heating the cell with a steam jacket.

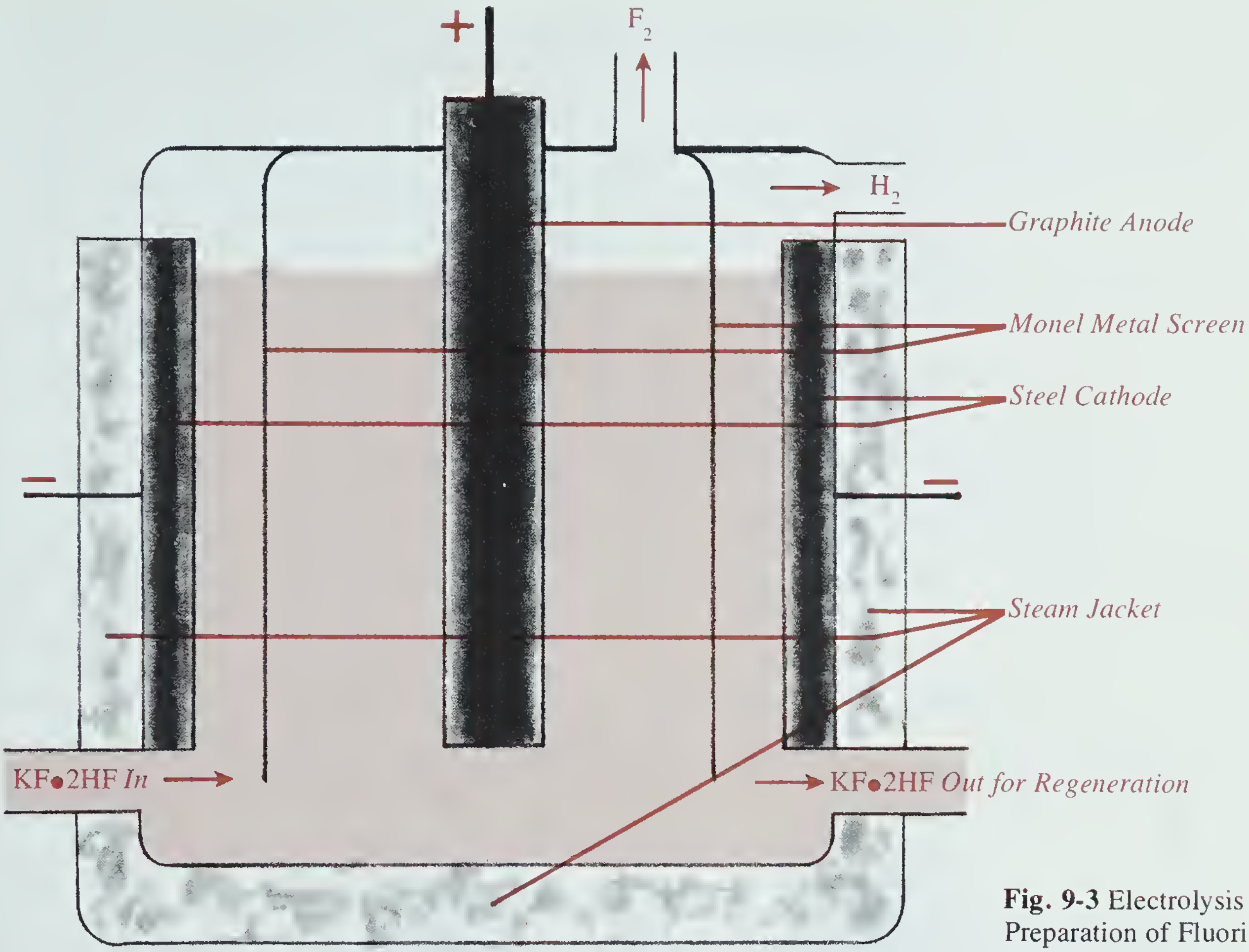


Fig. 9-3 Electrolysis Cell for the Preparation of Fluorine

An electrolytic cell for the preparation of fluorine is shown in Fig. 9-3. The cell is constructed of copper, which reacts with fluorine to form an inert coating of copper fluoride protecting the copper from further attack. At the anode, fluoride ions give up electrons to form fluorine atoms which combine to form fluorine molecules:

$$\text{Oxidation:}\quad 2\,F^- \rightarrow F_2(g) + 2e^-$$

At the cathode, hydrogen ions accept electrons and become reduced to hydrogen molecules:

$$\text{Reduction:}\quad 2\,H^+ + 2e^- \rightarrow H_2(g)$$

Thus the overall reaction is:

$$2\,H^+ + 2\,F^- \rightarrow H_2(g) + F_2(g)$$

Hydrogen is a by-product, and since it reacts explosively with fluorine, a Monel metal screen must be used to keep the gases separate. As the hydrofluoric acid is decomposed, more $KF \cdot 2\,HF$ is added so that the cell can be operated continuously.

Fluorine is used industrially in the preparation of organic compounds such as fluorocarbons (Teflon®, Freon®, etc.) and in the preparation of uranium(VI) fluoride, UF_6. Many toothpastes contain fluorine in the form of fluoride ions.

Chlorine (from Greek *chloros*, greenish yellow) was discovered by the Swedish chemist Karl Wilhelm Scheele in 1774. It is now prepared industrially by electrolysis of aqueous sodium chloride solution.

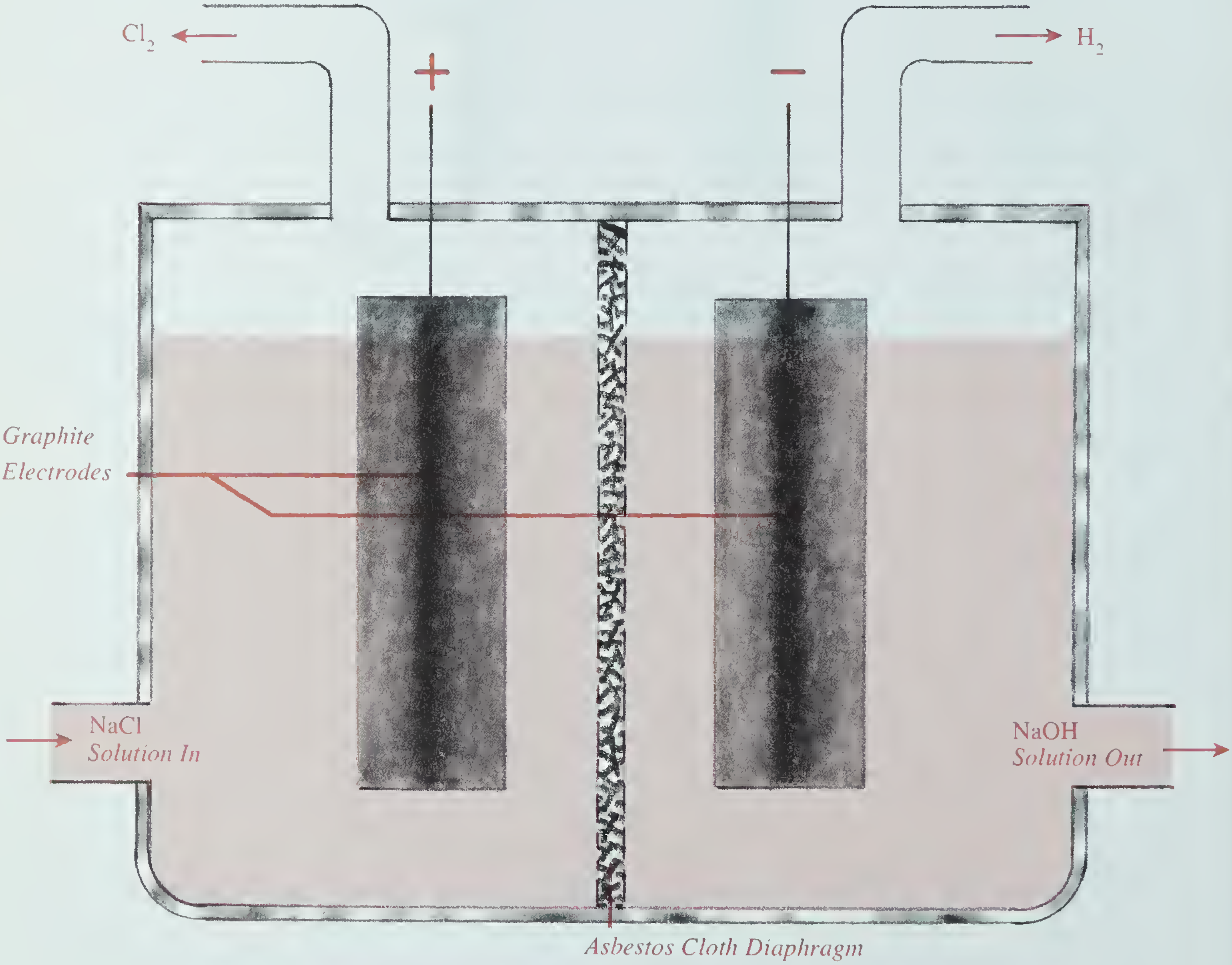


Fig. 9-4 Electrolysis Cell for the Preparation of Chlorine

Several electrolytic processes are used, but one type of cell can be represented schematically as in Fig. 9-4. The following reactions occur:

At the anode: $2\,Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (oxidation)

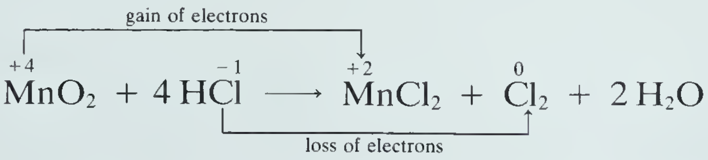
At the cathode: $2\,H_2O + 2e^- \rightarrow H_2(g) + 2\,OH^-(aq)$ (reduction)

Overall reaction: $2\,Cl^-(aq) + 2\,H_2O \rightarrow Cl_2(g) + H_2(g) + 2\,OH^-(aq)$

Chloride ions are oxidized to chlorine atoms at the anode. At the cathode water is reduced, yielding hydrogen gas and hydroxide ions. (Even though the sodium ions are attracted to the cathode, there is less tendency for them to gain electrons than there is for the water molecules to gain electrons.) Since the solution contains sodium ions, the products are chlorine gas, hydrogen gas, and an aqueous solution of sodium hydroxide.

Again, the halogen (chlorine) can react explosively with the hydrogen that is formed as a by-product. The two gases are kept apart by asbestos cloth diaphragms which, when wet, prevent the passage of gases but allow aqueous ions to pass through to reach the electrodes.

Chlorine is prepared in the laboratory by oxidizing hydrochloric acid with manganese(IV) oxide:



$$\overset{+4}{Mn}O_2 + 4\,H\overset{-1}{Cl} \longrightarrow \overset{+2}{Mn}Cl_2 + \overset{0}{Cl}_2 + 2\,H_2O$$

In aqueous solution the hydrochloric acid and manganese(II) chloride are almost completely ionized. The reaction is better represented by the equation:

$$MnO_2(s) + 4\,H_3O^+(aq) + 4\,Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2\,Cl^-(aq) + Cl_2(g) + 6\,H_2O$$

It is apparent that two of the chloride ions are simply spectator ions. They take no part in the reaction and can be omitted from the equation:

$$MnO_2(s) + 4\,H_3O^+(aq) + 2\,Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 6\,H_2O$$

Chlorine is highly poisonous when inhaled, yet it is safely used in purification of drinking water, to kill bacteria and remove undesirable tastes and odors. It is also used in enormous quantities in the bleaching of paper and textiles, where the unwanted colored substances are oxidized to colorless compounds.

Bromine (from Greek *bromos*, stench) was discovered by the French chemist A. J. Balard in 1824. It is now obtained commercially from the bromides present in certain brine wells and from seawater. The process is based on the fact that chlorine has a greater tendency to accept electrons than does bromine. Hence chlorine gas is a cheap oxidizing agent for obtaining bromine from its salts:

$$Cl_2 + 2\ Br^-(aq) \rightarrow 2\ Cl^-(aq) + Br_2$$

This reaction also serves as the basis of a laboratory test for bromide ion. Chlorine water (a solution of chlorine in water) is added to an aqueous solution of the suspected bromide. A small amount of carbon tetrachloride is added and the mixture is shaken vigorously. The elemental bromine concentrates in the carbon tetrachloride, which settles out as a reddish layer at the bottom.

Bromine vapor is highly poisonous, and the liquid causes painful burns on the skin. Bromine is used mainly to make other bromine compounds. Some of these are medicinal compounds. Much bromine is used in making ethylene dibromide, a gasoline additive, and in making silver bromide, the light-sensitive compound in most photographic films and papers.

Iodine (from Greek *iodos*, violet) was discovered by the French chemist B. Courtois in 1811. Iodide ion is the most easily oxidized of the halide ions. Hence any of the laboratory preparations of bromine and chlorine can be used for the preparation of iodine:

$$MnO_2 + 4\ H_3O^+(aq) + 2\ I^- \rightarrow Mn^{2+}(aq) + I_2 + 6\ H_2O$$

$$Cl_2 + 2\ I^-(aq) \rightarrow 2\ Cl^-(aq) + I_2$$

Iodide ions are so easily oxidized that even bromine will convert them to iodine:

$$Br_2 + 2\ I^-(aq) \rightarrow 2\ Br^-(aq) + I_2$$

In the laboratory, iodine is used as a sensitive test for starch. An intense blue-black color is formed when iodine is added to starch. Iodine is used medicinally as a germicide. A small amount of iodine in the form of potassium iodide is added to table salt; the product is called iodized salt. Lack of iodine in the diet results in goiter, an enlargement of the thyroid gland, due to the inability of that gland to secrete an iodine-containing substance called thyroxin.

9-8/REACTIONS OF THE HALOGENS

Fluorine and chlorine react with all metals:

$$F_2 + 2\,Na \rightarrow 2\,NaF$$

$$Cl_2 + Hg \rightarrow HgCl_2$$

Bromine and iodine are not as capable of acquiring electrons and are less reactive. However, they still combine with all except the least reactive metals (such as copper, silver, gold, and platinum).

$$Br_2 + Ca \rightarrow CaBr_2$$

$$I_2 + 2\,K \rightarrow 2\,KI$$

When a halogen reacts with a metal, the product in each case is called a metal halide.

Fluorine and chlorine form covalent compounds with almost all the nonmetals. Bromine and iodine also form covalent compounds with nonmetals, but fewer examples are known.

All halogens react with hydrogen gas to produce the corresponding hydrogen halide:

$$H_2 + F_2 \rightarrow 2\,HF \quad \text{(explosive)}$$

$$H_2 + Cl_2 \rightarrow 2\,HCl \quad \text{(fast but controllable)}$$

$$H_2 + Br_2 \rightarrow 2\,HBr$$

$$H_2 + I_2 \rightarrow 2\,HI \quad \text{(slow and incomplete)}$$

The hydrogen halides are colorless gases with pungent, disagreeable odors. They are all soluble in water, giving acidic solutions called the **hydrohalic acids.** Examples are hydrochloric acid, hydrobromic acid, and hydriodic acid:

$$HX + H_2O \rightarrow H_3O^+(aq) + X^-(aq); \qquad X = Cl, Br, I$$

The hydrogen halides are usually prepared in the laboratory by heating a metal halide with a strong acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF(g)$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl(g)$$

$$NaBr + H_3PO_4 \rightarrow NaH_2PO_4 + HBr(g)$$

$$NaI + H_3PO_4 \rightarrow NaH_2PO_4 + HI(g)$$

Bromides and iodides are so easily oxidized that it is impossible to prepare hydrogen bromide and hydrogen iodide by the sulfuric acid method. Hot concentrated sulfuric acid is a mild oxidizing agent, and the hydrogen halide is always contaminated by the free halogen formed in a reaction such as:

$$2\ NaBr + 3\ H_2SO_4 \rightarrow Br_2(g) + SO_2(g) + 2\ NaHSO_4 + 2\ H_2O$$

QUESTIONS

1. Explain what is meant by the terms: addition reaction; decomposition reaction; displacement reaction; double decomposition reaction. Give an example of each type.
2. Classify each of the following reactions as addition, decomposition, displacement, or double displacement reactions:

   (a) $CaCO_3 \rightarrow CaO + CO_2$

   (b) $K_2SO_4 + Ba(NO_3)_2 \rightarrow BaSO_4 + 2\ KNO_3$

   (c) $2\ H_2 + O_2 \rightarrow 2\ H_2O$

   (d) $CaC_2 + 2\ H_2O \rightarrow C_2H_2 + Ca(OH)_2$

   (e) $2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2$

3. Balance the following equations:

   (a) $Fe_3O_4 + H_2 \rightarrow Fe + H_2O$

   (b) $Ga + H_2SO_4 \rightarrow H_2 + Ga_2(SO_4)_3$

(c) $Fe_2O_3 + C \rightarrow Fe + CO$

(d) $Ca(OH)_2 + HCl \rightarrow CaCl_2 + H_2O$

(e) $P + O_2 \rightarrow P_2O_5$

4. What is an oxidizing agent? A reducing agent? How would you expect electronegativity to be related to oxidizing and reducing power?
5. In which of the following reactions is electron transfer involved?

(a) $2\ Ca + O_2 \rightarrow 2\ CaO$

(b) $CaO + H_2O \rightarrow Ca(OH)_2$

(c) $Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$

6. In each of the following oxidation-reduction reactions, indicate the oxidizing agent, the reducing agent, the substance oxidized, and the substance reduced:

(a) $2\ Fe + O_2 \rightarrow 2\ FeO$

(b) $2\ Fe + 3\ Br_2 \rightarrow 2\ FeBr_3$

(c) $Fe + 2\ HCl \rightarrow FeCl_2 + H_2$

7. The physical properties change in a regular way as one goes from the top to the bottom of the periodic table within a group. Discuss this statement with respect to the following properties of the halogens: melting point; boiling point; atomic radius; ionization potential.
8. What is the electronic configuration of the valence electrons in an atom of each of the halogens?
9. Using the information in Table 9-1, predict the physical properties of astatine. Write equations for three chemical reactions that would be typical of the element.
10. Write an equation for the reaction of hydrogen chloride with water, giving the electron dot formula for each ionic product.
11. Write an equation for the reaction of hot concentrated sulfuric acid with potassium fluoride; with potassium chloride; with potassium bromide.
12. Write electron dot formulas for CaF_2 and PF_3.
13. A chlorine atom has a much higher ionization potential than a sodium atom. What does this mean in terms of the behavior of the two elements?

14. What is the difference, if any, between hydrogen chloride and hydrochloric acid?
15. Balance the following equations:

    (a) $Zn + HCl \rightarrow ZnCl_2 + H_2$

    (b) $Mg + CO_2 \rightarrow MgO + C$

    (c) $Al_2O_3 + H_2 \rightarrow Al + H_2O$

    (d) $Cu(NO_3)_2 + H_2S \rightarrow CuS + HNO_3$

    (e) $CaO + HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$

16. Draw a diagram of a cell that can be used to obtain energy from the spontaneous reaction:

    $$Zn + Pb(NO_3)_2 \rightarrow Zn(NO_3)_2 + Pb$$

    Label the anode and the cathode. Indicate the directions of the electron flow in the external circuit and of the ion movements in the internal circuit. Write the equation for the reactions occurring at each electrode.
17. Describe schematically an electrolytic cell which uses molten potassium chloride as the electrolyte. Write the equations for the reactions which occur at each electrode and for the overall reaction. Indicate the direction of motion of particles in the external and internal circuits.

10

THE MOLE AND ITS USE

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Define the mole in terms of Avogadro's number.
2. Given the number of atoms, molecules, or formula units of a substance, calculate the number of moles present.
3. Given the number of moles of a substance, calculate the number of atoms, molecules, or formula units present.
4. Given the molecular formula of a substance, calculate its molecular mass, molar mass, and percentage composition.
5. Given the percentage composition of a compound, calculate its empirical formula.
6. Given the molecular mass and either the empirical formula or the percentage composition of a compound, calculate its molecular formula.
7. Summarize the information contained in a balanced equation.
8. Given a balanced equation and the number of grams or moles of one substance involved in the reaction, calculate the corresponding number of grams or moles of any other substance appearing in the equation.
9. Define molarity.
10. Given any two of: mass of solute, volume of solution, and molarity of solution, calculate the third quantity.

10-1/THE MOLE CONCEPT

One of the most important concepts to follow from the theory of the atom is that of atomic mass. Actually, the mass of an atom is extremely small. For example, the absolute mass of an atom of the most common isotope of oxygen is 2.66×10^{-23} g. This small number indicates that the gram is too large a mass unit to be used for determining the mass of an oxygen atom. In fact, the gram is much too large a mass unit to be used for determining the mass of any atom.

As we have learned, the atomic mass unit (u) is the unit of mass one uses when obtaining the mass of any atom. One atomic mass unit is 1/12 the mass of a carbon-12 atom. The carbon-12 atom has been assigned a mass of 12 u. The mass of the most common oxygen isotope is about 4/3 as great as the mass of carbon-12. Therefore, the mass of an atom of oxygen is about 16 u ($12 \times 4/3 = 16$). A more accurate value is 15.994 91 u. This is an extremely small unit of mass. No balance is capable of measuring such a small quantity of matter.

Let us consider a simple chemical reaction. Iron and sulfur will react to form iron(II) sulfide. The chemical equation for this reaction is:

$$\mathrm{Fe} + \mathrm{S} \rightarrow \mathrm{FeS}$$

As the equation suggests, one atom of iron will react with one atom of sulfur to produce iron(II) sulfide. It is impossible to measure the mass of one atom of iron or one atom of sulfur. However, it is possible to measure the mass of a large number of iron atoms and react them with an *equal* number of sulfur atoms, since iron and sulfur atoms react on a one-to-one basis to form iron(II) sulfide.

The **mole** is a certain number of atoms called Avogadro's number. Avogadro's number has been carefully defined. If a single atom of sulfur has a mass of 32 u, one mole (or Avogadro's number) of sulfur atoms has a mass of 32 g.

If a single oxygen atom has a mass of 16 u (half the mass of a single sulfur atom), and if Avogadro's number (one mole) of sulfur atoms has a mass of 32 g, then Avogadro's number of oxygen atoms will have a mass of 16 g ($1/2 \times 32\ \mathrm{g} = 16\ \mathrm{g}$).

In the same way, if a single hydrogen atom has a mass of 1 u (1/32 × the mass of a single sulfur atom), then Avogadro's number of hydrogen atoms will have a mass of 1 g (1/32 × 32 g = 1 g).

Thus a mole is Avogadro's number of atoms. Avogadro's number is very large: there are 6.02×10^{23} atoms in a mole. A mole of atoms is a collection of atoms whose total mass in grams is numerically equal to the atomic mass of an atom of the same element in atomic mass units. Therefore a mole of atoms is the atomic mass of an element expressed in grams. One sulfur atom has a mass of 32 u. One mole of sulfur atoms has a mass of 32 g. Remember that 32 g of sulfur is not made up of one single sulfur atom. Thirty-two grams of sulfur is composed of many sulfur atoms: Avogadro's number of sulfur atoms.

10-2/ DETERMINING AVOGADRO'S NUMBER

One method for determining Avogadro's number makes use of radioactive substances which emit alpha particles. Alpha particles are helium nuclei (He^{2+}). Experiments have shown that one mole of any gas will occupy 22.4 ℓ at 0°C and 1 atm pressure (101.3 kPa). Therefore one mole of helium will occupy 22.4 ℓ at 0°C and 1 atm pressure. If a radioactive element emits alpha particles, it is possible to design the experiment so that the charges of the alpha particles are neutralized and helium atoms are produced:

$$He^{2+} + 2\,e^{-} \rightarrow He$$

One can then count the number of alpha particles emitted with a Geiger counter, measure the volume of helium gas produced, correct this volume to 0°C and 1 atm pressure, and calculate Avogadro's number (N).

$$N = \frac{\text{alpha particles counted}}{\text{litres of He produced}} \times \frac{22.4\ \ell}{1\ \text{mol}}$$

Experiments like this have shown that Avogadro's number is 6.02×10^{23}. Therefore, if the average mass of one iron atom is 55.8 u, then the mass of 6.02×10^{23} iron atoms is 55.8 g. If the average mass of one sulfur atom is 32 u, the mass of 6.02×10^{23} sulfur atoms is 32 g. If the average mass of an atom of any element is x u, the mass of 6.02×10^{23} atoms of that element is x g. One mole of atoms of an element is 6.02×10^{23} atoms of that element. One mole of atoms of an element is also the atomic mass of that element expressed in grams.

EXERCISE/10-1

In an actual experiment 1.82×10^{17} alpha particles were counted. The helium gas which was produced occupied a volume of 0.006 73 cm^3 at 0°C and 1 atm pressure. Show that this experiment gives a value of 6.06×10^{23} for Avogadro's number.

10-3/THE NUMBER OF ATOMS IN A GIVEN MASS OF AN ELEMENT

One mole (1 mol) of atoms of an element consists of 6.02×10^{23} atoms. One mole of sulfur has a mass of 32 g. That is, 6.02×10^{23} atoms of sulfur have a total mass of 32 g. Suppose 8.0 g of sulfur were measured. How many atoms of sulfur would be present? If 32 g of sulfur is 1 mol, then 8.0 g of sulfur is $8.0/32 = 0.25$ mol. Now 1 mol of sulfur is 6.02×10^{23} atoms, and 0.25 mol of sulfur is $0.25 \times 6.02 \times 10^{23} = 1.5 \times 10^{23}$ atoms. There would be 1.5×10^{23} sulfur atoms present in an 8.0 g sample of sulfur.

SAMPLE PROBLEM/10-1

How many iron atoms are present in a 167.4 g sample of iron?

$$1 \text{ mol of iron} = 55.8 \text{ g}$$

$$167.4 \text{ g of iron} = \frac{167.4 \text{ g}}{55.8 \text{ g/mol}} = 3.00 \text{ mol of iron}$$

$$1 \text{ mol of iron contains } 6.02 \times 10^{23} \text{ atoms}$$

$$3.00 \text{ mol of iron contains}$$

$$3.00 \times 6.02 \times 10^{23} = 18.1 \times 10^{23}$$
$$= 1.81 \times 10^{24} \text{ atoms of iron}$$

EXERCISE/10-2

How many argon atoms are present in a 10.0 g sample of argon? (*Answer:* 1.51×10^{23})

10-4/MOLECULAR MASS AND FORMULA MASS

When atoms combine to form molecules, mass is neither created nor destroyed. Thus the mass of a molecule such as carbon dioxide (CO_2) can be obtained by adding the masses of each atom in the molecule. In the case of carbon dioxide there is one carbon atom (12 u) and two oxygen atoms (16 u each) in every molecule. Therefore the **molecular mass** of carbon dioxide is $12 + 16 + 16 = 44$ u.

In the case of a crystal of ionically-bonded material like NaCl, CaF_2, or AlF_3 the formulas do not describe molecules. The formula NaCl should suggest that a crystal of sodium chloride is made up of positive sodium ions attracted to negative chloride ions and that there is one sodium ion for every one chloride ion in the crystal. The formula CaF_2 should suggest that there are two fluoride ions for every one calcium ion in a crystal of calcium fluoride, and the formula $Al(NO_3)_3$ should suggest that there are three nitrate ions for every one aluminum ion in a crystal of aluminum nitrate. Thus, in solid ionic materials like sodium chloride there are no molecules—only arrangements of ions. Therefore, we do not speak of the molecular mass of NaCl. We speak of the **formula mass**. However, there is no problem in obtaining the formula mass of sodium chloride. One merely adds the mass of sodium (23 u) to the mass of chlorine (35.5 u) and obtains a formula mass of 58.5 u for NaCl.

SAMPLE PROBLEM/10-2

What is the molecular mass of alanine, $C_3H_7NO_2$?

$$\begin{aligned} 3\ \mathrm{C} &= 3 \times 12\ \mathrm{u} = 36\ \mathrm{u} \\ 7\ \mathrm{H} &= 7 \times 1\ \mathrm{u} = 7\ \mathrm{u} \\ 1\ \mathrm{N} &= 1 \times 14\ \mathrm{u} = 14\ \mathrm{u} \\ 2\ \mathrm{O} &= 2 \times 16\ \mathrm{u} = \underline{32\ \mathrm{u}} \\ & \qquad\qquad\qquad 89\ \mathrm{u} \end{aligned}$$

The molecular mass of alanine is 89 u.

SAMPLE PROBLEM/10-3

What is the formula mass of aluminum nitrate, $Al(NO_3)_3$?

$$\begin{aligned} 1\ \mathrm{Al} &= 1 \times 27\ \mathrm{u} = 27\ \mathrm{u} \\ 3\ \mathrm{N} &= 3 \times 14\ \mathrm{u} = 42\ \mathrm{u} \\ 9\ \mathrm{O} &= 9 \times 16\ \mathrm{u} = \underline{144\ \mathrm{u}} \\ & \qquad\qquad\qquad 213\ \mathrm{u} \end{aligned}$$

The formula mass of aluminum nitrate is 213 u.

EXERCISE/10-3

What is the molecular mass of H_2SO_4? What is the formula mass of $Ca(HSO_4)_2$? (*Answers:* 98.1 u; 234.3 u)

10-5/EXPANDING THE MOLE CONCEPT

So far we have said that the mole is Avogadro's number of atoms and that it is the atomic mass of an element expressed in grams. However, the idea of the mole can be generalized. A mole is Avogadro's number of atoms, molecules, formula units, ions, or particles (or anything!).

One mole of alanine is Avogadro's number of alanine molecules. One mole of alanine molecules has a mass of 89 g. It can now be said that one mole is also the molecular mass of a compound expressed in grams. Eighty-nine grams of alanine consists of 6.02×10^{23} molecules of alanine.

One mole of aluminum nitrate is Avogadro's number of $Al(NO_3)_3$ units. One mole of $Al(NO_3)_3$ has a mass of 213 g. One mole is the formula mass of an ionic substance expressed in grams. Therefore 6.02×10^{23} $Al(NO_3)_3$ units will have a total mass of 213 g.

The mole stands for gram atomic mass, gram molecular mass, or gram formula mass. It can also stand for gram ionic mass. Thus one mole of Na^+ ions is the ionic mass of the sodium ions expressed in grams (23 g). However, the mole is always Avogadro's number of particles.

10-6/PERCENTAGE COMPOSITION

In Sample Problem 10-2 the molecular mass of alanine was calculated to be 89 u. How much of this mass was contributed by the 3 carbon atoms, by the 7 hydrogen atoms, by the nitrogen atom, and by the 2 oxygen atoms? In other words, what is the percentage composition of alanine? The percentage composition of a substance can be calculated as shown in Sample Problems 10-4, 10-5, and 10-6.

SAMPLE PROBLEM/10-4

What is the percentage composition of hydrogen peroxide, H_2O_2?

The total atomic mass of hydrogen

$$\text{in } H_2O_2 \text{ is } 2 \times 1.0\text{ u} = \quad 2.0\text{ u}$$

The total atomic mass of oxygen

$$\begin{array}{r} \text{in } H_2O_2 \text{ is } 2 \times 16.0\text{ u} = \underline{32.0\text{ u}} \\ 34.0\text{ u} \end{array}$$

The total molecular mass of H_2O_2 is 34.0 u.

$$\%\text{H} = \frac{\text{mass of H in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= 2.0\text{ u}/34.0\text{ u} \times 100\% = 5.9\%$$

$$\%\text{O} = \frac{\text{mass of O in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= 32.0\text{ u}/34.0\text{ u} \times 100\% = 94.1\%$$

SAMPLE PROBLEM/10-5

What is the percentage composition of nitric acid, HNO_3?

The total atomic mass of hydrogen

$$\text{in } HNO_3 \text{ is } 1 \times \ 1.0\text{ u} = \ 1.0\text{ u}$$

The total atomic mass of nitrogen

$$\text{in } HNO_3 \text{ is } 1 \times 14.0\text{ u} = 14.0\text{ u}$$

The total atomic mass of oxygen

$$\begin{array}{r} \text{in } HNO_3 \text{ is } 3 \times 16.0\text{ u} = \underline{48.0\text{ u}} \\ 63.0\text{ u} \end{array}$$

The total molecular mass of HNO_3 is 63.0 u.

$$\%\text{H} = \frac{\text{mass of H in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= 1.0\text{ u}/63.0\text{ u} \times 100\% = 1.6\%$$

$$\%\text{N} = \frac{\text{mass of N in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= 14.0\text{ u}/63.0\text{ u} \times 100\% = 22.2\%$$

$$\%\text{O} = \frac{\text{mass of O in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= 48.0\text{ u}/63.0\text{ u} \times 100\% = 76.2\%$$

SAMPLE PROBLEM/10-6

What is the percentage composition of alanine, $C_3H_7NO_2$?

The total atomic mass of carbon
in alanine is $3 \times 12.0\ \text{u} = 36.0\ \text{u}$

The total atomic mass of hydrogen
in alanine is $7 \times 1.0\ \text{u} = 7.0\ \text{u}$

The total atomic mass of nitrogen
in alanine is $1 \times 14.0\ \text{u} = 14.0\ \text{u}$

The total atomic mass of oxygen
in alanine is $2 \times 16.0\ \text{u} = \underline{32.0\ \text{u}}$
$89.0\ \text{u}$

The total molecular mass of alanine is 89.0 u.

$$\%\text{C} = \frac{\text{mass of C in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= \frac{36.0\ \text{u}}{89.0\ \text{u}} \times 100\% = 40.4\%$$

$$\%\text{H} = \frac{\text{mass of H in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= \frac{7.0\ \text{u}}{89.0\ \text{u}} \times 100\% = 7.9\%$$

$$\%\text{N} = \frac{\text{mass of N in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= \frac{14.0\ \text{u}}{89.0\ \text{u}} \times 100\% = 15.7\%$$

$$\%\text{O} = \frac{\text{mass of O in 1 molecule}}{\text{mass of molecule}} \times 100\%$$

$$= \frac{32.0\ \text{u}}{89.0\ \text{u}} \times 100\% = 36.0\%$$

EXERCISE/10-4

What is the percentage composition of barium peroxide, BaO_2? (*Answer*: 81.1% Ba; 18.9% O)

EXERCISE/10-5

What is the percentage composition of sulfuric acid, H_2SO_4? (*Answer:* 2.0% H; 32.7% S; 65.2% O)

EXERCISE/10-6

What is the percentage composition of potassium hydrogen oxalate, KHC_2O_4? (*Answer:* 30.5% K; 0.8% H; 18.7% C; 50.0% O)

10-7/EMPIRICAL FORMULA DETERMINATION

When a new compound is prepared, chemists are interested in obtaining its empirical formula. They do this by analyzing the molecule to find out its percentage composition. The percentage composition information is then used to determine the empirical formula.

The **empirical formula** is the simplest formula. It gives a bare minimum of information about the compound because it shows only the relative numbers of moles of each type of atom in the compound. In writing the empirical formula, one writes the symbols of the elements with subscripts to designate the relative numbers of moles of these elements. The empirical formula CH_2O represents a compound in which there is 1 mol of carbon atoms and 2 mol of hydrogen atoms for every 1 mol of oxygen atoms. However, 1 mol of atoms of any element contains the same number (Avogadro's number) of atoms as 1 mol of atoms of any other element. Therefore we can also state that the empirical formula CH_2O represents a compound in which there is 1 atom of carbon and 2 atoms of hydrogen for every 1 atom of oxygen.

The empirical formula tells us the relative number of atoms in a compound. It does not tell us how many atoms of each type are in a molecule of the compound.

Suppose that a certain compound contains 5.9% hydrogen and 94.1% oxygen. For the empirical formula we need only the relative number of moles of hydrogen and moles of oxygen in the compound. Since only relative numbers are involved, we can consider any amount of the compound. For example, 100 g of compound contains 5.9 g of hydrogen and 94.1 g of oxygen.

1 g of hydrogen is 1 mol of atoms
∴ 5.9 g of hydrogen is 5.9 mol of atoms
16 g of oxygen is 1 mol of atoms
1 g of oxygen is 1/16 mol of atoms
∴ 94.1 g of oxygen is 94.1/16 = 5.9 mol of atoms

The ratio of hydrogen atoms to oxygen atoms is 5.9 to 5.9 or 1 to 1. This gives an empirical formula of HO.

At this point it should be stated that to change from grams of an element to moles of the element, one divides the given mass by the molar mass. For example, 84 g of sulfur can be converted to moles of sulfur by dividing 84 g by the molar mass of sulfur which is 32 g/mol:

$$\frac{84\ \text{g}}{32\ \text{g/mol}} = 2.6\ \text{mol}$$

One can change from the number of moles of an element to grams of the element by multiplying the number of moles by the molar mass. For example, 5.6 mol of carbon can be converted to grams of carbon by multiplying 5.6 mol by the molar mass of carbon which is 12 g/mol:

$$5.6\ \text{mol} \times 12\ \text{g/mol} = 67\ \text{g}$$

SAMPLE PROBLEM/10-7

What is the empirical formula of a compound which is found by analysis to contain 92.3% carbon and 7.7% hydrogen?

In 100 g of the compound there would be 92.3 g of carbon and 7.7 g of hydrogen.

$$\mathrm{C}\ 92.3\ \mathrm{g} \qquad \mathrm{H}\ 7.7\ \mathrm{g}$$

$$\mathrm{C}\ \frac{92.3\ \mathrm{g}}{12.0\ \mathrm{g/mol}} \qquad \mathrm{H}\ \frac{7.7\ \mathrm{g}}{1.0\ \mathrm{g/mol}}$$

$$\mathrm{C}\ 7.69\ \mathrm{mol} \qquad \mathrm{H}\ 7.7\ \mathrm{mol}$$

To obtain the simplest molar ratios, both molar quantities are divided by the smaller number of moles present (7.69):

$$\mathrm{C}\ \frac{7.69\ \mathrm{mol}}{7.69} \qquad \mathrm{H}\ \frac{7.7\ \mathrm{mol}}{7.69}$$

$$\mathrm{C}\ 1\ \mathrm{mol} \qquad \mathrm{H}\ 1\ \mathrm{mol}$$

The empirical formula of the substance is CH.

SAMPLE PROBLEM/10-8

What is the empirical formula of a compound which on analysis shows 2.2% H, 26.7% C, and 71.1% O?

In 100 g of the compound there would be 2.2 g H, 26.7 g C, and 71.1 g O.

$$\mathrm{H}\ 2.2\ \mathrm{g} \qquad \mathrm{C}\ 26.7\ \mathrm{g} \qquad \mathrm{O}\ 71.1\ \mathrm{g}$$

$$\mathrm{H}\ \frac{2.2\ \mathrm{g}}{1.0\ \mathrm{g/mol}} \qquad \mathrm{C}\ \frac{26.7\ \mathrm{g}}{12\ \mathrm{g/mol}} \qquad \mathrm{O}\ \frac{71.1\ \mathrm{g}}{16\ \mathrm{g/mol}}$$

$$\mathrm{H}\ 2.2\ \mathrm{mol} \qquad \mathrm{C}\ 2.2\ \mathrm{mol} \qquad \mathrm{O}\ 4.4\ \mathrm{mol}$$

To obtain the simplest molar ratios, all molar quantities are divided by the smallest number of moles present (2.2):

$$\mathrm{H}\ \frac{2.2\ \mathrm{mol}}{2.2} \qquad \mathrm{C}\ \frac{2.2\ \mathrm{mol}}{2.2} \qquad \mathrm{O}\ \frac{4.4\ \mathrm{mol}}{2.2}$$

$$\mathrm{H}\ 1\ \mathrm{mol} \qquad \mathrm{C}\ 1\ \mathrm{mol} \qquad \mathrm{O}\ 2\ \mathrm{mol}$$

The empirical formula of the substance is HCO_2.

SAMPLE PROBLEM/10-9

What is the empirical formula of a compound which on analysis shows 69.9% Fe and 30.1% O?

In 100 g of the compound there would be 69.9 g Fe and 30.1 g O.

Fe 69.9 g	O 30.1 g
Fe $\frac{69.9\text{ g}}{55.85\text{ g/mol}}$	O $\frac{30.1\text{ g}}{16.0\text{ g/mol}}$
Fe 1.25 mol	O 1.88 mol
Fe $\frac{1.25\text{ mol}}{1.25}$	O $\frac{1.88\text{ mol}}{1.25}$
Fe 1.00 mol	O 1.50 mol

The ratio of Fe atoms to O atoms is 1 to 1.5 or 2 to 3. Therefore the empirical formula is Fe_2O_3.

EXERCISE/10-7

What is the empirical formula of a compound which is found by analysis to contain 80.0% carbon and 20.0% hydrogen? (*Answer:* CH_3)

EXERCISE/10-8

What is the empirical formula of a compound which contains 35.9% aluminum and 64.1% sulfur? (*Answer:* Al_2S_3)

EXERCISE/10-9

What is the empirical formula of a compound which contains 26.6% K, 35.4% Cr, and 38.1% O? (*Answer:* $K_2Cr_2O_7$)

10-8/MOLECULAR FORMULA DETERMINATION

If one knows the molecular mass and the empirical formula one can determine the molecular formula. The **molecular formula** shows the actual number of atoms of each element in a molecule of the compound.

Suppose one knows that one mole of the compound from Sample Problem 10-8 has a mass of 90 g. This is the same as stating that 1 molecule of the compound has a mass of 90 u. The empirical formula was found to be HCO_2. The empirical formula mass may be calculated:

$$\begin{aligned} \text{Mass of hydrogen is } 1 \times 1\text{ u} &= 1\text{ u} \\ \text{Mass of carbon is } 1 \times 12\text{ u} &= 12\text{ u} \\ \text{Mass of oxygen is } 2 \times 16\text{ u} &= \underline{32\text{ u}} \\ & 45\text{ u} \end{aligned}$$

Thus 1 molecule of the compound must contain 2 empirical formula units, $(HCO_2)_2$. This is usually written as $H_2C_2O_4$.

SAMPLE PROBLEM/10-10

CH_2O is the empirical formula of a certain compound whose molecular mass is 180 u. What is the molecular formula of the compound?

$$\begin{aligned} (CH_2O)_x &= 180 \\ (12 + 2 \times 1 + 16)_x &= 180 \\ (30)_x &= 180 \\ x &= 6 \end{aligned}$$

The molecular formula is $C_6H_{12}O_6$.

SAMPLE PROBLEM/10-11

The analysis of a compound shows that it is made up of 21.9% Na, 45.7% C, 1.9% H, and 30.5% O. What is the molecular formula of the compound if its molecular mass is 210 u?

One mole of the compound is 210 g, and in 210 g of this compound there will be:

$$
\begin{aligned}
0.219 \times 210\ \text{g} &= 46.0\ \text{g Na} \\
0.457 \times 210\ \text{g} &= 96.0\ \text{g C} \\
0.019 \times 210\ \text{g} &= \ \ 4.0\ \text{g H} \\
0.305 \times 210\ \text{g} &= 64.0\ \text{g O}
\end{aligned}
$$

$$
\begin{array}{llll}
\text{Na}\ \ 46.0\ \text{g} & \text{C}\ \ 96.0\ \text{g} & \text{H}\ \ 4.0\ \text{g} & \text{O}\ \ 64.0\ \text{g} \\[6pt]
\text{Na}\ \dfrac{46.0\ \text{g}}{23\ \text{g/mol}} & \text{C}\ \dfrac{96.0\ \text{g}}{12\ \text{g/mol}} & \text{H}\ \dfrac{4.0\ \text{g}}{1\ \text{g/mol}} & \text{O}\ \dfrac{64.0\ \text{g}}{16\ \text{g/mol}} \\[6pt]
\text{Na}\ \ 2\ \text{mol} & \text{C}\ \ 8\ \text{mol} & \text{H}\ \ 4\ \text{mol} & \text{O}\ \ 4\ \text{mol}
\end{array}
$$

$$Na_2C_8H_4O_4$$

The molecular formula of the compound is $Na_2C_8H_4O_4$.

EXERCISE/10-10

A certain compound was found to have empirical formula CH. Its molecular mass was found to be 52.0 u. What is its molecular formula? (*Answer:* C_4H_4)

EXERCISE/10-11

An unknown compound is found to have a molecular mass of 75.0 u and to contain 32.0% carbon, 6.7% hydrogen, and 18.7% nitrogen, with the rest of the molecule consisting of oxygen. What is the molecular formula of the compound? (*Answer:* $C_2H_5NO_2$)

10-9/THE MOLE AND CHEMICAL EQUATIONS

The chemical equation is a shorthand method for describing a chemical change. The symbols and formulas are used to indicate the substances involved in the change. In order to balance a chemical equation one must know what substances react, what substances are produced, and the correct symbols and formulas for all of the substances involved in the reaction. One must also obey the Law of Conservation of Mass. That is, there must be as many atoms of each element on the right side of the "yields" sign as there are on the left side.

Let us consider a simple equation:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

This balanced equation states that 1 atom of carbon reacts with 1 molecule of oxygen to give 1 molecule of carbon dioxide. It also means that 12 u of carbon react with 32 u of oxygen to give 44 u of carbon dioxide. However, 10 carbon atoms (120 u) would also react with 10 oxygen molecules (320 u) to give 10 molecules of carbon dioxide (440 u). Furthermore, 6.02×10^{23} carbon atoms (12 g or 1 mol) would react with 6.02×10^{23} oxygen molecules (32 g or 1 mol) to give 6.02×10^{23} molecules of carbon dioxide (44 g or 1 mol). This information is summarized below:

$C(s)$	$+ O_2(g)$	$\rightarrow CO_2(g)$
1 atom	+ 1 molecule	→ 1 molecule
12 u	+ 32 u	→ 44 u
10 atoms	+ 10 molecules	→ 10 molecules
120 u	+ 320 u	→ 440 u
6.02×10^{23} atoms	$+ 6.02 \times 10^{23}$ molecules	$\rightarrow 6.02 \times 10^{23}$ molecules
12 g	+ 32 g	→ 44 g
1 mol	+ 1 mol	→ 1 mol

10-10/MASS CALCULATIONS INVOLVING CHEMICAL EQUATIONS

We can use our knowledge of chemical equations and moles to calculate mass relationships among the substances involved in a chemical reaction. For example, how many grams of oxygen would be needed to react with 60 g of carbon to produce carbon dioxide, and how many grams of carbon dioxide would result? We write the equation:

$$\begin{array}{ccccc} C(s) & + & O_2(g) & \rightarrow & CO_2(g) \\ 1\ \text{mol} & & 1\ \text{mol} & & 1\ \text{mol} \\ 12\ \text{g} & & 32\ \text{g} & & 44\ \text{g} \end{array}$$

Thus 1 mol (12 g) of carbon will react with 1 mol (32 g) of oxygen to produce 1 mol (44 g) of carbon dioxide. How many moles of carbon is 60 g?

$$\text{moles of C} = \frac{60\ \text{g}}{12\ \text{g/mol}} = 5.0\ \text{mol}$$

According to the equation 1 mol of carbon reacts with 1 mol of oxygen. Therefore 5.0 mol of carbon will react with 5.0 mol of oxygen. How many grams of oxygen are present in 5.0 mol?

$$\text{grams of } O_2 = 5.0\ \text{mol} \times 32\ \text{g/mol} = 160\ \text{g}$$

Also, 5.0 mol of carbon will produce 5.0 mol of carbon dioxide. How many grams of carbon dioxide are present in 5.0 mol?

$$\text{grams of } CO_2 = 5.0\ \text{mol} \times 44\ \text{g/mol} = 220\ \text{g}$$

SAMPLE PROBLEM/10-12

How many moles of oxygen are required to react with 9.7 g of magnesium to produce magnesium oxide? How many grams of oxygen are required?

$$\begin{array}{rccccc} \text{Unbalanced Equation:} & Mg(s) & + & O_2(g) & \rightarrow & MgO(s) \\ \text{Balanced Equation:} & 2\,Mg(s) & + & O_2(g) & \rightarrow & 2\,MgO(s) \\ & 2\ \text{mol} & & 1\ \text{mol} & & 2\ \text{mol} \\ & 1\ \text{mol} & & 0.5\ \text{mol} & & 1\ \text{mol} \end{array}$$

$$\text{moles of Mg} = \frac{9.7\ \text{g}}{24.3\ \text{g/mol}} = 0.40\ \text{mol}$$

1 mol of Mg reacts with 0.5 mol O_2

$\therefore$ 0.40 mol of Mg reacts with $0.40 \times 0.5 = 0.20$ mol of O_2

$$\text{Grams of } O_2 = 0.20 \text{ mol} \times 32 \text{ g/mol} = 6.4 \text{ g of } O_2$$

There is a similar but somewhat different method for solving this type of problem. The method is called the proportion method. Sample Problem 10-13 illustrates the use of both the mole method and the proportion method.

SAMPLE PROBLEM/10-13

How many grams of $KClO_3$ must be decomposed to give 0.96 g of oxygen?

$$\text{Unbalanced Equation: } KClO_3(s) \xrightarrow{\Delta} KCl(s) + O_2(g)$$

$$\begin{array}{lccc} \text{Balanced Equation: } & 2\,KClO_3(s) \xrightarrow{\Delta} & 2\,KCl(s) + & 3\,O_2(g) \\ & 2 \text{ mol} & 2 \text{ mol} & 3 \text{ mol} \\ & 2(122.6 \text{ g}) & 2(74.6 \text{ g}) & 3(32 \text{ g}) \\ & 245.2 \text{ g} & 149.2 \text{ g} & 96 \text{ g} \end{array}$$

Mole Method:

$$\text{moles of } O_2 = \frac{0.96 \text{ g}}{32 \text{ g/mol}} = 0.030 \text{ mol}$$

3 mol of O_2 are produced from 2 mol of $KClO_3$

1 mol of O_2 is produced from 2/3 mol of $KClO_3$

0.030 mol of O_2 are produced from $0.030 \times 2/3$ mol $= 0.020$ mol of $KClO_3$

Grams of $KClO_3 = 0.020 \text{ mol} \times 122.6 \text{ g/mol} = 2.5$ g of $KClO_3$

Proportion Method:

$$\begin{array}{ccc} x & & 0.96 \text{ g} \\ 2\,KClO_3(s) \xrightarrow{\Delta} & 2\,KCl(s) + & 3\,O_2(g) \\ 245.2 \text{ g} & & 96 \text{ g} \end{array}$$

$$\frac{x}{245.2 \text{ g}} = \frac{0.96 \text{ g}}{96 \text{ g}}$$

$$x = \frac{0.96 \text{ g} \times 245.2 \text{ g}}{96 \text{ g}} = 2.5 \text{ g of } KClO_3$$

EXERCISE/10-12

How many moles of hydrogen are required to react with 15.4 g of nitrogen to produce ammonia, NH_3? How many grams of hydrogen are required? (*Answer:* 1.65 mol; 3.30 g)

EXERCISE/10-13

In the reaction $Mg + 2\,HCl \rightarrow MgCl_2 + H_2$, how many grams of magnesium are required to produce 5.00 g of hydrogen? (*Answer:* 60.8 g)

10-11/MOLARITY

In Chapter 8, solutions were discussed. The idea of the quantity of solute dissolved in a certain volume of solution was not mentioned specifically. This is the idea of **concentration**. We all know that some solutions are more concentrated than others. We often hear the terms "concentrated" and "dilute" mentioned with respect to commercial products.

Chemists have several methods of expressing concentration. However, one method used frequently by chemists is called molarity. **Molarity** refers to the number of moles of a solute dissolved in a litre of solution. For example, a one-molar (abbreviated, 1 M) solution of sodium chloride in water contains one mole of sodium chloride dissolved in enough water to make up one litre of solution.

If you were asked to make up one litre of 1 M NaCl, you would first determine the mass of 58.5 g (23 + 35.5) of dry NaCl. The NaCl would then be placed in a special flask, called the *volumetric flask*, which is calibrated to contain one litre at normal temperature. Distilled water is added to the flask, and the contents are swirled until the NaCl dissolves completely. Then more distilled water is added until the water level (the bottom of the meniscus) reaches the one-litre mark on the neck of the flask. You do not know how much water you have added to the volumetric flask. You know only that you have *one* litre of solution ($NaCl + H_2O$) in the flask.

If you were asked to make up one litre of 2 M NaCl, you would place 117 g of dry NaCl in the one-litre volumetric flask and dissolve in it enough distilled water to fill the flask to the one-litre mark. If you were asked to make up one litre of 0.5 M NaCl, you would use 29.2 g of dry NaCl and dissolve it in one litre of solution.

Volumetric flasks come in many sizes (e.g., 50 cm^3, 100 cm^3, 250 cm^3, 500 cm^3, 1000 cm^3, 2000 cm^3, etc.). Therefore, it is possible to make up almost any quantity of a solution of any required molarity.

SAMPLE PROBLEM/10-14

How many grams of sugar, $C_{12}H_{22}O_{11}$, are contained in 50 cm^3 of a 0.40 M solution of sugar in water?

$$x\ \mathrm{M} = \frac{y\ \mathrm{mol}}{z\ \ell}$$

$$50\ \mathrm{cm}^3 = 0.050\ \ell$$

$$\therefore \quad 0.40\ \mathrm{M} = \frac{y\ \mathrm{mol}}{0.050\ \ell}$$

$$\begin{aligned} y\ \mathrm{mol} &= 0.40\ \mathrm{M} \times 0.050\ \ell \\ &= 0.020\ \mathrm{mol} \end{aligned}$$

$$1\ \mathrm{mol\ of}\ C_{12}H_{22}O_{11} = 342\ \mathrm{g}$$

$$\begin{aligned} \therefore \quad 0.020\ \mathrm{mol\ of}\ C_{12}H_{22}O_{11} &= 342\ \mathrm{g/mol} \times 0.020\ \mathrm{mol} \\ &= 6.8\ \mathrm{g\ of}\ C_{12}H_{22}O_{11} \end{aligned}$$

SAMPLE PROBLEM/10-15

What is the molarity of a solution that contains 49 g of sulfuric acid (H_2SO_4) in 3.0 ℓ of solution?

$$x\ \mathrm{M} = \frac{y\ \mathrm{mol}}{z\ \ell}$$

$$1\ \mathrm{mol\ of}\ H_2SO_4 = 98\ \mathrm{g}$$

$$\therefore \quad 49\ \mathrm{g\ of}\ H_2SO_4 = \frac{49\ \mathrm{g}}{98\ \mathrm{g/mol}} = 0.50\ \mathrm{mol}$$

$$x \text{ M} = \frac{0.05 \text{ mol}}{3.0 \ \ell}$$

$$x \text{ M} = 0.17 \text{ mol}/\ell = 0.17 \text{ M}$$

The solution of sulfuric acid is 0.17 M.

EXERCISE/10-14

How many grams of formaldehyde, CH_2O, are contained in 500 cm^3 of a 13 M aqueous solution of formaldehyde? (*Answer:* 195 g)

QUESTIONS

1. What is the mass of one mole of mercury? Of sodium? Of argon?
2. How many atoms are present in one mole of any element?
3. How many atoms are present in 5 mol of argon?
4. How many atoms are present in 100 g of argon? In 10 g of argon?
5. What is the molecular mass of $C_{12}H_{22}O_{11}$? Of $HC_2H_3O_2$?
6. What is the formula mass of $(NH_4)_2SO_4$? Of Na_3PO_4?
7. What is the molar mass of C_2H_5OH? Of $Al_2(SO_4)_3$?
8. What is the percentage composition of CaO? Of H_2S?
9. What is the percentage composition of Na_2SO_4? Of C_4H_9SH?
10. What are the empirical formulas for compounds whose percentage compositions are given:
    - (**a**) Fe = 63.53%, S = 36.47%
    - (**b**) Na = 21.6 %, Cl = 33.3 %, O = 45.1 %
    - (**c**) Cr = 26.52%, S = 24.52%, O = 48.96%
    - (**d**) C = 63.1 %, H = 11.92%, F = 24.97%
11. What is the molecular formula for a compound whose molecular mass is 116 u and whose empirical formula is CHO?

12. What is the molecular formula for a compound whose molecular mass is 238 u and whose percentage composition is Na = 19.3%, S = 26.9%, and O = 53.8%?
13. What is the molecular formula for a compound whose molecular mass is 198 u and whose percentage composition is C = 48.48%, H = 5.05%, N = 14.14%, O = 32.32%?
14. What does the equation $2\ VO(s) + 3\ Fe_2O_3(s) \rightarrow 6\ FeO(s) + V_2O_5(s)$ tell us about the relative number of moles of each substance involved in the reaction? (I.e., how many moles of VO react with how many moles of Fe_2O_3 to give how many moles of FeO and 1 mol of V_2O_5?)
15. In the reaction $2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g)$, how many moles of sulfur will react with 9 mol of oxygen?
16. How many grams of $O_2(g)$ are needed to react with 6.4 g of methane (CH_4) to produce $CO_2(g)$ and $H_2O(g)$?

    $$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

    How many grams of $CO_2(g)$ will be formed?
17. How many grams of nitrogen dioxide (NO_2) will be produced when 128 g of $O_2(g)$ react completely with nitrogen(II) oxide (NO)? Write a balanced equation before solving the problem.
18. Sodium carbonate and hydrochloric acid react to give sodium chloride, carbon dioxide, and water. How many grams of sodium carbonate and hydrochloric acid would be required to produce 286 g of carbon dioxide?
19. What is the mass in grams of one atom of sulfur? Of iron? Of fluorine?
20. How many grams of $C_6H_{12}O_6$ are contained in 250 cm^3 of a 0.050 M solution of $C_6H_{12}O_6$ in water?
21. How many grams of $CuSO_4 \cdot 5\ H_2O$ are required to prepare 2.0 ℓ of a 3.0 M copper sulfate solution?
22. What is the molarity of a solution that contains 39.2 g of H_3PO_4 in 500 cm^3 of solution?
23. What is the molarity of a solution that contains 100 g of Na_2SO_4 in 10.0 ℓ of solution?
24. What volume of 0.14 M hydrochloric acid would contain 5.0 g of HCl?

11

GASES

Long before Dalton's time, scientists knew of gases, liquids, and solids. They understood, in some cases, how to bring about changes from one state to another. However, they did not understand exactly what was happening within the sample of matter as it changed from one state to another. This was especially true in the case of liquids changing to gases. It was largely as a result of Dalton's experiments with gases that he proposed his atomic theory. How do the physical properties of gases and the physical laws that describe these properties suggest that matter is atomic in nature? Let us look at some of the properties and laws and at the men who discovered them.

When you have completed this chapter you should be able to attain the following objectives:

1. State Boyle's Law, Charles' Law, Dalton's Law of Partial Pressures, and the ideal gas law, in words and mathematically.
2. Use Boyle's Law and Charles' Law, singly or together, to solve gas problems involving pressure, volume, and temperature.
3. Convert Celsius temperatures to Kelvin temperatures and vice versa.
4. Define standard temperature and pressure.

5. Given the volume of a gas at a given temperature and pressure, calculate the volume at STP.
6. Correct for the vapor pressure of water in gas law calculations involving gases collected over water.
7. State the numerical value of the universal gas constant.
8. Given any three of the variables *P*, *V*, *T*, and *n*, calculate the fourth variable using the ideal gas law.
9. Define Brownian motion.
10. State the assumptions of the kinetic molecular theory.
11. Explain the compressibility of gases, Boyle's Law, Charles' Law, Dalton's Law of Partial Pressures using the postulates of the kinetic molecular theory.
12. Explain how the postulates of the kinetic molecular theory predict Gay-Lussac's Law.

11-1/THE DISCOVERY OF AIR PRESSURE

Galileo Galilei, an Italian physicist, discovered that if he pumped the air out of the top of a tube, the bottom of which was immersed in water, the water rose in the tube (Fig. 11-1A). However, it was not possible to raise the water

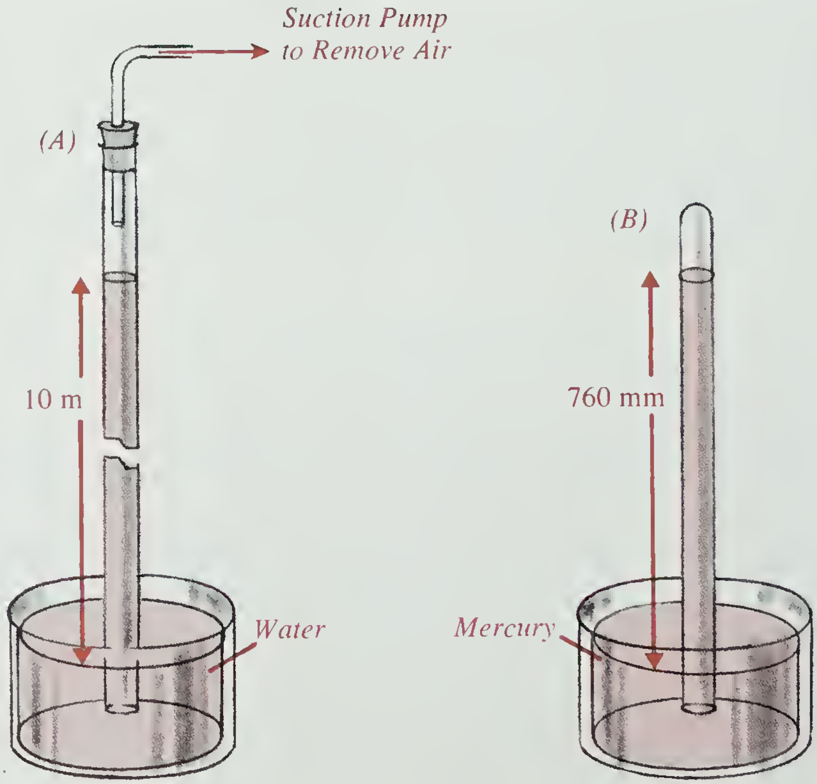


Fig. 11-1A Galileo's Apparatus Using Water
Fig. 11-1B Torricelli's Mercury Barometer

higher than about 10 m, no matter how hard he pumped.

Galileo called this problem to the attention of his pupil and assistant, Evangelista Torricelli. Eventually it dawned on Torricelli that it was the pressure of the atmosphere on the surface of the water outside the tube that forced the water up into the tube. At a height of about 10.3 m the pressure exerted by the column of water would just balance the pressure exerted by the atmosphere. He next theorized that the atmosphere should balance a much shorter column of mercury than water. Mercury is 13.6 times as dense as water, so the column ought to be only 1/13.6 as high as 10.3 m, or about 0.8 m. Torricelli tried the experiment in 1643 using a closed tube and found that the mercury column stayed at a level of about 760 mm (0.76 m). This experiment led him to the invention of the mercury barometer, a device which measures the small variations in atmospheric pressure (Fig. 11-1B).

11-2/ROBERT BOYLE

Robert Boyle (Fig. 11-2) was the seventh son and fourteenth child of the Earl of Cork. He remained single throughout his life and devoted all his effort to the study of science and religion. By 1659 he had constructed a new and superior air pump. With this he tried many experiments. In one experiment he placed a barometer inside a container from which he could pump the air. He found that the mercury level fell as the air was removed from the container (Fig. 11-3). Boyle felt this proved conclusively that it was the pressure of the air on the surface of the mercury which supported the column, thus confirming Torricelli's findings.

Fig. 11-2 Robert Boyle (1627-1691) *(Photo courtesy of The Bettmann Archive)*

Boyle published his results the following year. His conclusions were immediately attacked by Franciscus Linus, a Jesuit priest. Linus explained the action of a barometer by supposing that the mercury column was held up by an invisible internal cord. Boyle naturally felt this was a poor hypothesis and immediately began a series of experiments to support his own. In the process he formulated Boyle's Law, which stated the mathematical relationship between the pressure of a gas and its volume.

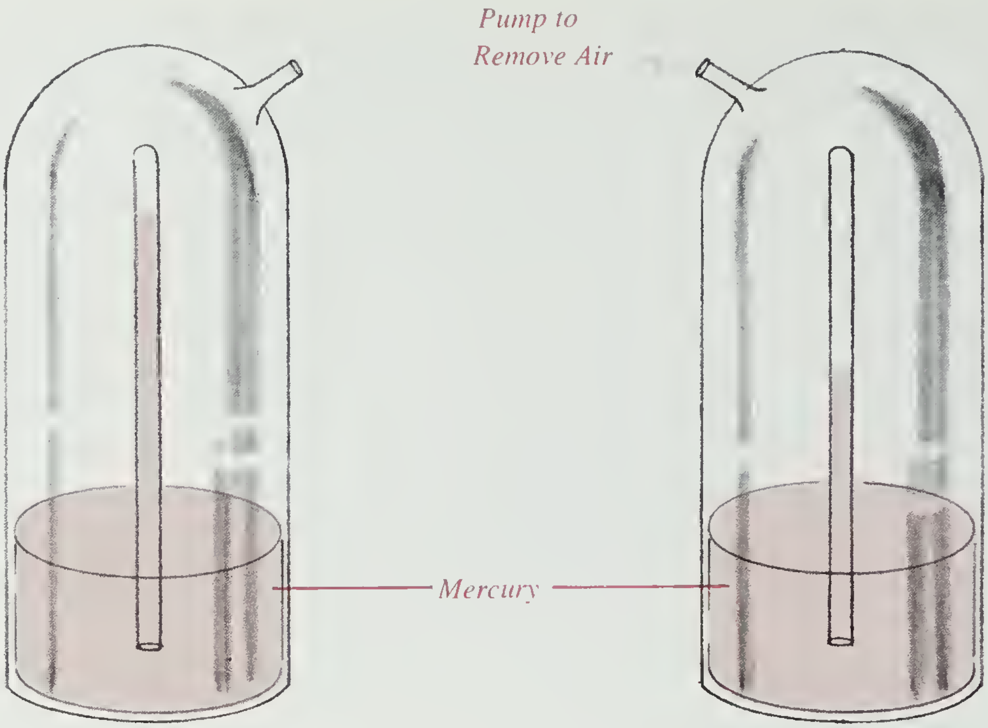


Fig. 11-3 The level of mercury falls as air is pumped from the container.

11-3/BOYLE'S LAW

With a J-shaped tube similar to that shown in Fig. 11-4, Boyle used a column of mercury to trap a sample of air in the short closed end. When he added more mercury to the longer open end, the air was compressed to a smaller volume. When he decreased the pressure by removing mercury, the air expanded to a greater volume. When he measured the air volumes corresponding to varying pressures, he noticed a simple relationship. Some of his data are given in Table 11-1.

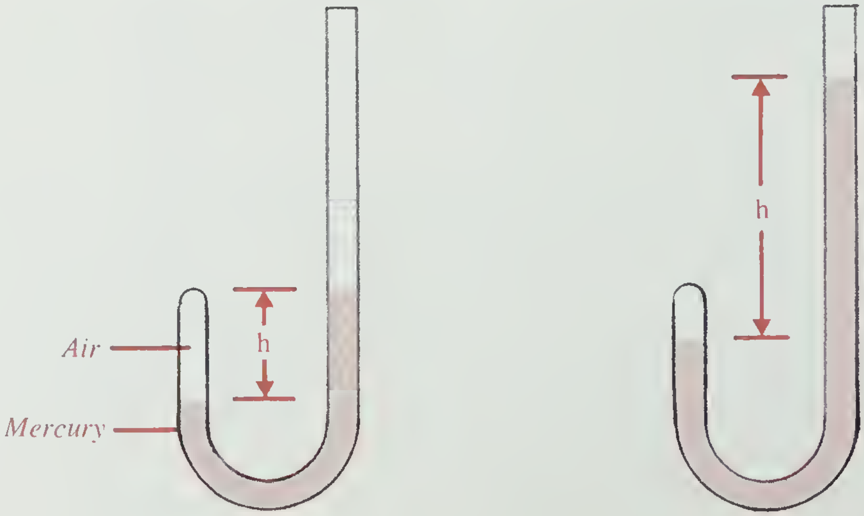


Fig. 11-4 Boyle's Apparatus
The longer the column of mercury, h, *the more the air is compressed.*

TABLE 11-1

SOME OF ROBERT BOYLE'S DATA

Volume of air V(m)*	*Pressure* P(m)†	*PV Product*
0.305	0.74	0.226
0.254	0.90	0.229
0.203	1.12	0.227
0.152	1.49	0.226
0.102	2.23	0.227

Boyle noticed that the product of the volume of air times the pressure exerted on it was very nearly a constant (in this case 0.227), or $PV = \text{constant}$. This can be rearranged as:

$$P = \frac{\text{constant}}{V} \quad \text{or} \quad V = \frac{\text{constant}}{P}$$

Note that if V increases, P decreases proportionately, and vice versa. Such relations are called inverse relations or inverse proportions. These expressions are simply the mathematical statement of **Boyle's Law** which states: *the volume of a fixed mass of a gas varies inversely with the pressure, provided the temperature remains constant.* Actually Boyle was not really concerned about the effects of temperature. Luckily for him the temperature stayed roughly constant during his experiments.

Since gases tend to resist being squeezed into a smaller volume, Boyle thought in terms of the "spring" of gases. He thought that gases were made up of very small particles similar to extremely minute coiled springs. Gases exerted a pressure because the "ether" (a mysterious "something" that

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* Boyle actually estimated the volume of the air by measuring the length of the air space in the tube. The actual volume of the air in cubic metres was unknown.

† Boyle expressed the pressure as the height (h) in metres of the mercury column plus the pressure of the atmosphere above the open end, which he estimated at 0.74 m. The metre is not an SI unit of pressure and will not be used as such in this book again. It is used here for historical reasons only.

was thought to fill the spaces between the gas particles) whirled the particles so violently that each particle tried to prevent all others from coming into its own little neighborhood.

11-4/CHARLES' LAW

Boyle had investigated the relationship between the volume and the pressure of a gas in 1659. However, it was not until 1787, over a century later, that the French physicist J. A. Charles discovered the relationship between the volume and the temperature of a gas at constant pressure.

We are all familiar with the fact that gases expand when heated and contract on cooling. A balloon's size becomes larger when held over a hot stove, and decreases when the balloon is removed from the heat. Many motorists release air from their tires to relieve the pressure caused by heat build-up from sustained high-speed driving. The problem is that they may forget to replace this air when tire temperatures return to normal, and the tire may wear excessively because of under-inflation.

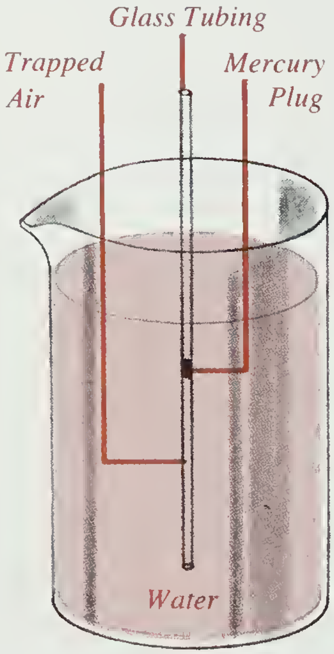

Fig. 11-5 Charles' Law Experiment

Charles' experiments were rather crude and were later performed more accurately in 1801 by John Dalton and in 1802 by the French chemist Joseph Louis Gay-Lussac. Nevertheless Charles deserves the credit for the early investigations.

We can repeat Charles' early observations by using a mercury "piston," made by trapping a quantity of air in a piece of narrow-bore glass tubing (Fig. 11-5) with a small plug of mercury. Since the tube is open to the atmosphere and the mercury is free to move up and down the tube, the pressure exerted on the trapped air remains constant. If the tube is immersed in hot water, the air expands and the mercury plug moves up the tube. Typical data for Charles' law experiment are shown on Table 11-2.

It is obvious that the volume increases as the Celsius temperature increases. The relationship is not a direct proportionality, however, because doubling the temperature from 50°C to 100°C results in a volume increase of only 885/766 or 1.155 times. A graph of volume versus temperature is a straight line, showing that the increase in volume is regular and uniform (Fig. 11-6).

TABLE 11-2

TYPICAL DATA FOR CHARLES' LAW EXPERIMENT

Temperature, T (°C)	*Gas Volume, V* (mm^3)
0	648
25	714
50	766
75	817
100	885

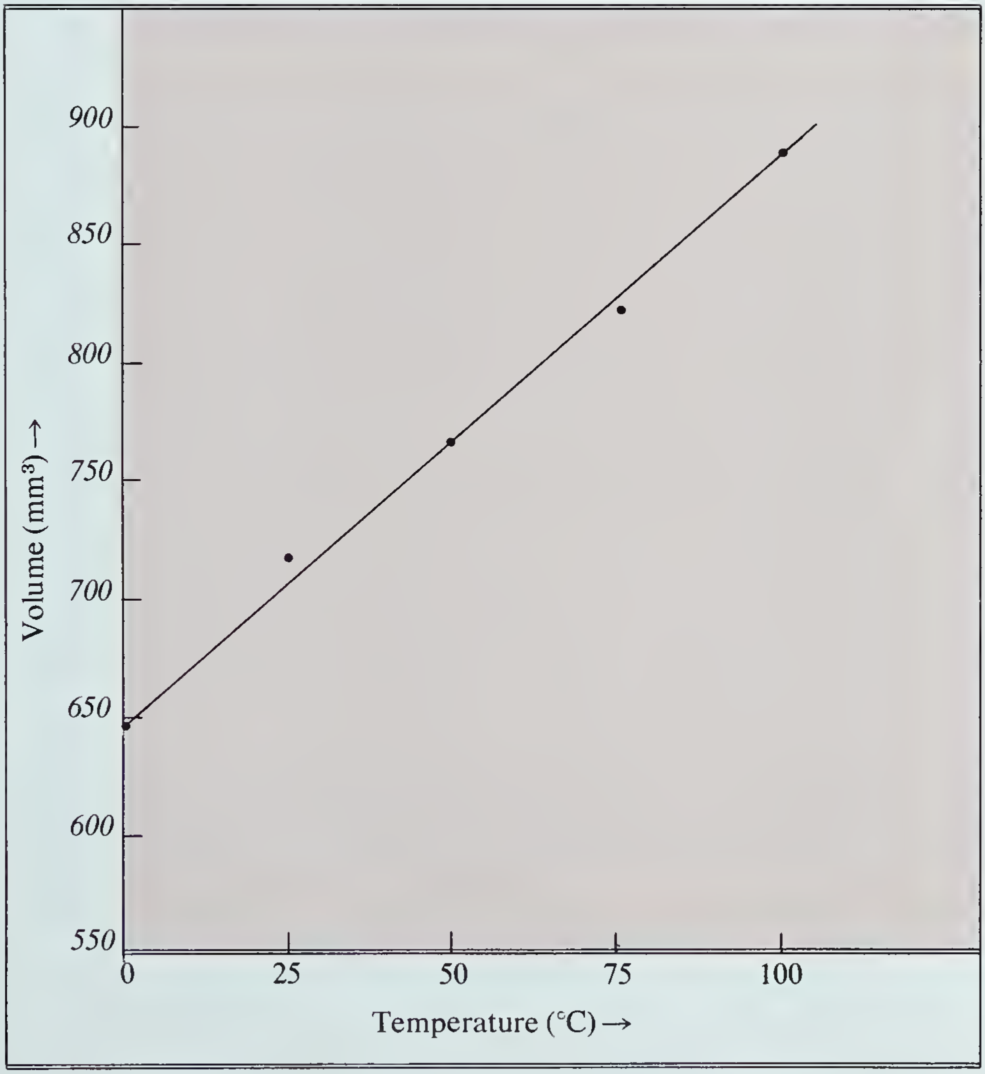

Fig. 11-6 Graph of Charles' Law Data

What is the relationship? We notice that at 100°C the volume is 885/648 or 1.366 times the volume at 0°C. An increase in temperature of 100°C causes a volume increase of 0.366 times the volume at 0°C. So an increase in temperature of 1°C causes an increase in volume of 0.366/100 or 0.003 66 times its volume at 0°C. The decimal fraction 0.003 66 is equivalent to the proper fraction 1/273. So another way of stating the results of the experiment is: the volume of a sample of gas at 0°C increases by 1/273 of its original volume for each degree it is warmed above 0°C. We can check this statement: at 75°C the volume should be 1 75/273 or 1.275 times the volume at 0°C. The predicted volume is $1.275 \times 648\ \text{mm}^3 = 826\ \text{mm}^3$. The experimental value is $817\ \text{mm}^3$. The difference can be attributed to the difficulty of making sufficiently precise measurements (experimental error!).

If the results of the experiment are valid, we should be able to state the results in a different way: the volume of a gas at 0°C decreases by 1/273 of its original volume for each degree it is cooled below 0°C. At some temperature, the volume of the gas should become zero. What is this temperature? It is −273°C. In practice, this zero volume has never been observed because all gases liquefy and the majority solidify before reaching −273°C. Nevertheless, −273°C is a theoretically important temperature and a new temperature scale, the *Kelvin scale*, is based on it. In this scale, −273°C becomes zero degrees Kelvin (0 K). This is called *absolute zero.* Other temperatures are obtained simply by adding 273 to the corresponding Celsius temperature. Thus, the freezing point of water is 273 K and the boiling point of water is 373 K. (Notice that the degree symbol is omitted when writing Kelvin temperatures.)

Let us now reexamine the data of Table 11-2, expressing the temperatures in the Kelvin scale shown in Table 11-3. Now we see that increasing the temperature from 273 K to 373 K (a factor of $373/273 = 1.366$) causes the volume to increase from $648\ \text{mm}^3$ to $885\ \text{mm}^3$; also a factor of $885/648 = 1.366$. There is now a direct proportionality. We can now state **Charles' Law** in modern terms: *the volume of a fixed mass of gas varies directly with the Kelvin temperature, provided the pressure remains constant.*

$$V = \text{constant} \times T$$

TABLE 11-3

DATA FOR CHARLES' LAW EXPERIMENT

Temperature		*Volume*
°C	K	mm^3
0	273	648
25	298	714
50	323	766
75	348	817
100	373	885

11-5/APPLICATION OF BOYLE'S AND CHARLES' LAW

If we know the volume and the pressure of a fixed mass of gas at a given temperature, then we can use Boyle's Law to calculate the volume at any other pressure, or the pressure at any other volume. For example, a 2.00 ℓ sample of a gas at a pressure of 1000 kPa is allowed to expand until its pressure drops to 300 kPa.* If the temperature remains constant, what will be the new volume?

To solve this problem, let us first list the quantities we know and those we are to find:

$$P_{\text{old}} = 1000 \text{ kPa} \qquad P_{\text{new}} = 300 \text{ kPa}$$

$$V_{\text{old}} = 2.00\ \ell \qquad V_{\text{new}} = ?$$

We know that since volume depends on the pressure, the new volume should equal the old volume multiplied by a quantity which we shall call a pressure factor:

$$V_{\text{new}} = V_{\text{old}} \times (\text{pressure factor})$$

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* *Note:* The symbol for the SI unit of pressure called the kilopascal is kPa. The normal atmospheric pressure at sea level is about 101 kPa. Laboratory barometers are usually calibrated to measure atmospheric pressure in millimetres of mercury. One millimetre of mercury exerts a pressure of 133 Pa or 0.133 kPa.

The pressure factor is the ratio of the two pressures. It is either 1000 kPa/300 kPa or 300 kPa/1000 kPa. The first of these is a number greater than one. The second is a number smaller than one. Since a gas expands as the pressure decreases, the new volume must be larger than the old volume, and the pressure factor must be a number greater than one:

$$V_{\text{new}} = 2.00\ \ell \times \frac{1000\ \text{kPa}}{300\ \text{kPa}} = 6.67\ \ell$$

If the 6.67 ℓ of gas in the previous example was originally at a temperature of 300 K and is now cooled to 150 K, what will be its new volume?

In this case the new volume is the old volume multiplied by a temperature factor:

$$V_{\text{new}} = V_{\text{old}} \times (\text{temperature factor})$$

The temperature factor is either 150 K/300 K or 300 K/150 K. Since Charles' Law tells us that gases contract on cooling, the temperature factor is a number less than one, and we can write:

$$V_{\text{new}} = 6.67\ \ell \times \frac{150\ \text{K}}{300\ \text{K}} = 3.33\ \ell$$

It is possible to combine the two laws into one mathematical operation. The question might have been worded like this: a certain mass of a gas occupies a volume of 2.00 ℓ at a pressure of 1000 kPa and a temperature of 300 K. What will be its volume at a pressure of 300 kPa and a temperature of 150 K?

We could then write:

$$V_{\text{new}} = V_{\text{old}} \times (\text{pressure factor}) \times (\text{temperature factor})$$

Using the same arguments as before we would find:

$$V_{\text{new}} = 2.00\ \ell \times \frac{1000\ \text{kPa}}{300\ \text{kPa}} \times \frac{150\ \text{K}}{300\ \text{K}} = 3.33\ \ell$$

EXERCISE/11-1

If a given mass of a gas occupies a volume of 8.4 ℓ at a pressure of 101 kPa, what is its volume at a pressure of 112 kPa and the same temperature? (*Answer:* 7.6 ℓ)

EXERCISE/11-2

If a given mass of a gas occupies a volume of 4.2 ℓ at a temperature of 0°C, what is its volume at a temperature of 91°C, if the pressure remains constant? (*Answer:* 5.6 ℓ)

EXERCISE/11-3

If a given mass of a gas occupies a volume of 6.3 ℓ at a pressure of 101 kPa and 0°C, what volume will it occupy at a pressure of 143 kPa and a temperature of 113°C? (*Answer:* 6.3 ℓ)

11-6/STANDARD TEMPERATURE AND PRESSURE

Since the volume of a gas varies with temperature and pressure, it is customary to choose some standard conditions of temperature and pressure so that the properties of different gases can be compared on a uniform basis. The choice is rather arbitrary, but usually the pressure of the atmosphere at sea level (101.3 kPa) is chosen as **standard pressure.** The freezing point of water (0°C or 273 K) is chosen as **standard temperature.** These two conditions together are usually referred to as **standard temperature and pressure,** or **STP.** Scientists do not usually measure gas volumes at STP, but they usually use Boyle's and Charles' Laws to "correct" their experimental values to standard conditions.

For example, a chemist may find that a sample of a gas occupies a volume of 43.4 cm^3 at a pressure of 97.3 kPa and a temperature of 27°C. What is its volume at STP?

We can summarize the data as:

$V_{\text{old}} = 43.4\ \text{cm}^3$ $\qquad$ $V_{\text{new}} = ?$

$P_{\text{old}} = 97.3\ \text{kPa}$ $\qquad$ $P_{\text{new}} = 101.3\ \text{kPa}$

$T_{\text{old}} = 27°\text{C} = 300\ \text{K}$ $\qquad$ $T_{\text{new}} = 0°\text{C} = 273\ \text{K}$

$$V_{\text{new}} = V_{\text{old}} \times (\text{pressure factor}) \times (\text{temperature factor})$$

Since pressure increases, volume decreases, and the pressure factor <1. Since temperature decreases, volume decreases, and the temperature factor <1.

$$\therefore \quad V_{\text{new}} = 43.4\ \text{cm}^3 \times \frac{97.3\ \text{kPa}}{101.3\ \text{kPa}} \times \frac{273\ \text{K}}{300\ \text{K}} = 37.9\ \text{cm}^3$$

EXERCISE/11-4

What is the STP volume of a sample of gas which occupies 500 cm^3 at a temperature of 100°C at a pressure of 200 kPa? (*Answer:* 723 cm^3)

11-7/DALTON'S LAW OF PARTIAL PRESSURES

We have already noted that John Dalton performed experiments with gases. He had a keen interest in the weather, and his early experiments dealt with measuring the water content of the air. In Dalton's time air was generally thought to be a compound of oxygen, nitrogen, and water. Dalton showed that air always contained 21 parts of oxygen for every 79 parts of nitrogen, but the amount of water vapor in the air varied. He concluded that air was a mixture. He demonstrated that if he added water vapor to a sample of dry air, the pressure exerted by the air increased. The increase in pressure was just equal to that exerted by the water vapor alone at the same temperature. As a result of these observations and his experiments with other gas mixtures as well, Dalton formulated the law which is now called **Dalton's Law of Partial Pressures.** The total pressure exerted by a mixture of gases is the sum of the pressures of each gas when measured alone:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$$

For example, let us add 1.00 ℓ of nitrogen with a pressure of 100 kPa to 1.00 ℓ of oxygen with a pressure of 200 kPa. If the temperature is constant and the volume remains at 1.00 ℓ, the new pressure will be 300 kPa:

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{oxygen}} = 100\ \text{kPa} + 200\ \text{kPa} = 300\ \text{kPa}$$

Dalton's studies led him to believe that a gas consisted of particles which could move throughout a volume already occupied by the particles of another gas, without being affected by the gas particles already there, provided the gases did not react. This was a reasonable assumption provided that gas particles were extremely small compared to the distances between them.

Oxygen is usually prepared by heating potassium chlorate and collecting the gas over water (Fig. 11-7). The gas collected is not pure oxygen. It is a mixture of oxygen and water vapor. We must correct for (allow for) the presence of this water vapor whenever we wish to make calculations involving the pressure or volume of a gas collected over water. Say, for example, that we have collected 400 cm^3 of oxygen over water at a temperature of 27°C (300 K) and at an atmospheric pressure of 100.0 kPa. According to Dalton's Law:

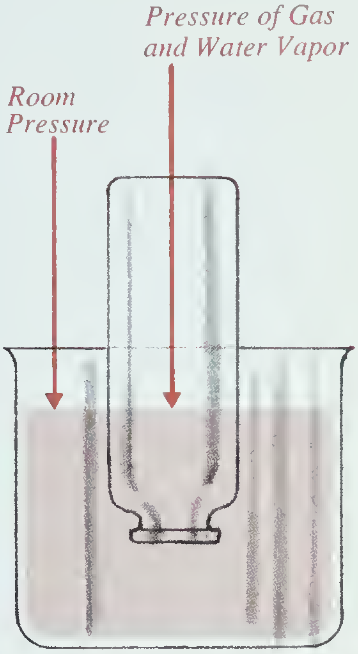


Fig. 11-7 Collecting a Gas Over Water
The pressure exerted by the wet gas (gas + water vapor) is equal to the atmospheric pressure when the water level is the same inside and outside the bottle.

$$P_{\text{total}} = P_{\text{oxygen}} + P_{\text{water vapor}}$$

or

$$P_{\text{oxygen}} = P_{\text{total}} - P_{\text{water vapor}}$$

At 27°C the vapor pressure of the water is 3.78 kPa. (See the Appendix for a table of water vapor pressures at various temperatures.)

$$\therefore\ P_{\text{oxygen}} = 100.0\text{ kPa} - 3.78\text{ kPa} = 96.2\text{ kPa}$$

What will be the volume of the dry oxygen at 27°C? According to Boyle's Law:

$$V_{\text{new}} = V_{\text{old}} \times (\text{pressure factor})$$

$$V_{\text{new}} = 400\text{ cm}^3 \times \frac{96.2\text{ kPa}}{100.0\text{ kPa}} = 384\text{ cm}^3$$

EXERCISE/11-5

A volume of 110 cm^3 of hydrogen is collected over water at a temperature of 17°C and an atmospheric pressure of 95.0 kPa. What is the volume of the dry hydrogen at STP? (*Answer:* 95.2 cm^3)

11-8/THE IDEAL GAS LAW

We can combine Boyle's Law and Charles' Law. According to Boyle's Law, volume is inversely proportional to pressure:

$$V \propto \frac{1}{P}$$

According to Charles' Law, volume is directly proportional to Kelvin temperature:

$$V \propto T$$

Volume is also directly proportional to the number of moles (n) of gas present. That is, the more gas particles that are present, the more volume the gas occupies:

$$V \propto n$$

We can combine these three statements:

$$V \propto \frac{1}{P} \cdot T \cdot n$$

or

$$V \propto \frac{nT}{P}$$

By inserting a proportionality constant, R, the expression becomes:

$$V = R \cdot \frac{nT}{P}$$

This can be rearranged as:

$$PV = nRT$$

R is the **universal gas constant.**

This equation is usually known as the **ideal gas law.** It is the simplest example of an **equation of state**—an equation that gives the relationship between the pressure, volume, temperature, and mass of a substance. Any gas that obeys the ideal gas law is called an **ideal gas.** The value of R must be determined by performing an experiment on one gas. Once its value is determined, however, it can be used in calculations involving all other gases. Experimentally, it is found that one mole of an ideal gas at 273 K and 101.3 kPa occupies a volume of 22.4 ℓ. From the ideal gas law we find:

$$R = \frac{PV}{nT} = \frac{101.3 \text{ kPa} \times 22.4 \ \ell}{1 \text{ mol} \times 273 \text{ K}} = 8.314 \text{ kPa} \cdot \ell/\text{K} \cdot \text{mol}$$

Now that we know the value of R, a knowledge of any three of the variables in the ideal gas law will enable us to calculate the value of the fourth variable.

For example, what volume is occupied by 0.0330 mol of a gas at 91°C and 50.0 kPa?

$$91°\text{C} = (273 + 91) \text{ K} = 364 \text{ K}$$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{0.0330 \text{ mol} \times 8.314 \text{ kPa} \cdot \ell/\text{K} \cdot \text{mol} \times 364 \text{ K}}{50.0 \text{ kPa}}$$

$$V = 2.00 \ \ell$$

EXERCISE/11-6

What volume is occupied by 0.0273 mol of oxygen at 27°C and 107 kPa? (*Answer:* 636 cm^3)

11-9/A MODEL FOR GASES—THE KINETIC MOLECULAR THEORY

If a bottle of concentrated ammonia is opened in a room, the odor of the ammonia will soon be detected throughout the room. This suggests that the particles of a gas can move or diffuse through another gas. A Scottish botanist, Robert Brown, discovered in 1827 that small particles suspended in a gas or a liquid are in constant zigzag motion. This so-called **Brownian motion** was assumed to be due to collisions of the gas particles with the suspended material.

We can now make assumptions concerning the nature of gases. That is, we will now develop a model by making the simplest possible assumptions.

Building on the results of Boyle, Charles, and others, as well as the results of his own experiments, John Dalton in 1801 proposed a kinetic molecular model for gases. This was refined and developed by J. C. Maxwell, a British physicist, in 1859. The basic assumptions of the model are:

1. Gases consist of extremely small particles called molecules. These molecules are so small that their volume is negligible in comparison with the volume of the container.

2. The molecules of a gas are in rapid, random, straight-line motion. They collide with each other and with the walls of the container.

3. All collisions are perfectly elastic, that is, there are no energy losses due to friction.

4. There are no attractive forces between the molecules.

5. At constant temperature, the average velocity of the molecules of all gases is a constant. If the temperature increases, the average velocity increases; if the temperature decreases, the average velocity decreases.

The last postulate was added to Dalton's theory by Maxwell. These few postulates are sufficient to explain all the observations about gases that we have discussed.

Postulate 1 explains the compressibility of gases. Since the volume of a gas is mostly empty space, it should be fairly easy to force the molecules into a smaller volume.

Postulate 3 is necessary because, if molecules lost energy during nonelastic collisions, they would gradually slow down and come to rest at the bottom of the container. This has never been observed for any gas.

The first four postulates together explain Dalton's Law of Partial Pressures. Since the distance between molecules is relatively large, it is always possible to add more gas molecules, and since there are no intermolecular forces, the gases will act independently in their collisions with the walls of the container. Thus the total pressure is equal to the sum of the individual partial pressures.

The kinetic molecular theory of gases explains Boyle's Law. Pressure must be due to the collisions of the gas molecules with the walls of the container. What would happen if the volume of the container were decreased? The gas molecules would hit the walls of the container more often, and therefore the pressure on the container walls would be increased. If the volume of the container were increased, the gas molecules would collide with the walls less frequently because they have further to travel. Therefore the pressure would be decreased.

The kinetic molecular theory also explains Charles' Law.

Consider a container which can easily expand, such as a balloon. If the balloon is heated, Postulate 5 states that the gas molecules will speed up. They will strike the wall of the balloon more often and with more force, and therefore the balloon will expand. Thus the volume of a gas increases as its temperature increases.

The kinetic molecular theory of gases predicts a relationship we have not yet mentioned, that is, the relation between pressure and temperature. Consider a gas-filled container that cannot easily expand. If the container is heated, the gas molecules will speed up. They will strike the walls of the container more frequently and with more force. Therefore the pressure will increase. The pressure of a gas increases as its temperature increases, and decreases with a decrease in temperature. The pressure exerted by a gas is directly proportional to its Kelvin temperature, provided the volume remains constant. This holds true experimentally and is called **Gay-Lussac's Law.**

Real gases do not obey the ideal gas law equation exactly. There are two main reasons for this. First, there are some attractive forces between gas molecules. This causes gas volumes to be slightly smaller than the gas law equation would predict. Second, the volume of a molecule is not completely negligible, and this causes gas volumes to be slightly larger than the gas law equation would predict. Under ordinary conditions of temperature and pressure, these effects are small and tend to cancel each other. At high pressures or low temperatures the effects are more noticeable.

QUESTIONS

1. The pressure on 220 cm^3 of a gas is 110 kPa. What will be the volume if the pressure is changed to 55.0 kPa, keeping the temperature constant?
2. The pressure on 6.00 ℓ of a gas is 200 kPa. What will be the volume if the pressure is doubled, keeping the temperature constant?
3. A gas initially at a pressure of 300 kPa is allowed to expand at constant temperature until its volume has increased from 100 to 225 cm^3. What is the final pressure?

4. The initial pressure of a gas is 150 kPa. What will be the final pressure if the gas is compressed to one half its original volume?
5. Convert the following Celsius temperatures to Kelvin temperatures: 27°C; 273°C; −162°C; 727°C.
6. Convert the following Kelvin temperatures to Celsius temperatures: 0 K; 273 K; 1000 K; 328 K; 225 K.
7. If a sample of gas measures 2.00 ℓ at 25°C, what is its volume at 50°C if the pressure remains constant?
8. If a sample of gas measures 500 cm^3 at STP, what is its volume at 101.3 kPa and 34°C?
9. A sample of a gas whose volume at 27°C is 127 cm^3 is heated at constant pressure until its volume becomes 317 cm^3. What is the final Celsius temperature of the gas?
10. Correct the following volumes to STP:
    - **(a)** 24.5 ℓ at 25°C and 104 kPa.
    - **(b)** 1000 mm^3 at 100°C and 75.0 kPa.
    - **(c)** 45.0 cm^3 at −40°C and 140 kPa.
11. A 200 cm^3 sample of gas is collected at 50.0 kPa and a temperature of 271°C. What volume would this gas occupy at 100 kPa and a temperature of −1°C?
12. Air is a mixture of many gases. The partial pressure of nitrogen is 80.0 kPa. The partial pressure of oxygen is 20.3 kPa. Atmospheric pressure is 101.3 kPa. What is the partial pressure due to all the other gases present in air?
13. If oxygen is collected over water at 18°C and standard pressure, what is the partial pressure of the oxygen when the water level inside the flask equals the water level outside the flask?
14. A student collects 45.0 cm^3 of hydrogen over water at 19°C and 104.2 kPa. What is this volume at STP?
15. If 80.0 cm^3 of oxygen are collected over water at 20°C and 95.0 kPa, what volume will the oxygen occupy at STP?
16. Calculate the volume occupied by half a mole of carbon dioxide gas at 33.0 kPa and −35°C.
17. How many moles of gas are there in a sample that occupies a volume of 570 cm^3 at 78°C and a pressure of 103 kPa?
18. One litre of a gas at 100 kPa and −20°C is compressed to half a litre at 40°C. What is its final pressure?

19. A sample of a gas occupies a volume of 119 cm^3 at STP. To what temperature must the sample be heated to occupy a volume of 92 cm^3 at 225 kPa?
20. A gas mixture consists of 60.0% argon, 30.0% neon, and 10.0% krypton by volume. If the pressure of this gas mixture is 80.0 kPa, what is the partial pressure of each of the gases?
21. If 2.00 ℓ of dry nitrogen at STP are collected over water at 20°C and 95.0 kPa, what volume will be occupied by the wet gas?
22. What volume would 250 cm^3 of pure, dry oxygen at STP occupy if collected over water at 20°C and at an atmospheric pressure of 98.0 kPa?
23. If 450 cm^3 of hydrogen at STP occupy 511 cm^3 when collected over water at 18°C, what is the atmospheric pressure?

12

GASES AND THE MOLE

When you have finished studying this chapter, you should be able to attain the following objectives:

1. State Gay-Lussac's Law of Combining Volumes and Avogadro's hypothesis.
2. Using the arguments of Cannizzaro, calculate the numbers of atoms in each molecule of reactants and products of gas phase reactions.
3. Given the pressure, volume, and temperature of a fixed mass of gas, calculate its molar mass and molecular mass.
4. Perform mass-volume and volume-volume calculations for reactions involving gases.

12-1/DALTON'S PROBLEM

Dalton's atomic theory suggested that atoms of different elements should have different atomic masses. The question naturally arose, what is the mass of an atom?

Since it was impossible to weigh individual atoms, Dalton and his contemporaries had to use data obtained from chemical analyses of various compounds. For example, water was found to contain hydrogen and oxygen in a ratio of one gram of hydrogen to eight grams of oxygen. Dalton had no way of knowing how many atoms of hydrogen were combined with one atom of oxygen in a molecule of water. He arbitrarily assumed that there was one atom of each element in water, and assigned water the formula HO. This gave oxygen an atomic mass eight times that of a hydrogen atom. If the formula were HO_2, then an oxygen atom had only four times the mass of a hydrogen atom, and so on. Dalton recognized this, but having nothing better to go on, he stuck to his assumption that equal numbers of atoms react to form compounds. He analyzed many compounds and constructed a table of relative atomic masses. Many of his numbers were wrong, of course, because of his wrong assumption. It was therefore necessary to modify the model. The key was provided several years later as the result of a study of chemical reactions of gases.

12-2/GAY-LUSSAC'S LAW OF COMBINING VOLUMES

In 1805 Joseph Louis Gay-Lussac, a French chemist, and Alexander von Humboldt, a German scientist, worked together to measure the exact proportions by volume in which gases react with each other. They found that, no matter which gas was in excess, one volume of oxygen always reacted with two volumes of hydrogen to form two volumes of water vapor. The experimental error was less than 0.1%. Gay-Lussac investigated other gas reactions and found that all gases combine in simple whole-number ratios by volume—1:1, 2:1, 1:2, 1:3, 3:1, 3:2, etc. Also, the volumes of the product gases were in simple whole-number ratios to the volumes of the reactants. We can summarize some of his results as follows:

Hydrogen + Oxygen → Water Ratio = 2:1:2

$$\boxed{\text{1 vol}}\boxed{\text{1 vol}} \qquad \boxed{\text{1 vol}} \qquad \boxed{\text{1 vol}}\boxed{\text{1 vol}}$$

Ammonia + Hydrogen Chloride → Solid Ammonium Chloride
Ratio = 1:1

$$\boxed{\text{1 vol}} \qquad \boxed{\text{1 vol}}$$

Nitrogen + Oxygen → Nitrogen(I) Oxide Ratio = 2:1:2

$\boxed{1\text{ vol}}\boxed{1\text{ vol}}\quad\boxed{1\text{ vol}}\quad\boxed{1\text{ vol}}\boxed{1\text{ vol}}$

Nitrogen + Oxygen → Nitrogen (II) Oxide Ratio = 1:1:2

$\boxed{1\text{ vol}}\quad\boxed{1\text{ vol}}\quad\boxed{1\text{ vol}}\boxed{1\text{ vol}}$

These findings can be summarized in **Gay-Lussac's Law of Combining Volumes:** when gases react, they do so in simple, whole-number ratios by volume.

Gay-Lussac knew that the particles of a gas were small in relation to the total volume of the container. He supposed that the effective volume of a gas particle (the total volume divided by the total number of particles) might be the same for all gases. If this were so, and if the gas particles were atoms, then equal volumes of gases would contain equal numbers of atoms. In this case one could determine relative atomic masses by measuring equal volumes of gases under identical conditions.

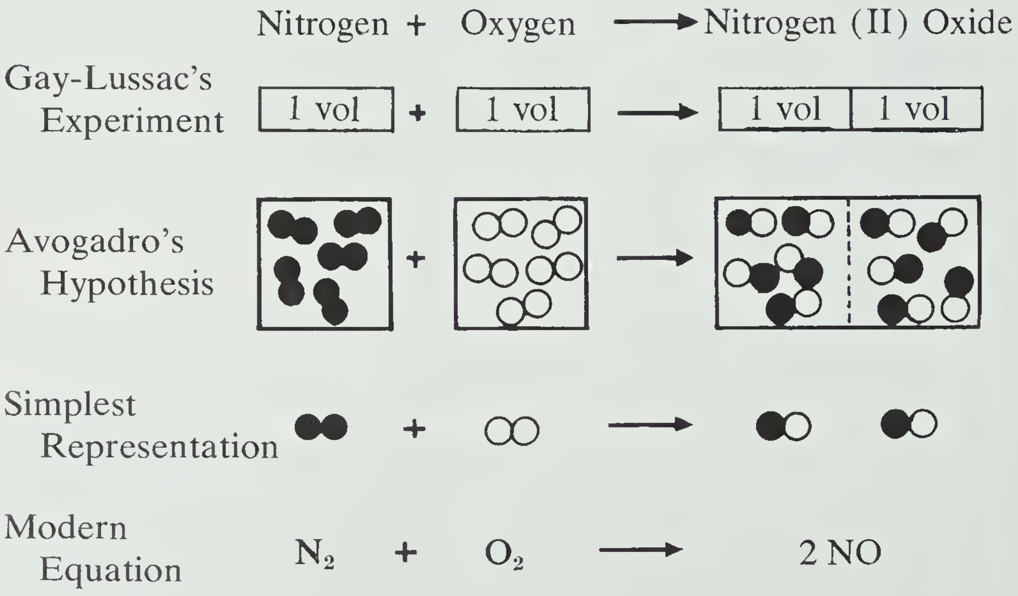
Dalton rejected Gay-Lussac's conclusions for two reasons. He thought (erroneously) that Gay-Lussac's data were less accurate than his own. Also, he argued (correctly) that equal volumes of a gas did not contain equal numbers of atoms. For if that were the case, then the reaction between 1 volume of nitrogen "atoms" and 1 volume of oxygen "atoms" should give 1 volume of nitrogen(II) oxide "atoms." Gay-Lussac had found 2 volumes of nitrogen(II) oxide were formed. Someone was wrong.

12-3/AVOGADRO'S HYPOTHESIS

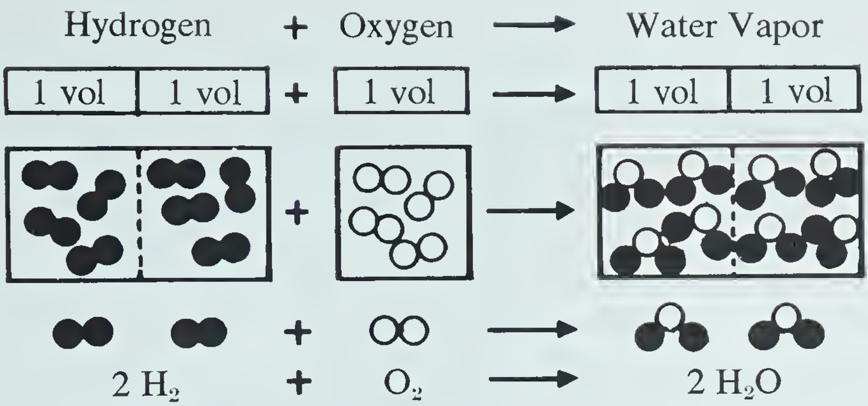
In 1811 Amadeo Avogadro, an Italian physicist, finally solved the problem. He suggested that the smallest particles of gases were not atoms but molecules. These molecules could contain one, two, three, or more atoms, depending on the individual gases. His rewording of Gay-Lussac's original guess is now called **Avogadro's hypothesis:** equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. That is, a litre of nitrogen contains the same number of molecules as a litre of oxygen at the same temperature and pressure.

At this time Jöns Jakob Berzelius, the great Swedish chemist, had developed a theory that atoms in molecules are held together by attractive forces between oppositely charged atoms. He did not believe that atoms of the same element could possibly pair up, and his influence was so great that no attention was paid to Avogadro's hypothesis. It was not until 1860, twelve years after Berzelius' death and four years after Avogadro's death, when Avogadro's student Stanislao Cannizzaro made such a clear and forceful presentation to a meeting of chemists at Karlsruhe, that Avogadro's hypothesis gained general acceptance.

Gay-Lussac's Law of Combining Volumes now made sense. For if one litre of nitrogen and one litre of oxygen combined to give two litres of nitrogen(II) oxide, then one molecule of nitrogen reacted with one molecule of oxygen to form two molecules of the oxide, each of which contained one atom of nitrogen and one atom of oxygen. These two nitrogen atoms must have come from a nitrogen molecule which contained two atoms, and the two oxygen atoms must have come from an oxygen molecule which also consisted of two atoms. The arguments can be summarized:



In the reaction of hydrogen with oxygen to form water, similar arguments lead to the conclusion that a hydrogen molecule is diatomic and the formula for water is H_2O:



EXERCISE/12-1

Review the arguments which show that a molecule of nitrogen(I) oxide contains two atoms of nitrogen and one atom of oxygen.

Avogadro's concept of a molecule consisting of one or more atoms marked an important turning point in the history of chemistry. From this point on chemistry developed rapidly as a science.

We should not leave Avogadro without asking why his ideas were rejected for fifty years even though they were correct. One reason may be that he offered no experimental evidence to support his hypothesis. Perhaps a more important reason is that any hypothesis or theory must not only explain a limited set of experimental data, but it must lead to the discovery of new facts and relationships. This was not possible in 1811, and hence a correct explanation was ignored for fifty years.

12-4/MOLAR VOLUME AND THE IDEAL GAS LAW

In Chapter 10 we learned that a mole of any gas contains Avogadro's number of molecules. Since equal volumes of gases contain equal numbers of molecules under identical conditions, one mole of a gas (6.02×10^{23} molecules) should occupy some definite volume under specified conditions. It has been determined that at STP the volume occupied by one mole of any gas is 22.4 ℓ. This volume is called its **molar volume.**

Since a mole of any gas occupies 22.4 ℓ at STP, it now becomes easy to determine the molar mass of any substance, provided it can be converted into a gas. All that we have to do is measure the mass of a given volume of the gas at STP, and then calculate what would be the mass of 22.4 ℓ of the gas.

For example, 2.00 g of liquid benzene can be converted into a vapor which occupies 903 cm^3 at 150°C and 99.7 kPa. What is its approximate molar mass?

There are two ways to solve this problem.

Solution 1

First, find the volume of the gas at STP.

$V_{\text{old}} = 0.903\ \ell$ $\quad V_{\text{new}} = ?$

$P_{\text{old}} = 99.7\ \text{kPa}$ $\quad P_{\text{new}} = 101.3\ \text{kPa}$

$T_{\text{old}} = 150°\text{C} = 423\ \text{K}$ $\quad T_{\text{new}} = 0°\text{C} = 273\ \text{K}$

$$\therefore\ V_{\text{new}} = 0.903\ \ell \times \frac{99.7\ \text{kPa}}{101.3\ \text{kPa}} \times \frac{273\ \text{K}}{423\ \text{K}} = 0.574\ \ell$$

If 0.574 ℓ of benzene have a mass of 2.00 g, then 1.00 ℓ of benzene has a mass of 2.00/0.574 g, and 22.4 ℓ of benzene have a mass of 22.4×2.00/0.574 = 78.0 g.
∴ The molar mass of benzene is 78.0 g.

Solution 2

We can use the ideal gas equation.

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{99.7\ \text{kPa} \times 0.903\ \ell}{8.314\ \text{kPa} \cdot \ell/\text{K} \cdot \text{mol} \times 423\ \text{K}} = 0.0256\ \text{mol}$$

If 0.0256 mol of benzene have a mass of 2.00 g, then 1.00 mol of benzene has a mass of 2.00/0.0256 = 78.1 g.
∴ The molar mass of benzene is 78.1 g.

EXERCISE/12-2

What is the molar mass of a vapor, 0.842 g of which occupy 450 cm^3 at a pressure of 100 kPa and a temperature of 100°C? (*Answer:* 58.0 g)

12-5/MASS-VOLUME RELATIONSHIPS IN REACTIONS INVOLVING GASES

One mole of any gas occupies 22.4 ℓ at STP. We can use this knowledge to calculate the volume of gases involved in chemical reactions. If any volumes are not at STP, they can be corrected to STP by using Boyle's and Charles' Laws.

SAMPLE PROBLEM/12-1

Calculate the volumes of hydrogen and oxygen at STP that can be obtained by electrolysis of 50.0 g of water.

Balanced Equation:

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

2 mol	2 mol	1 mol
2(18.0 g)	2(22.4 ℓ)	22.4 ℓ
36.0 g	44.8 ℓ	

36.0 g water produce 44.8 ℓ hydrogen

1.00 g water produces 44.8/36.0 ℓ hydrogen

50.0 g water produce 44.8/36.0 × 50.0 = 62.2 ℓ hydrogen at STP

Similarly, 50.0 g water produce 22.4/36.0 × 50.0 = 31.1 ℓ oxygen at STP

SAMPLE PROBLEM/12-2

What would have been the volumes of hydrogen and oxygen in the previous question if they had been collected at 93.0 kPa and 26°C?

$$\text{Volume of } H_2 = 62.2\ \ell \times \frac{101.3\ \text{kPa}}{93.0\ \text{kPa}} \times \frac{299\ \text{K}}{273\ \text{K}} = 74.2\ \ell$$

$$\text{Volume of } O_2 = 31.1\ \ell \times \frac{101.3\ \text{kPa}}{93.0\ \text{kPa}} \times \frac{299\ \text{K}}{273\ \text{K}} = 37.1\ \ell$$

SAMPLE PROBLEM/12-3

What volume of oxygen is required to burn 10.0 ℓ of acetylene gas, C_2H_2, to carbon dioxide and water, if all gases are at the same temperature and pressure? What is the total volume of gaseous products?

Unbalanced Equation:

$$C_2H_2(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Balanced Equation:

$2\,C_2H_2(g)$	$+\ 5\,O_2(g)$	$\rightarrow 4\,CO_2(g)$	$+\ 2\,H_2O(g)$
2 mol	5 mol	4 mol	2 mol
2 volumes	5 volumes	4 volumes	2 volumes

2 ℓ C_2H_2 requires 5 ℓ O_2.

1 ℓ C_2H_2 requires 5/2 ℓ O_2.

$\therefore$ 10.0 ℓ C_2H_2 require $10.0 \times 5/2 = 25.0$ ℓ O_2.

The 2 mol of C_2H_2 will give a total of 6 mol of gaseous products. So the total volume of products is three times the volume of C_2H_2, or $3 \times 10.0 = 30.0$ ℓ.

SAMPLE PROBLEM/12-4

How many grams of magnesium are required to react with hydrochloric acid to produce 300 cm^3 of hydrogen gas at 25°C and 105 kPa? The equation is:

$$Mg + 2\,HCl \rightarrow MgCl_2 + H_2$$

Solution 1

$$\begin{array}{lcl} Mg + 2\,HCl \rightarrow MgCl_2 + & H_2 \\ 1 \text{ mol} & 1 \text{ mol} \\ 24.3 \text{ g} & 22.4\ \ell \end{array}$$

First convert the volume of hydrogen to STP:

$$V_{new} = 300\ cm^3 \times \frac{273\ K}{298\ K} \times \frac{105\ kPa}{101.3\ kPa} = 285\ cm^3 = 0.285\ \ell$$

22.4 ℓ of hydrogen require 24.3 g of magnesium

1.00 ℓ of hydrogen requires 24.3/22.4 g of magnesium

0.285 ℓ of hydrogen require $0.285 \times 24.3/22.4$
$= 0.309$ g of magnesium

Therefore 0.309 g of magnesium are required to react with hydrochloric acid to produce 300 cm^3 of hydrogen gas at 25°C and 105 kPa.

Solution 2

We can use the ideal gas equation:

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{105\ kPa \times 0.300\ \ell}{8.314\ kPa \cdot \ell/K \cdot mol \times 298\ K} = 0.0127\ mol$$

0.0127 mol of hydrogen are produced by 0.0127 mol of magnesium.

0.0127 mol of magnesium = 0.0127 mol Mg × 24.3 g/mol
= 0.309 g Mg

SAMPLE PROBLEM/12-5

Decomposition of potassium chlorate produces 400 cm^3 of oxygen collected over water at 97.0 kPa and 20°C. How many grams of potassium chlorate are required?

Solution 1

$$
\begin{array}{ll}
2\,KClO_3 \xrightarrow{\Delta} & 2\,KCl + 3\,O_2 \\
2\text{ mol} & 3\text{ mol} \\
2(122.6) & 3(22.4) \\
245\text{ g} & 67.2\,\ell
\end{array}
$$

First, find the partial pressure of the oxygen. The vapor pressure of water at 20°C is 2.3 kPa.

$$\therefore P_{\text{oxygen}} = 97.0\text{ kPa} - 2.3\text{ kPa} = 94.7\text{ kPa}.$$

Then convert the volume to STP:

$$V = 400\text{ cm}^3 \times \frac{94.7\text{ kPa}}{101.3\text{ kPa}} \times \frac{273\text{ K}}{293\text{ K}} = 348\text{ cm}^3 = 0.348\,\ell$$

67.2 ℓ of oxygen are formed from 245 g of $KClO_3$

1.00 ℓ of oxygen is formed from 245/67.2 g of $KClO_3$

0.348 ℓ of oxygen are formed from $0.348 \times 245/67.2 = 1.27$ g of $KClO_3$

$\therefore$ 1.27 g of $KClO_3$ are required.

Solution 2

After finding the partial pressure of the oxygen, use the ideal gas law to find the number of moles of oxygen.

$$n = \frac{PV}{RT} = \frac{94.7\text{ kPa} \times 0.400\,\ell}{8.314\text{ kPa}\cdot\ell/\text{K}\cdot\text{mol} \times 293\text{ K}} = 0.0156\text{ mol}$$

3 mol of oxygen are formed from 245 g of $KClO_3$

1 mol of oxygen is formed from 245/3 g of $KClO_3$

0.0156 mol of oxygen are formed from $0.0156 \times 245/3 =$ 1.27 g of $KClO_3$

EXERCISE/12-3

How many litres of oxygen are required to burn 11 ℓ of hydrogen? How many litres of water vapor will be formed? (*Answers:* 5.5 ℓ; 11 ℓ)

EXERCISE/12-4

How many litres of hydrogen gas, measured at 23°C and 103 kPa, can be obtained by the reaction of 75.0 g of aluminum with excess sulfuric acid? The equation for the reaction is:

$$2\ Al + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2$$

(*Answer:* 99.5 ℓ)

EXERCISE/12-5

What volume of hydrogen, collected over water at 25°C and 97.0 kPa, will be formed by the reaction of 18.0 g of calcium hydride with water according to the equation:

$$CaH_2 + 2\ H_2O \rightarrow Ca(OH)_2 + 2\ H_2?$$

(*Answer:* 22.6 ℓ)

QUESTIONS

1. A compound containing only carbon and hydrogen atoms is found on analysis to consist of 3.00 g of carbon for every 1.00 g of hydrogen. If a hydrogen atom is arbitrarily assigned a mass of 1 u, what is the atomic mass of a carbon atom if the formula of the compound is CH? If the formula is CH_2? C_2H_3?
2. If you know that the atomic mass of a carbon atom is 12 u, what is a reasonable formula for the compound of Question 1?
3. One litre of nitrogen reacts with 3 ℓ of hydrogen to form 2 ℓ of ammonia, all at the same conditions of temperature and pressure. Review the arguments Gay-Lussac would use to show that hydrogen and nitrogen are diatomic and that ammonia has the formula NH_3.
4. It is found that 50 cm^3 of arsenic vapor reacts with 300 cm^3 of hydrogen to produce 200 cm^3 of a gaseous product. If each product molecule contains one arsenic atom, how many atoms are in a molecule of arsenic? What is the formula of the product?
5. When 2 ℓ of a gaseous compound containing only carbon, hydrogen, and nitrogen are burned, the products consist of 2 ℓ of carbon dioxide, 5 ℓ of water vapor, and 1 ℓ of nitrogen gas. What is the formula of the compound?
6. You are given 1.00 g of hydrogen gas. (a) How many moles of hydrogen are in this sample? (b) How many molecules? (c) How many atoms? (d) What is the volume of this gas at STP?
7. If 91.0 g of a gas occupy 14.0 ℓ at STP, what is the molar mass of the gas?
8. How many moles of a gas are present in 560 cm^3 of a gas at 500 kPa and 180°C?
9. What is the molecular mass of a compound if 560 cm^3 has a mass of 1.10 g at STP?
10. What is the molar mass of a gas if 2.40 g of the gas occupy a volume of 2.80 ℓ at 180°C and 50.0 kPa?
11. What is the molar mass of a compound that has a density of 1.87 g/ℓ at STP?
12. Tungsten metal is prepared by heating tungsten trioxide with hydrogen gas according to the equation:

$$WO_3(s) + 3\ H_2(g) \rightarrow W(s) + 3\ H_2O(g)$$

What volume of hydrogen at STP is required to prepare one mole of tungsten by this method?

13. How many grams of zinc are required to prepare 6.00 ℓ of hydrogen at STP? The reaction is:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2(g)$$

14. Aluminum oxide is decomposed on electrolysis according to the equation:

$$2\ Al_2O_3 \rightarrow 4\ Al + 3\ O_2(g)$$

What volume of oxygen at STP is obtained by electrolysis of 40.8 g of aluminum oxide?

15. Acetylene is prepared in the laboratory by dropping water on pieces of calcium carbide:

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2(g)$$

What volume of dry acetylene at STP can be prepared from 1.00 g of calcium carbide?

16. Zirconium metal and chlorine gas react to form zirconium(IV) chloride:

$$Zr + 2\ Cl_2 \rightarrow ZrCl_4(g)$$

What volume of chlorine gas must be used at 350°C and 50.0 kPa to produce 200 cm^3 of $ZrCl_4$ under the same conditions? What mass of zirconium will be used up?

17. What volume of oxygen at STP is required to react with one mole of ammonia according to the equation:

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

How many litres of NO are formed at STP?

18. Nitric acid is made commercially by the platinum-catalyzed air oxidation of ammonia. The first step in the sequence is the reaction given in Question 17. How many litres of air (21.0% oxygen) at 27°C and 100 kPa are needed to convert 50.0 kg of ammonia to NO by this method?
19. What volume of oxygen at STP is necessary to burn 14 g of methane, CH_4, to carbon dioxide and water?

13

ORGANIC CHEMISTRY

All chemical substances can be divided into two classes. One class includes sugar, starch, butter, rubber, paper, and penicillin. These substances are *organic* substances. The other class includes rocks, glass, air, water, salts, and metals. They are called *inorganic* substances. This chapter will deal with *organic* compounds.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Define organic chemistry.
2. State the structural features of each of the following types of compounds and give an example of each: hydrocarbons, alkanes, alkenes, alkynes, alkadienes, cycloalkanes, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, mercaptans, amines, amides.
3. Given a list of structural formulas, choose those which contain one or more of the structural groupings listed in the preceding objective.
4. Define and give an example of each of the following: saturated hydrocarbon, homologous series, structural formula, isomers, substitution reaction, cracking, unsaturated hydrocarbon, addition reaction, resonance hybrid, alkyl group, functional group, fermentation, polymer, condensation polymer, addition polymer, free radical.

5. Describe the structure of an aromatic hydrocarbon as a resonance hybrid of two or more contributing structures.
6. Write equations for organic reactions such as: preparation and reactions of alkanes, alkenes, and alkynes; preparation of ethanol; ionization and esterification of carboxylic acids; formation of addition polymers and condensation polymers.
7. Write the steps involved in the addition polymerization of an alkene and also in the formation of a condensation polymer.

13-1/INTRODUCTION

The division into organic and inorganic substances was first used in 1807 by Jöns Jakob Berzelius, a Swedish chemist. At that time one thing seemed clear: some substances had been present since the earth began, but other substances existed only because they had been manufactured by living things. Berzelius called substances that were obtained from living organisms, organic. Everything else he called inorganic.

At first this seemed to be a useful division. Organic materials differed from inorganic materials in several ways. For example, organic materials seemed to be more easily decomposed than inorganic substances. One could heat salt (inorganic) until it was red hot and melted; however, the salt was unchanged chemically. If sugar (organic) was heated, it would turn black and decompose. Cooling would not restore its original properties.

Another difference was that organic substances could be converted to inorganic substances. However, Berzelius believed that there was no way to convert an inorganic substance to an organic substance. It was believed that organic substances could be the products of living things only. At that time, chemists thought that a mysterious "vital force" was necessary to produce organic compounds. They believed that this "vital force" was present only in living things, and they did not expect to be able to prepare organic compounds in the laboratory.

In 1827 Friedrich Wöhler, a German chemist, accidentally found that by heating an inorganic compound called ammonium cyanate, he could prepare urea. Urea is an organic substance, one of the waste products of the body which is eliminated in urine. Wöhler had converted an inorganic compound into an organic compound. He repeated his experiment over and over before he dared to announce his results to the world. Before long, other chemists had prepared a number of other organic substances in the laboratory.

While the idea of a "vital force" later proved to be incorrect, the concept of organic substances was retained. Organic substances were found to be made up of molecules which always contained at least one carbon atom. Normally, inorganic compounds did not contain carbon. However, carbon dioxide, carbon monoxide, and the carbonate salts are examples of substances which do contain carbon but are considered to be inorganic.

Thus, **organic chemistry** is the study of carbon-containing compounds. Inorganic chemistry is the study of the compounds of the rest of the elements.

Organic compounds contain few elements. The atoms in most organic compounds are limited to carbon, hydrogen, nitrogen, oxygen, and sulfur. Despite this limitation, there are more organic compounds than inorganic compounds. The main reason for this stems from the fact that carbon atoms are the only atoms that can effectively join together in long chains or numerous rings. Thus, organic compounds are often made up of molecules containing hundreds or even thousands of atoms. The great variety of organic compounds is due to the ability of carbon atoms to bond to themselves.

13-2/TETRAVALENT CARBON

Carbon is element No. 6. Its ground state electronic configuration is:

$$1s^2 2s^2 2p^2$$

It appears then that before bonding, one of the $2s$ electrons is promoted to an empty $2p$ orbital:

$$\begin{array}{llcll} 2p & \underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ } & & 2p & \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow} \\ 2s & \underline{\uparrow\downarrow} & \longrightarrow & 2s & \underline{\uparrow} \\ 1s & \underline{\uparrow\downarrow} & & 1s & \underline{\uparrow\downarrow} \end{array}$$

This excited carbon atom has 4 unpaired electrons in its outer orbitals. The electron dot symbol for carbon is:

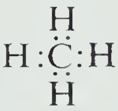
$$\cdot\dot{\underset{\cdot}{C}}\cdot$$

A carbon atom has four valence electrons, and it must form four bonds. Carbon is tetravalent.

13-3/THE ALKANES

One of the most important classes of organic compounds is the **hydrocarbons.** These compounds are made up of carbon and hydrogen atoms only. A hydrogen atom has only one valence electron, and it can form only one bond. The hydrocarbons are subdivided into a number of families. The first of the families is called the **alkane** family.

Four hydrogen atoms are required to bond with a single carbon atom:



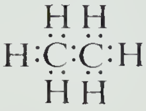
$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H \\ H \end{array}$$

This compound is the first member of the alkane family. It is called methane. Alkanes are called **saturated** hydrocarbons because the carbon atoms are bonded to as many hydrogen atoms as possible. In alkanes, the carbon atoms are saturated with hydrogen atoms.

Two carbon atoms can bond together:

$$\cdot\dot{\underset{\cdot}{C}}:\dot{\underset{\cdot}{C}}\cdot$$

By counting the unpaired electrons in this two-carbon system, one can see that 6 electrons are ready to bond to 6 hydrogen atoms. A second member of the series of alkanes is formed when 6 hydrogen atoms bond to the 2 carbon atoms:



$$\begin{array}{c} H\;H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H \\ H\;H \end{array}$$

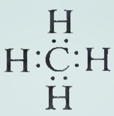
This compound, C_2H_6, is called ethane. In methane and ethane single bonding (two-electron bonds) is the rule. This is true for every alkane. All bonds are single bonds in alkane molecules.

The next alkane is the familiar fuel, propane. It has 3 carbon atoms per molecule, and its molecular formula is C_3H_8. The formula of every alkane differs from the alkane before it by a constant CH_2. The first three alkanes are CH_4, C_2H_6, and C_3H_8. In fact, one can write a general formula for the alkanes. The formula is C_nH_{2n+2}. The alkanes form a homologous series. A **homologous series** is one in which the formula of each member differs from the preceding member in a consistent regular way, such as by a CH_2 unit.

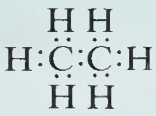
The following is a list of the simple alkanes and their molecular formulas:

methane	CH_4	hexane	C_6H_{14}
ethane	C_2H_6	heptane	C_7H_{16}
propane	C_3H_8	octane	C_8H_{18}
butane	C_4H_{10}	nonane	C_9H_{20}
pentane	C_5H_{12}	decane	$C_{10}H_{22}$

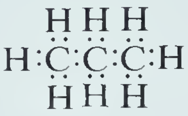
Note that the name of each alkane ends with the suffix "-ane." This indicates that the molecule contains only single bonds. The molecular formulas show the total number of carbon atoms and hydrogen atoms in each molecule. For methane, ethane, and propane the molecular formulas are sufficient because in each case the carbons and hydrogens can be assembled in only one way:



$$\begin{array}{ccc} & \mathrm{H} & \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & :\mathrm{H} \\ & \mathrm{H} & \end{array}$$

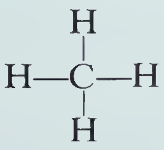


$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & :\mathrm{H} \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

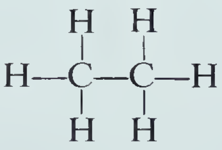


$$\begin{array}{ccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ \mathrm{H}: & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & : & \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{C}}} & :\mathrm{H} \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

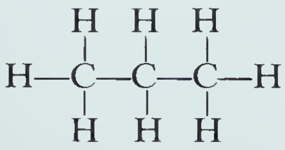
These more detailed formulas are called **structural formulas** since they show more about the structure of the molecule. A dash often represents each electron dot pair, so that the usual structural formulas for methane, ethane, and propane are:



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{H} \\ & | & \\ & \mathrm{H} & \end{array}$$



$$\begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{H} \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$



$$\begin{array}{ccccccc} & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \\ & | & & | & & | & \\ \mathrm{H}- & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & -\mathrm{H} \\ & | & & | & & | & \\ & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

There is only one structure for methane, one for ethane, and one for propane.

Before going any further, it is well to take a closer look at the structure of methane as an example of a carbon atom with four single bonds. It appears from the structural formula that all carbon-hydrogen bonds are at 90° angles to one another. This is unfortunate and it is due to the limitations imposed by trying to draw a three-dimensional object in two dimensions. Actually the structure of methane is three-dimensional, with the four C—H bonds pointing from the carbon atom toward the corners of a regular tetrahedron (Fig. 13-1A).

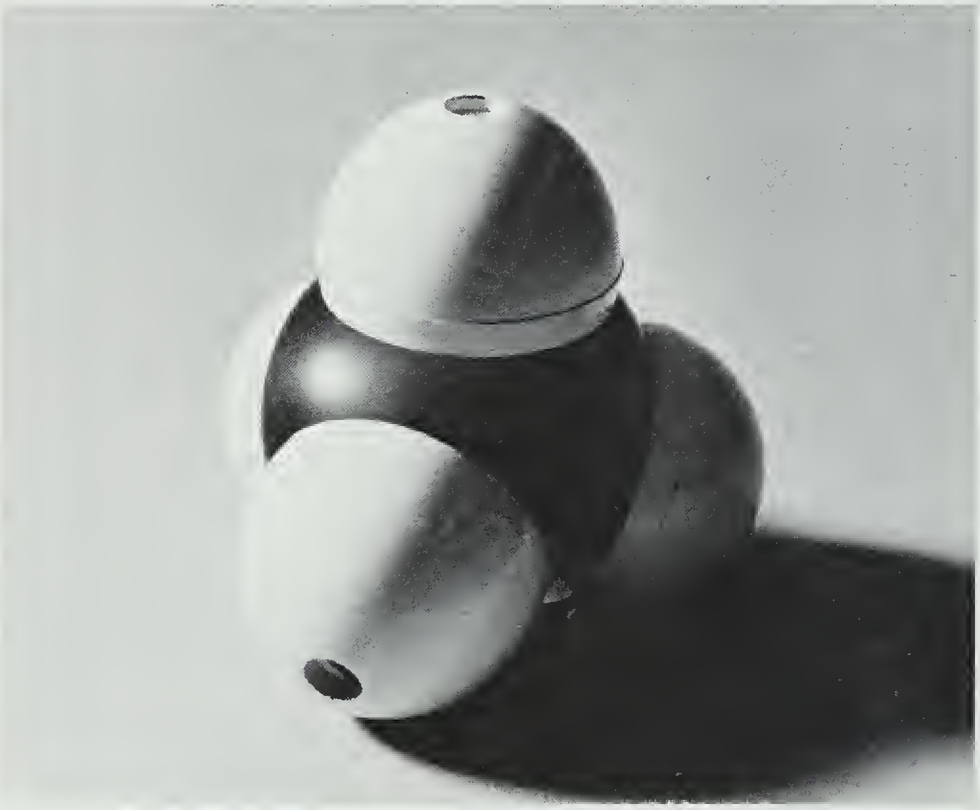


Fig. 13-1A Model of Methane (CH_4)

In Fig. 13-1B the carbon atom and the two hydrogens attached to it by solid lines are in the plane of the paper. The dotted line indicates that its hydrogen atom is behind the plane of the paper, and the wedge indicates that its hydrogen atom is in front of the plane of the paper. All carbon-hydrogen bond angles are about 109°. The maximum stability of the methane molecule occurs when it has a tetrahedral rather than a planar structure.

In the alkanes, each carbon atom always forms four single bonds which are at 109° to one another. Usually the structural

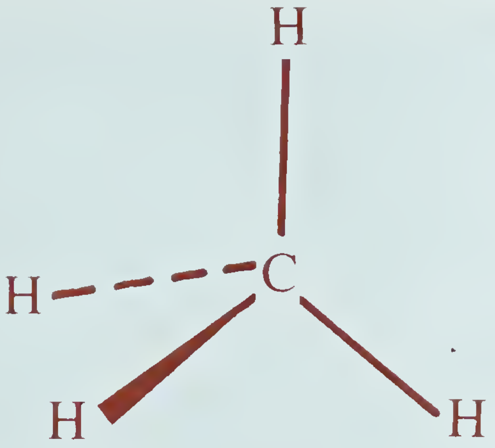
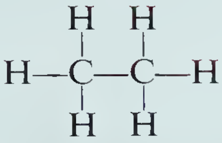


Fig. 13-1B Perspective Diagram of Methane

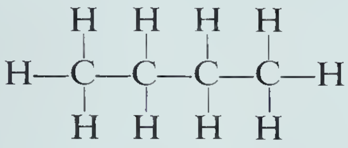
formula for ethane is drawn:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

However, we recognize that the molecule is not really planar, and the bonds are not at 90° to one another (Fig. 13-2).

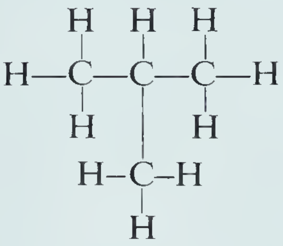
In the case of butane, C_4H_{10}, an interesting possibility occurs. Two legitimate structural formulas fit the one molecular formula. They are:



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

n-butane

and



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & | & & H & & \\ & & H & - & C & - & H & & \\ & & & & | & & & & \\ & & & & H & & & & \end{array}$$

isobutane

In both structures each carbon atom has four bonds, and each hydrogen atom has one bond. These two formulas represent butane molecules. The molecules are isomers. Molecules are **isomers** if they have the same molecular formula but different structural formulas. However, *isomers have different physical and chemical properties.*

The two isomers of butane differ in the way that the four carbon atoms and ten hydrogen atoms are assembled. The first isomer is called normal butane or *n*-butane. The "*n*" means that the carbon atoms are joined in one continuous chain. The second isomer is called isobutane. It is a branched-chain hydrocarbon.

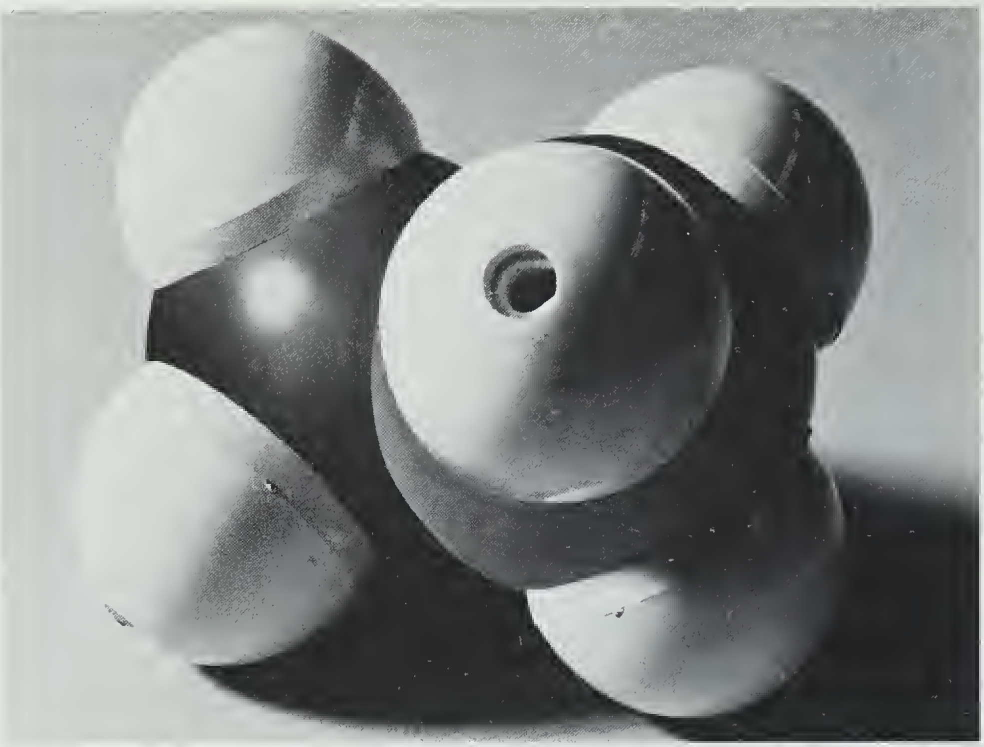
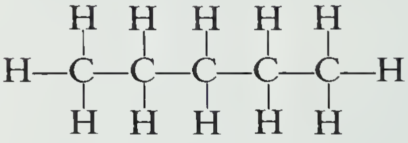


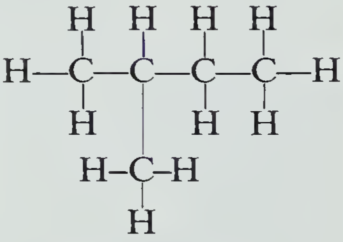
Fig. 13-2 Model of Ethane (C_2H_6)

Pentane, C_5H_{12}, has three isomers. Their structural formulas are:

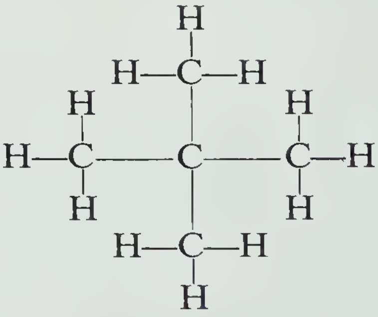


$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

n-pentane



isopentane



neopentane

Models of the butane and pentane isomers are illustrated in Figs. 13-3A and 13-3B. There are *five* isomers of hexane, *nine* isomers of heptane, and about *4 billion* isomers of $C_{30}H_{62}$.

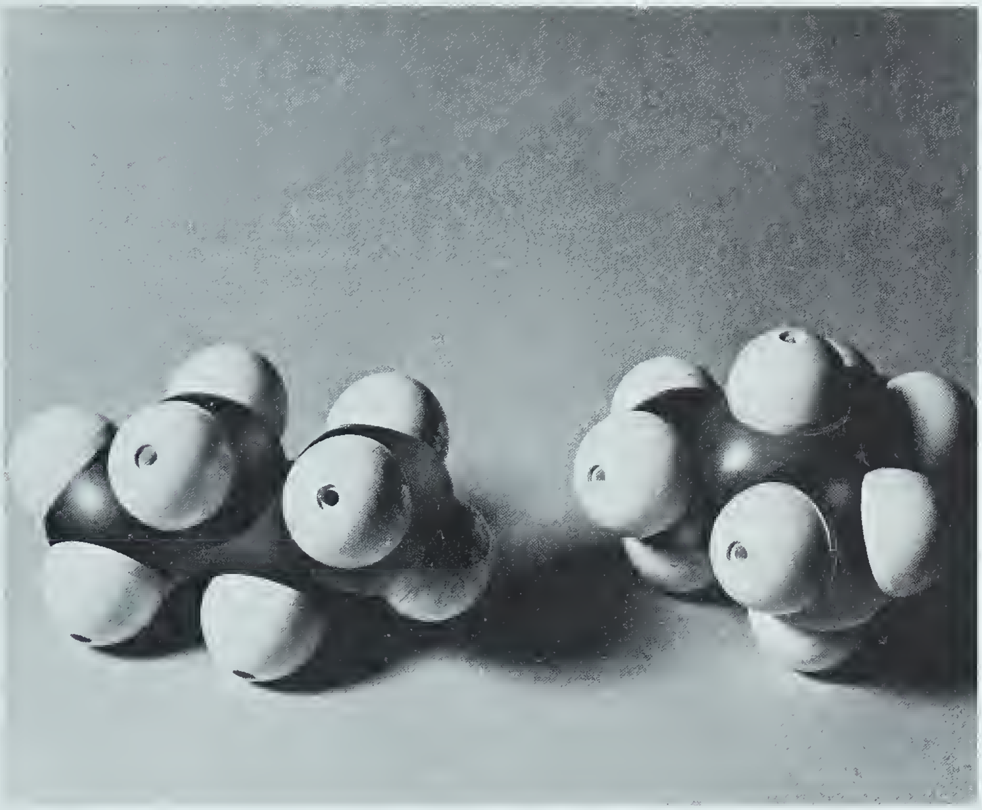


Fig. 13-3A Models of the Butane (C_4H_{10}) Isomers

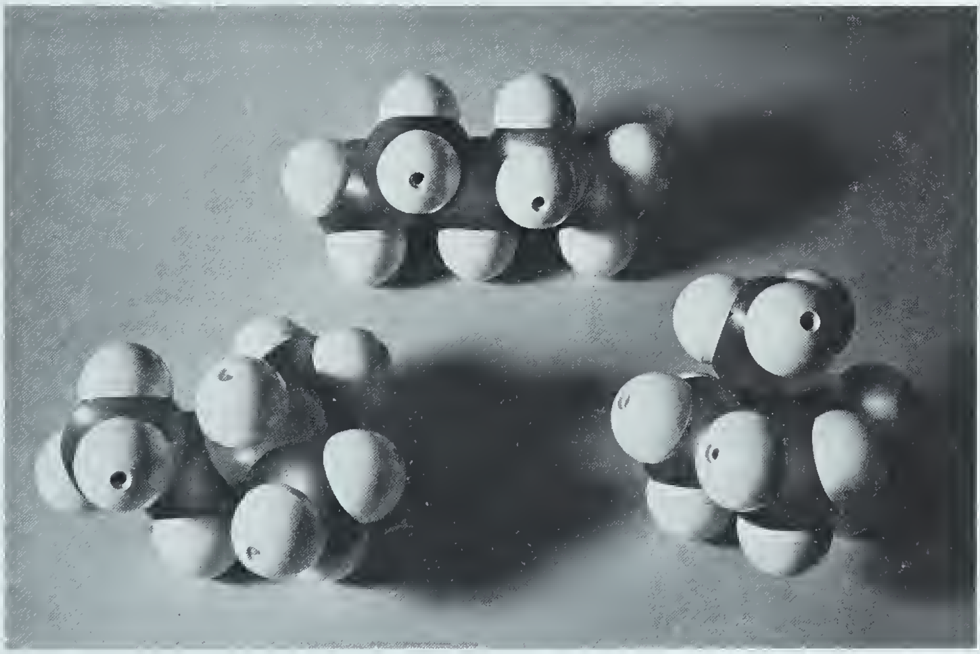


Fig. 13-3B Models of the Pentane (C_5H_{12}) Isomers

Thus, there is another reason for the large number of organic compounds. Not only can carbon atoms join together to make long chains, but also a compound such as octane can have many isomers with the same molecular formula but with different structural formulas. For example, the atoms which make up octane can be arranged in 18 different ways.

13-4/METHANE—A TYPICAL ALKANE

Methane is a common constituent of the gas found in coal mines. Methane makes up 20% to 40% of coal gas. Methane also forms about 90% of natural gas. Normally it burns quietly but it will explode if it is mixed with oxygen in the correct proportion. The equation for the combustion of methane is:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

Methane is prepared in the laboratory by heating sodium acetate and sodium hydroxide:

$$NaC_2H_3O_2 + NaOH \xrightarrow{\Delta} CH_4(g) + Na_2CO_3$$

Chemically, methane and the other alkanes are relatively inert. They are called saturated hydrocarbons because each carbon atom is bonded by single covalent bonds to four other atoms. They will, of course, burn in oxygen to form carbon dioxide and water, but they do not react easily with other compounds.

They will, however, undergo what are called **substitution reactions,** in which one or more hydrogen atoms is replaced by another atom. An example is:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

chloromethane
(*methyl chloride*)

In this reaction, a chlorine atom has been substituted for one of the four hydrogen atoms of methane. The substitution process could continue:

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

dichloromethane
(*methylene chloride*)

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

trichloromethane
(*chloroform*)

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

tetrachloromethane
(*carbon tetrachloride*)

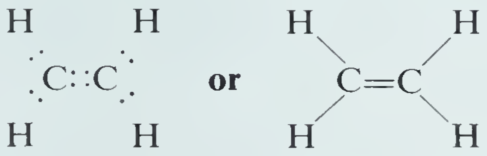
Because all of the carbon atoms in the alkanes are bonded by single covalent bonds to four other atoms, *nothing can add on to an alkane.* Substitution reactions are the only possible reactions.

13-5/ALKENES

As we have seen, when two carbon atoms bond together in ethane, there is a requirement for 6 hydrogen atoms to bond with the 2 carbon atoms. However, in the compound ethene only four hydrogen atoms are available:

$$\begin{array}{c}\mathrm{H:\underset{\cdot\cdot}{\dot{C}}:\underset{\cdot\cdot}{\dot{C}}:H}\\ \mathrm{H\ H}\end{array}$$

Each carbon atom has an unpaired electron, and neither carbon atom obeys the octet rule. Carbon is tetravalent, and it forms four bonds. Thus, the two unpaired electrons form a second bond between the two carbon atoms:



Each carbon atom now has four bonds: one bond to each of two hydrogen atoms and two bonds to the other carbon atom (Fig. 13-4).

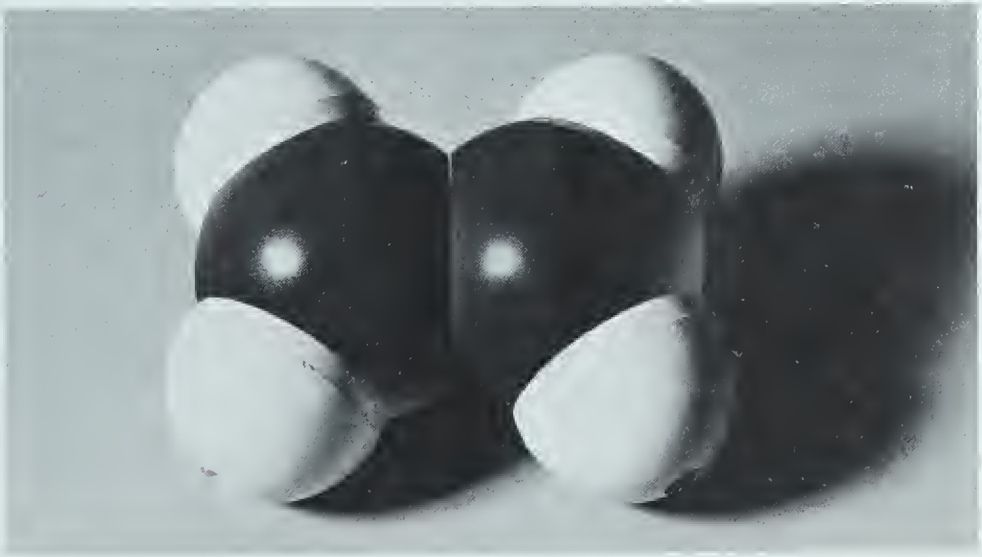
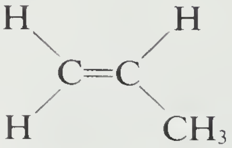


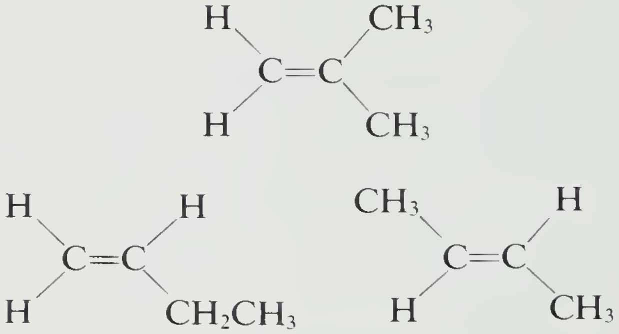
Fig. 13-4 Model of Ethene (C_2H_4)

This compound is called ethene. Like ethane, ethene has two carbon atoms. However, ethene, like the other alkenes, has one double bond in the molecule. All alkenes have names ending in the suffix "-ene" indicating the presence of a carbon-carbon double bond. The general formula of the alkenes is C_nH_{2n}.

Below is a table of some other simple alkenes:



propene, C_3H_6



butene, C_4H_8,

There are four possible isomers of butene (one is not shown). We notice that in addition to varying the arrangement of the carbon atoms in butene, the position of the double bond can also be varied.

13-6/ETHENE—A TYPICAL ALKENE

Ethene can be prepared by the cracking process. **Cracking** is a method by which organic molecules are broken down into simpler molecules by the action of heat and a catalyst. At 600°C ethane is converted to ethene:

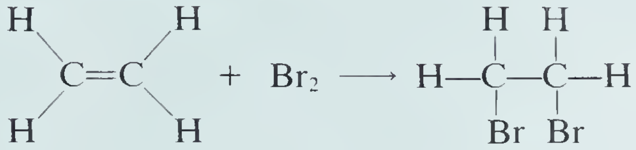
$$C_2H_6 \xrightarrow{\Delta} C_2H_4 + H_2$$

Ethene can also be prepared by the action of hot concentrated sulfuric acid on ethyl alcohol:

$$C_2H_5OH \xrightarrow[\Delta]{H_2SO_4} C_2H_4 + H_2O$$

In ethane, there are 6 hydrogen atoms for 2 carbon atoms, but in ethene there are 4 hydrogen atoms for 2 carbon atoms. Ethene is an *unsaturated hydrocarbon.* It is not saturated with hydrogen atoms. Any hydrocarbon which has one or more double bonds is **unsaturated.**

These double bonds are chemically reactive, and the alkenes will undergo what is called an **addition reaction.** For example, a bromine molecule will add on to an ethene molecule to form dibromoethane:



Notice that the suffix changes from "-ene" to "-ane." Since dibromoethane has no double bonds, its name ends in "-ane." In this reaction the bromine is not substituted for anything. It actually adds on to the ethene. This is why we call this type of reaction an addition reaction.

Ethene, like any hydrocarbon, will burn in air to form carbon dioxide and water vapor:

$$C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

13-7/ALKYNES

We have seen examples of 2 carbon atoms bonding to 6 hydrogen atoms, and 2 carbon atoms bonding to 4 hydrogen atoms. In the compound ethyne (acetylene), only 2 hydrogen atoms are bonded to the 2 carbon atoms:

$$\mathrm{H}:\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}:\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}:\mathrm{H}$$

Here each carbon atom has two unpaired electrons. The carbon atoms do not obey the octet rule. However, we recall that carbon is tetravalent, and forms four bonds. Thus the four unpaired electrons form a second and a third bond between the two carbon atoms:

$$\mathrm{H}:\mathrm{C}\vdots\vdots\mathrm{C}:\mathrm{H} \qquad \textbf{or} \qquad \mathrm{H{-}C{\equiv}C{-}H}$$

Now each carbon atom has four bonds: one bond is to a hydrogen atom, and the other three bonds are to the other carbon atom (Fig. 13-5). Any hydrocarbon that has one or more triple bonds is unsaturated.

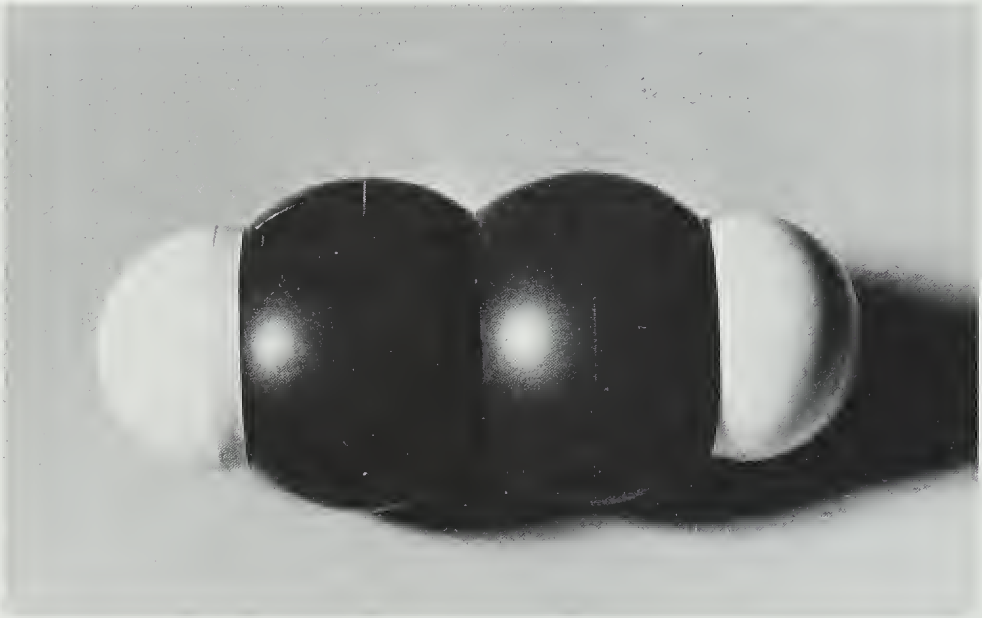


Fig. 13-5 Model of Ethyne (C_2H_2)

Ethyne, like the other two-carbon hydrocarbons, ethane and ethene, has the stem "eth-." Like the other alkynes the suffix is "-yne" indicating the presence of a carbon-carbon triple bond. All alkynes have one triple bond per molecule. The general formula of the alkynes is C_nH_{2n-2}. Some of the other simple alkynes are:

propyne C_3H_4 $H—C{\equiv}C—CH_3$
butyne C_4H_6 $H—C{\equiv}C—CH_2—CH_3$
and
$CH_3—C{\equiv}C—CH_3$

13-8/ETHYNE—A TYPICAL ALKYNE

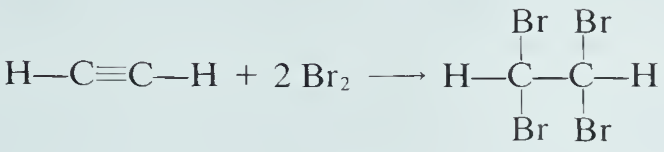
Ethyne is prepared by reacting calcium carbide with water to give calcium hydroxide and ethyne:

$$CaC_2 + 2\ H_2O \rightarrow C_2H_2(g) + Ca(OH)_2$$

Ethyne, or acetylene as it is usually called, will burn in air:

$$2\ C_2H_2 + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$$

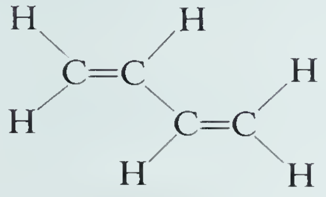
Because it is an unsaturated hydrocarbon, ethyne will undergo an addition reaction with 2 molecules of bromine:



$$\mathrm{H{-}C{\equiv}C{-}H} + 2\,\mathrm{Br_2} \longrightarrow \mathrm{H{-}CBr_2{-}CBr_2{-}H}$$

13-9/ALKADIENES

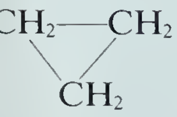
The *alkadienes* or *dienes* are molecules which have just what their name implies—two (di-) double bonds (-ene) per molecule. The most important diene is 1,3-butadiene. The stem "but-" tells us that the molecule has four carbon atoms. The numbers one and three tell us that the double bonds are attached to the first and the third carbon atoms:



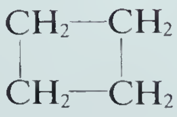
1,3-Butadiene is prepared by cracking petroleum samples which contain butane. Butadiene is used in making synthetic rubber. Canada's Polymer Corporation produced Buna-S at Sarnia in 1942. This synthetic rubber is made from butadiene and styrene.

13-10/CYCLOALKANES

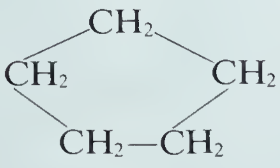
Hydrocarbons can take the form of a closed ring as well as an open chain. The simplest of such cyclic compounds are the cycloalkanes:



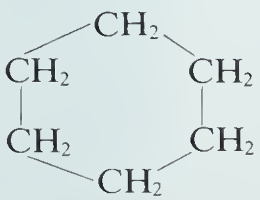
yclopropane



cyclobutane

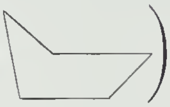
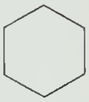


cyclopentane

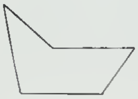
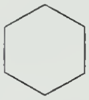


cyclohexane

These formulas are often drawn in the following manner:

   (**or** )  (**or** )

At each corner of the geometric symbol a carbon atom is understood to be present. The lines from corner to corner are carbon-carbon bonds. Unless otherwise indicated, hydrogens are assumed to be present at the corner carbons in sufficient quantity to give each carbon atom four bonds.

In cyclopropane and cyclobutane, the bond angles are 60° and 90°, which are much smaller than saturated carbon's normal 109°. These molecules are less stable because of the so-called ring strain. Ring strain is not a major factor in cyclopentane and cyclohexane. These molecules are not really planar (Fig. 13-6). For cyclopentane the molecule assumes a nonplanar shape with four carbons in plane and one carbon atom out of plane. Thus  is a better representation of cyclopentane than . In the same way  is a better representation of cyclohexane than . Five and six-membered carbon rings are common in organic chemistry. They are abundant in the molecules of living things.

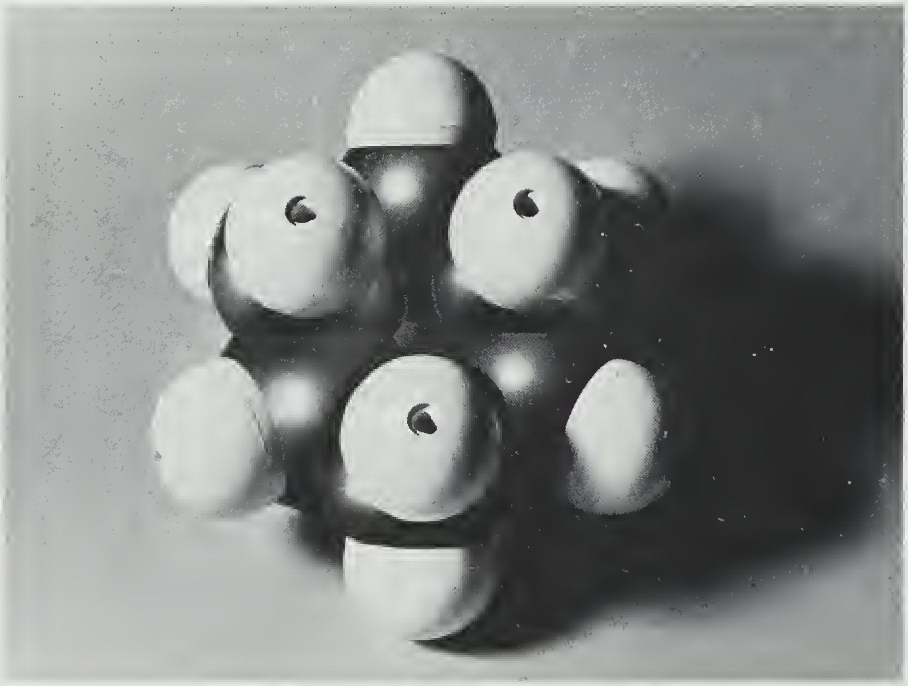


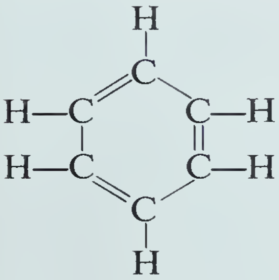
Fig. 13-6 Model of Cyclohexane (C_6H_{12})

13-11/AROMATIC HYDROCARBONS

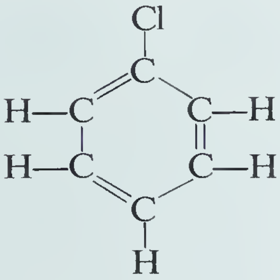
In 1825, Michael Faraday purified and analyzed an oily liquid given to him by the Portable Gas Company of London. Because of his careful work, he is credited with the discovery of benzene. Several of the aromatic, pleasant-smelling oils obtainable from plant sources were also found to consist of molecules similar in some ways to benzene. Later the term **aromatic compound** was applied to any substance whose molecules contained the benzene structural skeleton, even if the substance did not have a pleasant smell.

The molecular formula of benzene is C_6H_6. Any compound which has only six hydrogens for six carbon atoms must be highly unsaturated. However, unlike the other unsaturated families (e.g., alkenes and alkynes) benzene undergoes *substitution reactions rather than addition reactions.* Furthermore, when a monosubstituted benzene, such as C_6H_5Cl, reacts to form a disubstituted product, $C_6H_4Cl_2$, three isomers can be identified.

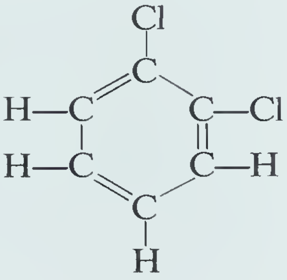
August Kekulé, a German chemist, attempted to explain some of these experimental results by proposing the following structures:



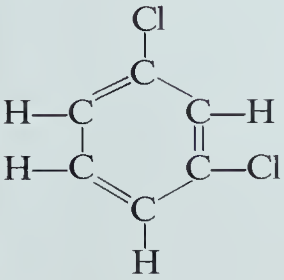
(1)



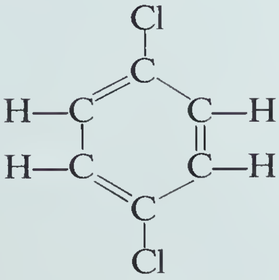
(2)



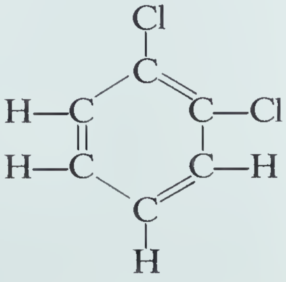
(3)



(4)



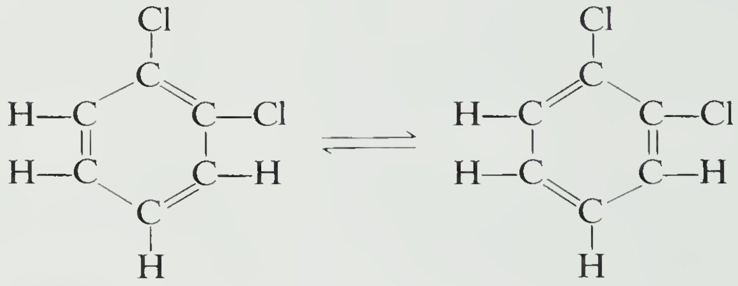
(5)



(6)

Kekulé proposed structure **1** for benzene, structure **2** for the monosubstituted product, and structures **3**, **4**, and **5** for the disubstituted products. It was pointed out to Kekulé that structure **3** should have an isomer (structure **6**) which differs in the location of the double bonds. In structure **3**, the carbon atoms holding the two chlorine atoms are joined by a single bond; in structure **6**, they are joined by a double bond.

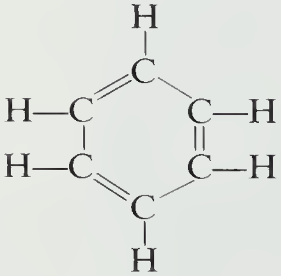
Kekulé modified his theory by suggesting that the double bonds shift back and forth rapidly so that structures **3** and **6** are isomers which can never be separated:



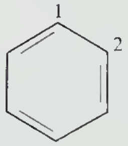
Later studies proved that double bonds are shorter than single bonds. However, all carbon–carbon bonds in benzene are the same length, and furthermore the carbon–carbon bonds in benzene are shorter than single bonds but longer than double bonds.

These observations require a modification of classical bonding theory in the case of benzene. One of the approaches taken is called **resonance theory.**

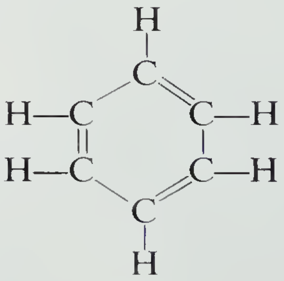
It is possible to draw two structures for benzene (**7** and **8**) differing only in the locations of electron pairs:



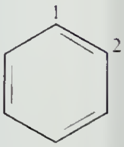
or



(7)



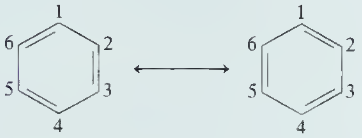
or



(8)

These Kekulé structures, as they are called, are not identical. The C-1 to C-2 bond in structure **7** is a single bond; in structure **8** it is a double bond.

Resonance theory suggests that whenever it is possible to draw two or more structures differing only in the location of the electrons, neither structure adequately represents the molecule. However, a good approximation of the molecular structure of benzene can be obtained by thinking of it as being a **resonance hybrid** or average of the classical Kekulé structures. These two classical Kekulé structures should not be considered as being real themselves but rather are said to be contributing structures:

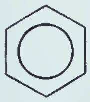


The two contributing structures can be averaged to get a structure for the resonance hybrid. The double-headed arrow is a signal that the structures are contributors to a resonance hybrid. The carbon atoms have been numbered for convenience. In the first structure the C-1 to C-2 bond is single; in the second structure it is double. The average of a single bond and a double bond is a partial double bond which is shown by drawing a dotted line instead of a solid line for the second of the two bonds:

$$\mathrm{C}\mathrel{\overset{\cdots}{-}}\mathrm{C}$$

In the first structure the C-1 to C-3 bond is double; in the second structure it is single. The average of a double bond and a single bond is again a partial double bond or a bond and a half. As one can see, the average of all carbon–carbon bonds in a benzene ring is a bond and a half. The resonance hybrid is written:

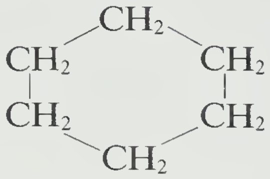
or sometimes



This hybrid structure explains why all carbon–carbon bonds in benzene are shorter than single bonds but are longer than double bonds. It also shows that benzene must not be thought of as a cycloalkene type of molecule with alternating double and single bonds. Benzene is a new type of molecule. The resonance hybrid is an average of the two contributing Kekulé structures. Benzene is more stable than one might expect. In fact, any compound that exhibits resonance is more stable than might be expected.

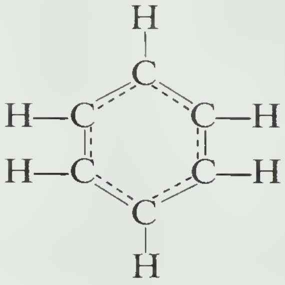
It is important to note that benzene does not behave as it does because of resonance theory. Rather, resonance theory attempts to explain the natural behavior of the benzene molecule.

We have now seen two molecules having six-membered rings. Cyclohexane,

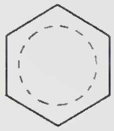


or

has single bonds between the carbon atoms. However, benzene,



or



is best considered as having 1-1/2 bonds between the carbon atoms (Fig. 13-7).

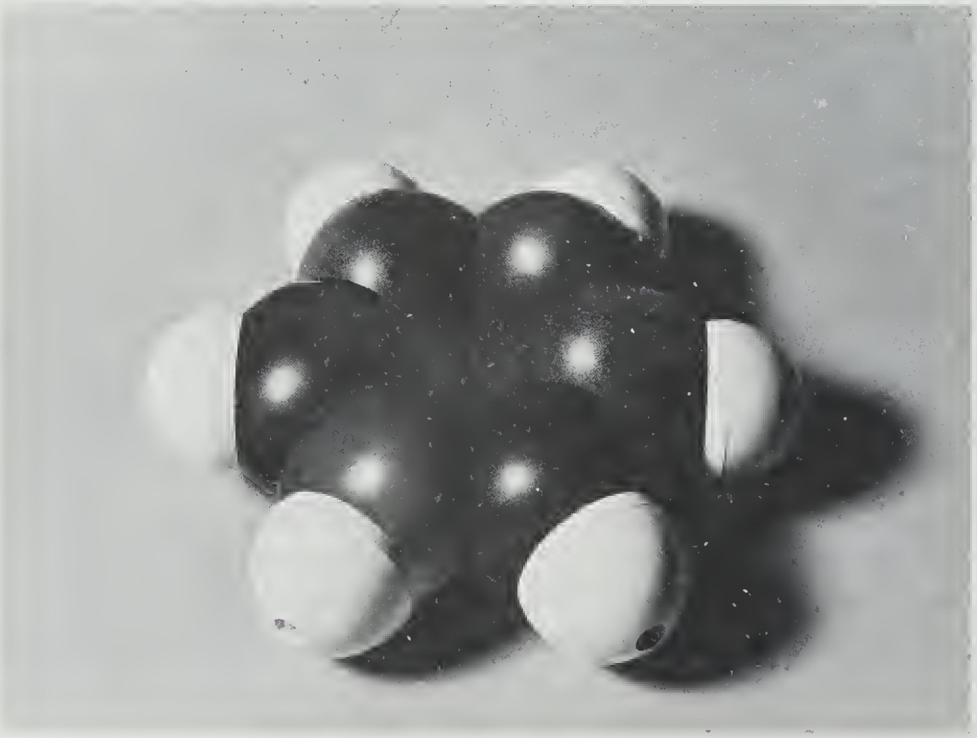
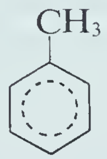


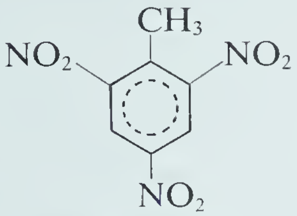
Fig. 13-7 Model of Benzene (C_6H_6)

Benzene is a liquid which is obtainable from coal tar. It is flammable and poisonous. It is a solvent and is a starting material for the manufacture of drugs, dyes, and explosives.

Toluene has a CH_3 group replacing one hydrogen atom of benzene. It is used as a solvent, and it is also used in the manufacture of the explosive, trinitrotoluene (TNT):

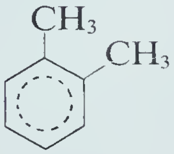


toluene

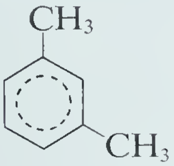


trinitrotoluene

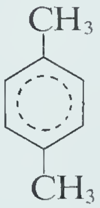
The xylenes have two CH_3 groups replacing two hydrogen atoms:



ortho xylene
(*o-xylene*)



meta xylene
(*m-xylene*)



para xylene
(*p-xylene*)

TABLE 13-1

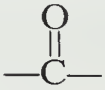
ALKYL GROUPS DERIVED FROM ALKANES

Parent Alkane	*Formula of Parent Alkane*	*Formula of Alkyl Group*	*Name of Alkyl Group*
Methane	CH_4	$CH_3—$	Methyl
Ethane	CH_3CH_3	$CH_3CH_2—$	Ethyl
Propane	$CH_3CH_2CH_3$	$CH_3CH_2CH_2—$	*n*-Propyl
n-Butane	$CH_3(CH_2)_2CH_3$	$CH_3(CH_2)_2CH_2—$	*n*-Butyl
n-Pentane	$CH_3(CH_2)_3CH_3$	$CH_3(CH_2)_3CH_2—$	*n*-Pentyl
n-Hexane	$CH_3(CH_2)_4CH_3$	$CH_3(CH_2)_4CH_2—$	*n*-Hexyl

13-12/SUBSTITUTION PRODUCTS

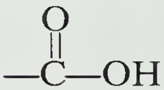
A large number of hydrocarbons of all kinds can be made. We should now consider organic compounds that contain other atoms in addition to carbon atoms and hydrogen atoms. Here the emphasis will be on the properties of the groups of atoms which can be attached to the hydrocarbon part of the molecule. The symbol R– will be used to designate that hydrocarbon part. The R– groups are often **alkyl groups** which are derived from alkanes (Table 13-1).

The atom or reactive group of atoms attached to the alkyl group is called a **functional group.** The term "functional group" is applied to any reactive atom or group of atoms in an organic compound to distinguish it from those which do not react. Examples of functional groups are —OH (hydroxyl), —NH_2 (amino),



$-\overset{\overset{O}{\|}}{C}-$

(carbonyl), —COOH or



$-\overset{\overset{O}{\|}}{C}-OH$

(carboxyl).

13-13/ALCOHOLS

The alcohols are characterized by the presence of the **hydroxyl** group which is attached to an alkyl group. The general formula is R—OH.

The simplest member of the family is methyl alcohol or methanol, CH_3OH. Methyl alcohol is a colorless liquid with a pleasant odor. It is a good fuel and was once used in antifreeze. Unfortunately some desperate individuals mistakenly take it as a drink. Since it is poisonous, even small quantities can bring about blindness or death. Often methyl alcohol is sold under the names wood alcohol, methyl hydrate, or methylated spirits. It is used as a thinner (solvent) for shellac.

The most familiar member of the alcohol family is ethyl alcohol, also called ethanol or grain alcohol, C_2H_5OH. It is colorless, has a pleasant odor, a sharp taste, and burns with a colorless flame. It is a derivative of the alkane, ethane. Ethyl alcohol is a good solvent for many organic compounds, including nitrocellulose lacquer.

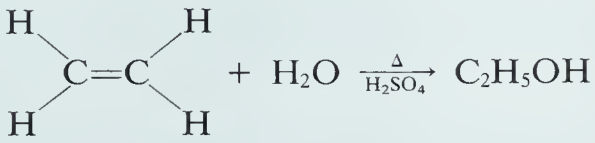
Since early times, man has known that certain fruit juices spoiled (fermented) upon standing. Drinking of these fermented liquids (wine) produced a euphoric state. About 1000 a ago someone discovered that the active substance in the liquid mixture could be concentrated by distillation. Since then many types of liquors have been developed. All of these alcoholic beverages contain ethyl alcohol in varying concentrations, from 5% to as high as 75%. Like the other lower members of the alcohol family (those with relatively few C-atoms in the hydrocarbon chain), ethyl alcohol is poisonous. A concentration of only 0.40% in the blood of an individual can cause death.

Ethanol is often prepared by fermentation of sugars by yeast:

$$\underset{\textit{glucose}}{C_6H_{12}O_6} \xrightarrow[\text{fermentation}]{} 2\ \underset{\textit{ethanol}}{C_2H_5OH} + 2\ CO_2(g)$$

$$\underset{\substack{\textit{sucrose}\\(\textit{sugar})}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{fermentation}]{} 4\ \underset{\textit{ethanol}}{C_2H_5OH} + 4\ CO_2(g)$$

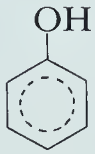
Ethanol is also made industrially from ethene:



Denatured alcohol is composed principally of ethyl alcohol to which other poisonous or nauseating materials have been added to make it unfit for drinking or use in foodstuffs.

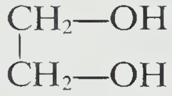
Other alcohols are derived from propane, butane, pentane, etc. They are propyl alcohol (propanol), butyl alcohol (butanol), and pentyl alcohol (pentanol or amyl alcohol). Isopropyl alcohol is sold as rubbing alcohol since it kills germs better than the other simple alcohols and has a temporary lubricating effect during the rubbing process. These more complicated alcohols are made by fermentation with special yeasts.

If the hydroxyl group replaces a hydrogen atom on a benzene ring, the resulting compound is called phenol:



Phenol is also called carbolic acid since it is an acidic compound. Phenol is a moderately potent germicide and has been used as a disinfectant in operating rooms. It is also used as a starting compound in the manufacture of dyes and other useful compounds.

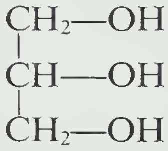
We should also look at two alcohols which have more than one hydroxyl group per molecule. Ethylene glycol (or dihydroxyethane) is a two-carbon, saturated molecule which has two hydroxyl groups:



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH_2\text{—}OH \end{array}$$

It is used as an antifreeze in the ratio of 1:1 by volume with water. The resultant mixture has a lower freezing point and a higher boiling point than water.

Glycerol is a three-carbon, saturated molecule which has three hydroxyl groups:



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2\text{—}OH \end{array}$$

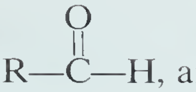
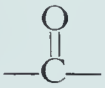
Glycerol is a colorless, odorless, viscous (thick) liquid with a sweet taste. It is used in cigarette tobacco to keep it moist, in the manufacture of hand lotions and cellophane, and in the manufacture of the explosive, nitroglycerine.

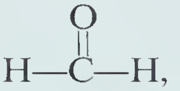
13-14/ETHERS

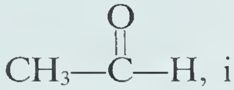
Ethers have been called organic oxides. Their general formula is R—O—R′. R can be the same as R′ as in $CH_3\text{—}O\text{—}CH_3$ (dimethyl ether) and $C_2H_5\text{—}O\text{—}C_2H_5$ (diethyl ether), or R can be different from R′ as in $CH_3\text{—}O\text{—}C_2H_5$ (methyl ethyl ether).

The most common ether is diethyl ether which is normally called ether. It is used as an organic solvent and has been used as an anesthetic. It is rarely used for the latter purpose today because of its unpleasant side-effects.

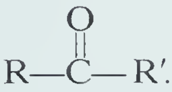
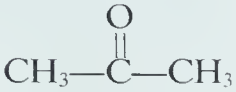
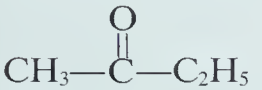
13-15/ALDEHYDES

Aldehydes have the general formula  $R-\overset{\overset{O}{\|}}{C}-H$, and they have a  $-\overset{\overset{O}{\|}}{C}-$ group which is called the **carbonyl** group.

Formaldehyde,  $H-\overset{\overset{O}{\|}}{C}-H$, is a gas with a sharp, suffocating odor. A solution of formaldehyde in water is called formalin. Formalin is used for preserving biological specimens because it reacts with the proteins in these specimens, making them harder and less susceptible to putrefaction (rotting).

Acetaldehyde,  $CH_3-\overset{\overset{O}{\|}}{C}-H$, is another simple aldehyde. It is used largely as an intermediate for the synthesis of other organic compounds.

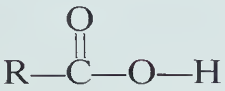
13-16/KETONES

Ketones have the general formula  $R-\overset{\overset{O}{\|}}{C}-R'$. Like the aldehydes, ketones contain the carbonyl group. As in ethers, R and R′ can be the same in ketones such as  $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (dimethyl ketone) or they can be different in ketones such as  $CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5$ (methyl ethyl ketone).

The most common ketone is dimethyl ketone which is usually called acetone. Acetone is used as a solvent and for synthesizing other compounds. Diabetics produce abnormally large quantities of acetone in their bodily metabolism. In severe cases of diabetes, an odor of acetone may be detected in the breath.

13-17/CARBOXYLIC ACIDS

The general formula of simple carboxylic acids is



$$R-\overset{\overset{O}{\|}}{C}-O-H$$

The functional group is the **carboxyl** group, $-\overset{\overset{O}{\|}}{C}-OH$.

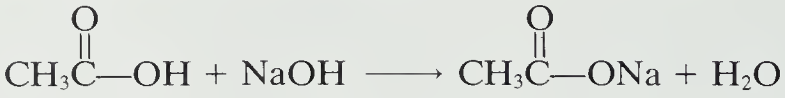
Acids are substances which ionize in water to generate H_3O^+ ions. A carboxylic acid molecule can ionize in the following way:

$$R-\overset{\overset{O}{\|}}{C}-O-H + H_2O \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^- + H_3O^+$$

When the oxygen–hydrogen bond breaks, the electron pair remains with the oxygen atom which now becomes negative. The hydrogen atom loses its electron and an H_3O^+ ion is formed.

Carboxylic acids are found in vinegar, fruits, rancid butter, etc. The first member of the family is formic acid, $H-\overset{\overset{O}{\|}}{C}-OH$. Formic acid is an acrid-smelling liquid which is the irritative component in the sting of bees and the "bite" of many types of ants.

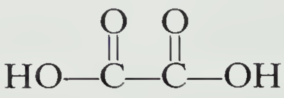
Acetic acid, $CH_3\overset{\overset{O}{\|}}{C}-OH$, is present in vinegar. Like the other carboxylic acids, it can react with a base such as sodium hydroxide to form a salt (sodium acetate) and water.



$$CH_3\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-ONa + H_2O$$

The carboxylic acids figure prominently in the metabolic processes of man and other organisms. They are also used by living systems as building blocks for the manufacture of larger molecules such as fats and steroids.

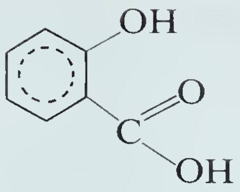
Oxalic acid is the simplest dicarboxylic acid. It consists of two carboxyl groups joined together:



$$HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

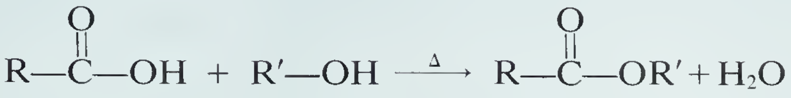
This acid is poisonous. It has been used in the preparation of blueprints and in products used for cleaning copper and brass, and the removal of rust.

A more complicated acid is salicylic acid. It consists of a phenol molecule with a carboxyl group attached to the carbon atom adjacent to the hydroxyl group:



13-18/ESTERS

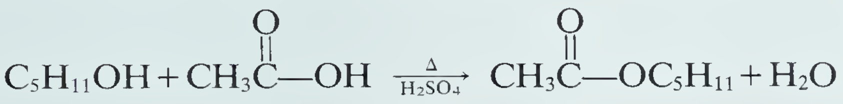
Organic acids react with alcohols to form esters and water. A general equation is:



$$\mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH} + \mathrm{R'}-\mathrm{OH} \xrightarrow{\Delta} \mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OR'} + \mathrm{H_2O}$$

Carboxylic Acid + Alcohol ⟶ Ester + Water

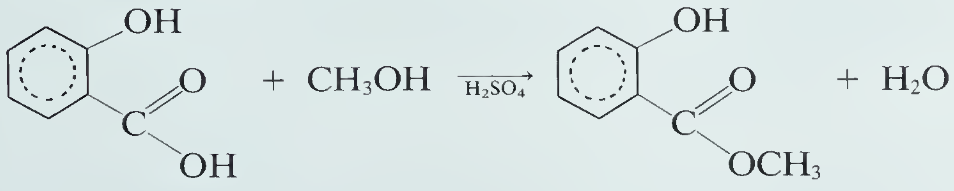
Esters have many commercial uses ranging from cosmetics and perfumes to synthetic fibers. Many vegetable oils are esters and some fruit odors are due to the presence of esters. The odor of bananas is due to pentyl (amyl) acetate which is an ester of acetic acid and pentyl alcohol:



$$\mathrm{C_5H_{11}OH} + \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH} \xrightarrow[\mathrm{H_2SO_4}]{\Delta} \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OC_5H_{11}} + \mathrm{H_2O}$$

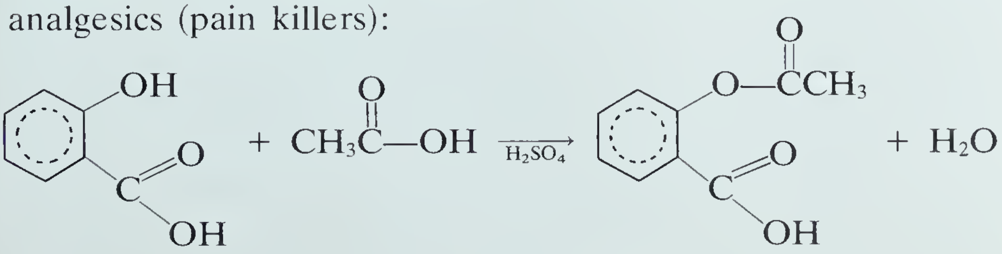
The odors of oranges, apples, and other fruits are also due to esters.

Salicylic acid reacts with methyl alcohol to form methyl salicylate which is called oil of wintergreen:



methyl salicylate

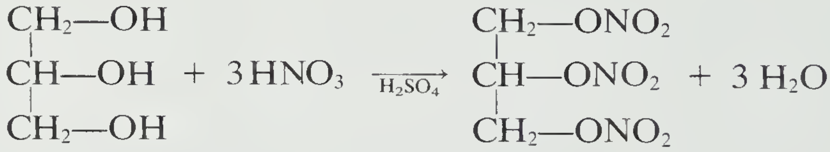
Salicylic acid also reacts with acetic acid to form acetylsalicylic acid (aspirin) which is the most common of all analgesics (pain killers):



aspirin

Aspirin is the most widely used drug in the world. During the 1960s the United States alone produced over 15 billion aspirin tablets annually.

Esters can also be prepared by reacting inorganic mineral acids with alcohols. One well-known ester is nitroglycerine. Glycerol reacts with nitric acid to give nitroglycerine and water:



$$\begin{array}{l} CH_2\text{—}OH \\ \vert \\ CH\text{—}OH \\ \vert \\ CH_2\text{—}OH \end{array} + 3HNO_3 \xrightarrow[H_2SO_4]{} \begin{array}{l} CH_2\text{—}ONO_2 \\ \vert \\ CH\text{—}ONO_2 \\ \vert \\ CH_2\text{—}ONO_2 \end{array} + 3H_2O$$

nitroglycerine

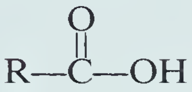
Nitroglycerine was first prepared by the Italian chemist Ascanio Sobrero in 1846. Alfred Nobel, a Swedish chemist, began to manufacture nitroglycerine in 1862. However, nitroglycerine is sensitive to shock and many fatal accidents occurred when workers used liquid nitroglycerine. Nobel discovered that the explosive capabilities of nitroglycerine were not seriously reduced when the liquid was diluted by mixing it with (adsorbing it on) kieselguhr, a powdery "earth" consisting of the skeletons of marine organisms called diatoms. The result was a pasty mixture called *dynamite*. In this way the explosive could be handled and shipped more safely since dynamite is harder to detonate than nitroglycerine. This discovery made Nobel wealthy, and he used part of this wealth to establish the annual Nobel Prizes.

13-19/OTHER TYPES OF ORGANIC COMPOUNDS

Alcohols can be related to water (H—O—H) by considering that an alkyl group has been substituted for one of the two hydrogen atoms (R—O—H). The *mercaptans* can be related to hydrogen sulfide (H—S—H) by considering that an alkyl group has been substituted for a hydrogen atom (R—S—H).

The mercaptans have an offensive "rotten egg" odor. *n*-Butyl mercaptan (C_4H_9SH) is the principal part of the well-known fluid that is the defensive weapon of the skunk. In the same way that alcohols relate to water and mercaptans relate to hydrogen sulfide, *amines* relate to ammonia (NH_3). Amines have the formula R—NH_2 and are often detected by their "fish-like" odor.

A compound in which the —OH group of an acid



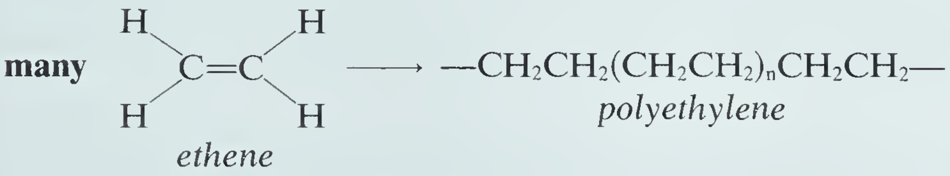
$$R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH$$

is replaced by an —NH_2 is called an *amide* ($R\text{—}\overset{\overset{O}{\|}}{C}\text{—}NH_2$). Amides are of special importance because the amide group $\text{—}\overset{\overset{O}{\|}}{C}\text{—}\underset{\underset{H}{|}}{N}\text{—}$ is the basic structural group in proteins and enzymes.

13-20/POLYMERS

A **polymer** is a substance which has a large molecular mass and which is composed of many fundamental building block molecules or *monomer* units. These monomer units have chemically united to form the polymer.

The well-known polymer, polyethylene, is made from the polymerization of the monomer ethene:



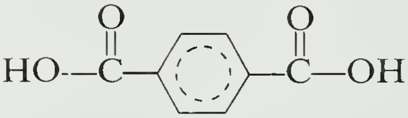
Each —CH_2CH_2— unit in the polyethylene is derived from an ethene molecule. The double bond in ethene has been converted to a single bond as the polymer is formed. A single polyethylene molecule can contain many thousands of these ethene monomer units.

There are both naturally occurring polymers and synthetic polymers. Proteins, nucleic acids, polysaccharides, and natural rubber are examples of naturally occurring polymers. The synthetic polymers include nylon, Dacron®, Lucite®, synthetic rubber, and polystyrene.

The two principal types of synthetic polymers are condensation polymers and addition polymers. Condensation polymers form slowly and require heating of the reaction mixture for several hours before the polymer reaches the proper chain lengths. Condensation polymers have relatively low molecular masses in comparison with addition polymers. The former have molecular masses which are generally less than 100 000 while addition polymer molecules can have masses of as much as 10 million atomic mass units. Addition polymers also form much more rapidly than condensation polymers. The formation of condensation polymers involves the splitting out of small molecules such as H_2O and NH_3 while in addition polymerization the monomer units merely add on to one another.

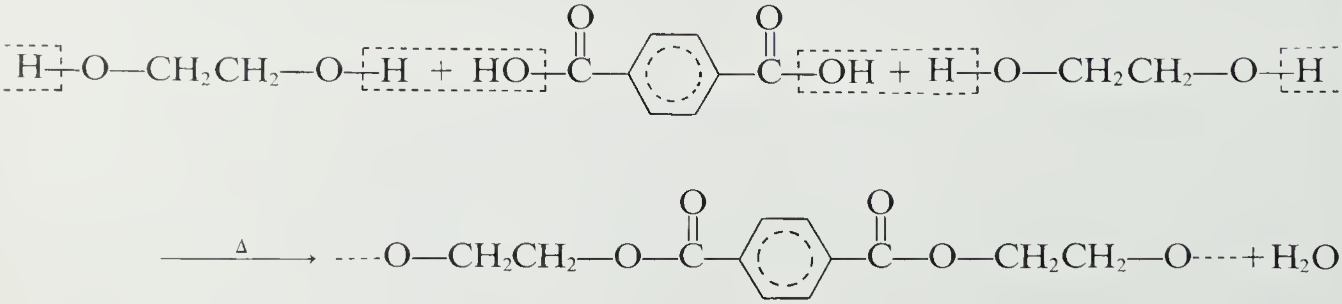
13-21/CONDENSATION POLYMERS

When ethylene glycol, $HO—CH_2—CH_2—OH$, reacts with paraphthalic acid,



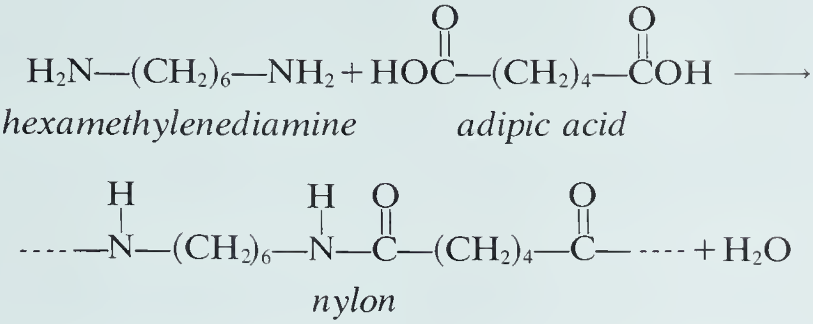
paraphthalic acid

a polymer of high molecular mass called Dracon® is produced:



Because an acid has reacted with an alcohol to form a polymeric substance containing many ester groups, the product is called a polyester.

Nylons are a well-known type of condensation polymer. One of the best known of the nylons is made by reacting hexamethylenediamine with adipic acid:



$$\mathrm{H_2N{-}(CH_2)_6{-}NH_2 + HO\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}OH \longrightarrow}$$

hexamethylenediamine *adipic acid*

$$\mathrm{\cdots\cdots{-}\overset{H}{\overset{|}{N}}{-}(CH_2)_6{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}\cdots\cdots + H_2O}$$

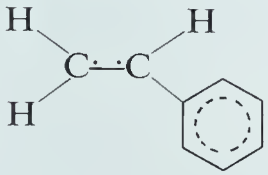
nylon

In the polymer, nylon, the hexamethylenediamine units alternate with adipic acid units. The $\mathrm{{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}}$ segments are amide groups, and nylon is a polyamide. Nylon has a molecular mass of around 25 000 u. It is used in textiles. If nylon is heated to 250°C and forced through a plate in which tiny holes have been drilled, nylon fibers are produced. This nylon in fiber form is subjected to mechanical stretching called cold drawing, and a strong fiber results. Nylon fiber is used in clothing, ropes, tire cord, and brushes while solid nylon is formed into gears or bearings.

13-22/ADDITION POLYMERS

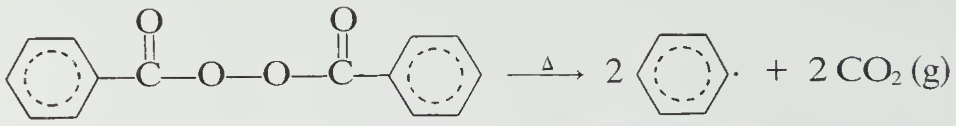
Many polymerization reactions proceed by means of a free radical mechanism. An atom, ion, or molecule which contains one or more unpaired electrons is a **free radical.** Unpaired electrons have a tendency to pair up with other electrons of opposite spins. Thus free radicals are *reactive.*

Styrene is a monomer which can be made to polymerize:



The second bond of the double bond between the two carbon atoms in styrene is shown as an electron pair. The reason for this will become clear as we proceed.

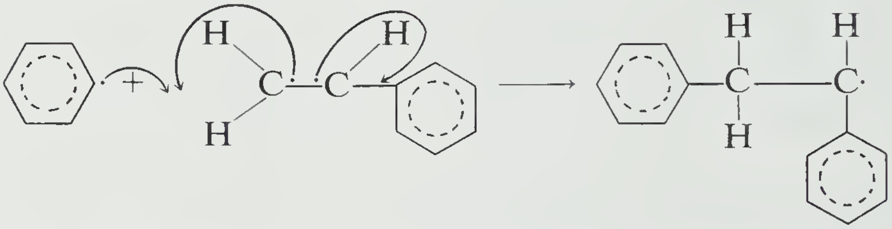
A small amount of an *initiator* (a substance which generates free radicals) is mixed in with the styrene monomer. Heating the mixture causes the initiator to break down into free radicals, as we see in the case of benzoyl peroxide:



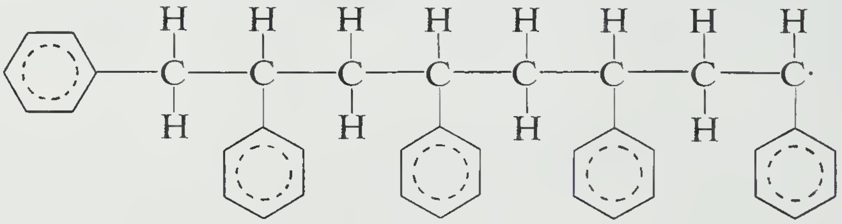
benzoyl peroxide
(*initiator*)

phenyl radical

The phenyl free radical then acts with one end of the carbon–carbon double bond of the styrene molecule:



Now an unpaired electron appears on one of the styrene carbon atoms. This new free radical then reacts with a second styrene molecule to form a new free radical which reacts with a third styrene, then a fourth, a fifth, and so on:



polystyrene

Finally, the growth of the addition polymer chain is stopped by a termination step. For example, the growing chain could react with a phenyl free radical. However, a more likely possibility is for two different growing chains to react together. When two free radicals come together, the unpaired electrons of the two species pair up and form a stable covalent bond.

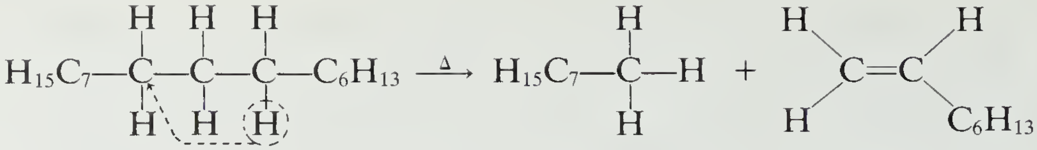
13-23/PETROLEUM

Crude oil as it comes from the ground consists of a highly complex mixture of compounds. Most of these are saturated hydrocarbons, but there are a number of aromatic hydrocarbons present as well. At the oil refinery crude oil is separated into a number of fractions by distillation. The division into fractions is largely determined on the basis of boiling point and the number of carbon atoms present in the hydrocarbon molecules. The gas fraction is made up of those compounds that boil at less than 30°C. It is really natural gas dissolved in the liquid petroleum. Natural gas is mainly methane mixed with some ethane and some propane. The naphtha or petroleum ether fraction consists of low boiling (30–65°C) hydrocarbons which have 5 or 6 carbon atoms per molecule. It is used primarily as a solvent or cleaning material. Gasoline boils from 60 to 150°C and contains 6 to 9 carbon atoms per molecule. Kerosene boils from 170 to 230°C and is used as a jet fuel and as a light diesel fuel. The molecules in the kerosene fraction have 10 to 13 carbon atoms. Light oils have 14 to 18 carbon atoms per molecule and are used as diesel fuel and for oil-fired furnaces. The heavy oils (18 to 21 carbon atoms per molecule) are used for lubrication. The C_{22} to C_{40} fraction is paraffin wax. After the distillation process, some nondistillable residues remain. These are the asphalts which are used in road surfacing and roofing materials.

Petroleum often contains undesirable quantities of organic sulfur and nitrogen compounds. One way of removing them is to treat the petroleum with high-pressure hydrogen which converts the sulfur and nitrogen to H_2S and NH_3. These two gases are removed from the petroleum by extraction with NaOH solution and water.

The automobile gets its power from the controlled ignition of a mixture of air and vaporized fuel. The gasoline fraction is the most useful fuel fraction since the naphtha fraction would evaporate in the gasoline tank, and the kerosene fraction is not volatile enough to evaporate sufficiently for efficient ignition. Only a small fraction of the original crude oil is actually useful in automobile engines without further treatment. The treatment is called *cracking*.

Large molecules in the lubricating oil range can be converted into more useful molecules in the gasoline range by the cracking process. This reaction occurs under the influence of heat and especially under the influence of appropriate catalysts. A typical reaction is:



$$C_{16}H_{34} \xrightarrow{\Delta} C_8H_{18} + C_8H_{16}$$

hexadecane *octane* *octene*

In this way smaller molecules in the gasoline range are made from larger, less useful molecules. The cracking process is carried out in large "cat crackers" (catalytic crackers).

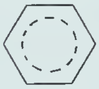
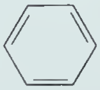
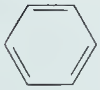
Branched-chain hydrocarbons burn more evenly and are less susceptible to premature ignition (engine knock) in an engine cylinder than straight-chain hydrocarbons. The knock is due to the explosion taking place in the cylinder before the piston has returned to its position of minimum displacement.

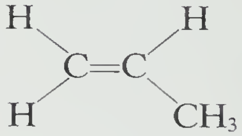
A gasoline is rated for performance in a test engine where its performance is compared to that of a known mixture of two pure hydrocarbons. Isooctane has a branched structure and knocks very little. Pure isooctane has an octane rating of 100. *n*-Heptane has a straight-chain structure and knocks very badly. It has an octane rating of 0. A gasoline is rated at "91-octane" if it behaves in a test engine the same as a mixture of 91% isooctane and 9% *n*-heptane. Poor-quality gasoline has a low octane rating.

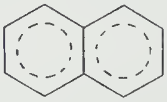
There are two ways of improving the octane rating of gasoline. One is to alter the structure of the molecules so as to increase the proportions of branched-chain hydrocarbons. During the 1930s it was discovered that a variety of catalysts such as aluminum chloride and sulfuric acid would promote the "reforming" of branched-chain molecules in the cracking process. Also, it became possible to combine molecules in the volatile C_4 to C_6 range to produce the larger gasoline range molecules.

The second way to improve the octane rating is to use additives. Lead tetraethyl is chief among the additives. A small quantity of this compound improves the anti-knock quality of the gasoline. However, about 0.1 g of lead per litre of gasoline burned finds its way into the atmosphere. Most of this lead eventually ends up in the soil. Like most heavy metals, lead is a poison, even in trace amounts. It is true that lead compounds already occur naturally in the soil; however, any extra amount deposited there by human activity could be dangerous. It appears that an important start on pollution control will involve the removal of lead from gasoline. The power in gasoline without lead will have to be maintained by structural modification of hydrocarbon molecules.

QUESTIONS

1. What was the experiment which indicated that a "vital force" is not necessary to produce organic compounds?
2. What is organic chemistry?
3. Why are there so many organic compounds?
4. What is the molecular formula of an alkane that has 16 carbon atoms?
5. Why are the alkanes considered to be a homologous series?
6. Draw the structural formulas of the isomers of hexane.
7. Write the equation for the substitution reaction involving ethane and bromine.
8. Why are the alkenes said to be unsaturated hydrocarbons?
9. Draw the structural formulas of any three isomers of pentene.
10. Write the equation for the addition reaction involving propene and bromine.
11. What is the molecular formula of an alkyne that has 20 carbon atoms?
12. Write the structural formula for 1,3-pentadiene.
13. What is meant by ring strain in cyclopropane?
14. Why is  a better representation of the benzene molecule than  **or**  ?
15. What does the dotted circle in  represent?
16. Write the structural formula for ortho dichlorobenzene.
17. Write the structural formula for *n*-propyl alcohol.
18. What is denatured alcohol?
19. Write the structural formula for ethyl propyl ether.
20. What functional group is found in both aldehydes and ketones?

21. Write the structural formula of a carboxylic acid which has four carbon atoms.
22. Write the equation for the reaction of propyl alcohol and acetic acid. This type of reaction is called an esterification.
23. How is dynamite related to nitroglycerine?
24. What are the differences between condensation polymers and addition polymers?
25. Show how ethylene glycol reacts with adipic acid to form a polyester.
26. How does a polymer of  (polypropene or polypropylene) differ from the polystyrene shown in Chapter 13?
27. What is the purpose of a "cat cracker?"
28. What is meant by the term "reforming" as it applies to the petroleum industry?
29. Name the group of compounds (e.g., alkane, alkyne, ketone, etc.) to which each of the following belongs:

(a) 

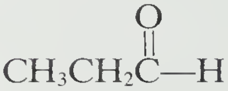
(b) $CH_2{=}C{=}CH_2$

(c) $CH_3CH_2CH_2OH$

(d) $CH_3—C{\equiv}C—CH_3$

(e) $C_{16}H_{30}$

(f) $CH_3CH_2—O—CH_2CH_3$

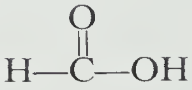
(g) 

$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}—H$

(h) 

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

(i) 

(j) 

$H—\overset{\overset{\displaystyle O}{\|}}{C}—OH$

QUESTIONS TO THINK ABOUT

30. In Section 13-5 the structures of three of the four isomeric butenes were given. What do you think is the structure of the missing isomer? (*Hint*: There is no free rotation about a carbon–carbon double bond).

31. The fermentation of glucose to ethanol by yeast consists of a series of reactions, each catalyzed by a different enzyme in the yeast. Look up the reactions in an advanced textbook. What functional groups are being transformed in each step?
32. Silicon is just below carbon in the periodic table. Predict the geometry of silane, SiH_4.
33. Occasionally one can identify an unknown compound by counting the number of isomeric products it forms in different reactions. For example, in the chlorination of propane four different isomeric products with formula $C_3H_6Cl_2$ were isolated and designated by the letters A, B, C, and D. Each was separated and reacted with more chlorine to give one or more trichloropropanes, $C_3H_5Cl_3$. A gave one trichloropropane, B gave two, and C and D each gave three trichloro compounds. One of the trichloro compounds from C was identical with the trichloro compound from A. Deduce structures for A, B, C, and D.

14

BIOCHEMISTRY

Living organisms are highly organized systems of organic compounds. These organisms derive the energy they require for life processes and produce the substances of which they are built by means of chemical reactions.

Biochemistry did not evolve as a discipline separate from organic chemistry until after the "vital force" theory was abandoned around the middle of the nineteenth century. Before that time, organic chemistry and the chemistry of life processes were virtually synonymous. It was believed that all organic compounds were produced as a result of chemical reactions taking place in the tissues of living things. It became apparent, however, that compounds, thought to be obtainable from living things only, could actually be produced in the laboratory.

Organic chemists study the chemistry related to carbon-containing compounds. Biochemists are concerned chiefly with the chemical processes that take place in living organisms. Biochemists use information gained from all branches of science. They are interested in learning about the kinds of molecules that make up living systems and the methods living systems use to produce energy and reproduce themselves.

The chemical system of even a very small plant or animal is extremely complex. It involves a multitude of compounds (many of which are polymers) taking part in a great number of chemical reactions influenced by a smaller number of specific catalysts. We will not attempt to study such a system. We shall consider some of the classes of compounds that are extremely important in biochemistry. Thus, instead of attempting to study a plant or animal cell, we will study some of the compounds that are essential components of most living things.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. State the structural features of each of the following types of compounds and give an example of each: fats and oils, triglyceride, carbohydrate, aldose, ketose, pentose, hexose, aldopentose, ketohexose, monosaccharide, disaccharide, polysaccharide, amino acid, protein, dipeptide.
2. Given a list containing structural formulas corresponding to the types of compounds listed in the preceding objective, identify the formulas which belong to each type of compound.
3. Write structural formulas for: a triglyceride, an aldose, a ketose, a pentose, a hexose, an aldopentose, a ketohexose, an amino acid, a dipeptide.
4. Define and give an example of each of the following: hydrogenation, peptide linkage, photosynthesis, enzyme, fermentation, aerobic and anaerobic respiration, hormone, drug, analgesic, antiseptic, antibiotic, toxin.
5. Explain the detergent action of a soap.
6. State the characteristics of living things.
7. Explain briefly the actions of antihistamines, antacids, corrosive poisons, cyanides, heavy metals, neurotoxins, hallucinogens.

14-1/FATS AND OILS

Fats and **oils*** are esters of glycerol, in which all three hydroxyl groups have reacted with carboxylic acids containing long hydrocarbon chains (fatty acids). Glycerol, for example, reacts with stearic acid to form the fat, glyceryl tristearate:

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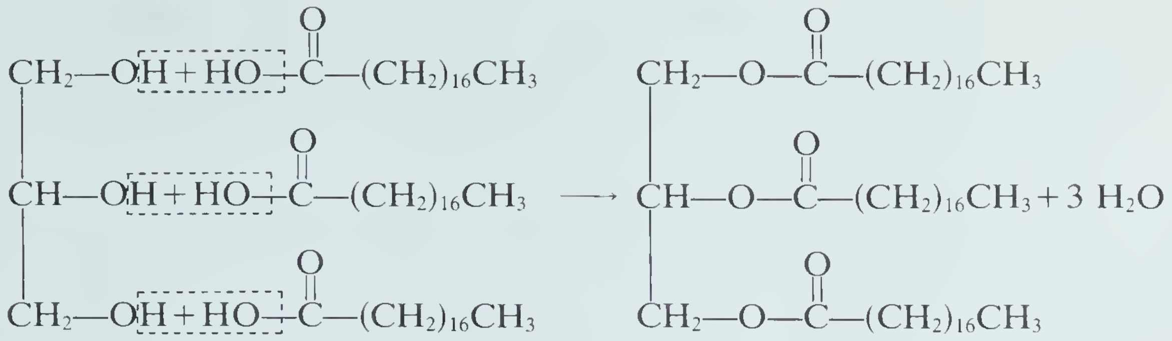
* Oils from animal or vegetable sources should not be confused with the petroleum-based oils discussed in Section 13-23.

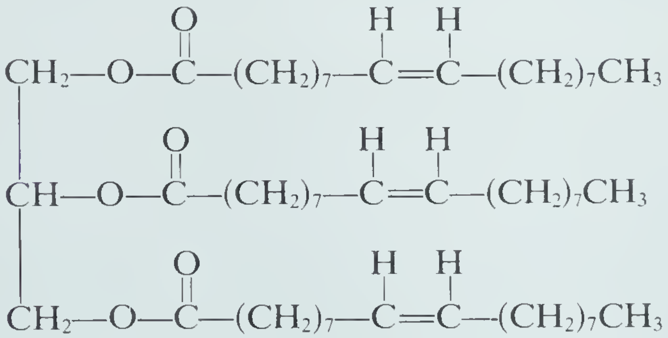


$$\begin{array}{lcl}
\mathrm{CH_2{-}O\boxed{H + HO{-}}\overset{\overset{O}{\|}}{C}{-}(CH_2)_{16}CH_3} & & \mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_{16}CH_3} \\
| & & | \\
\mathrm{CH{-}O\boxed{H + HO{-}}\overset{\overset{O}{\|}}{C}{-}(CH_2)_{16}CH_3} & \longrightarrow & \mathrm{CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_{16}CH_3 + 3\ H_2O} \\
| & & | \\
\mathrm{CH_2{-}O\boxed{H + HO{-}}\overset{\overset{O}{\|}}{C}{-}(CH_2)_{16}CH_3} & & \mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_{16}CH_3}
\end{array}$$

glycerol + stearic acid ⟶ *glyceryl tristearate + water*

Because they are esters of glycerol, the fats and oils belong to a class of compounds called **triglycerides.** Fats are solids at room temperature and are common constituents of animal tissues. They are actually a mixture of glycerides for there can be one, two, or three different long-chain carboxylic acid groups in the same molecule.

Oils are liquids at room temperature and are usually obtained from vegetable sources. We are familiar with olive oil, corn oil, and peanut oil. Structurally, oils are quite similar to fats. Both are triglycerides, but the main difference is that the long hydrocarbon chains in oil molecules contain one or more double bonds. Glyceryl trioleate is a typical oil:



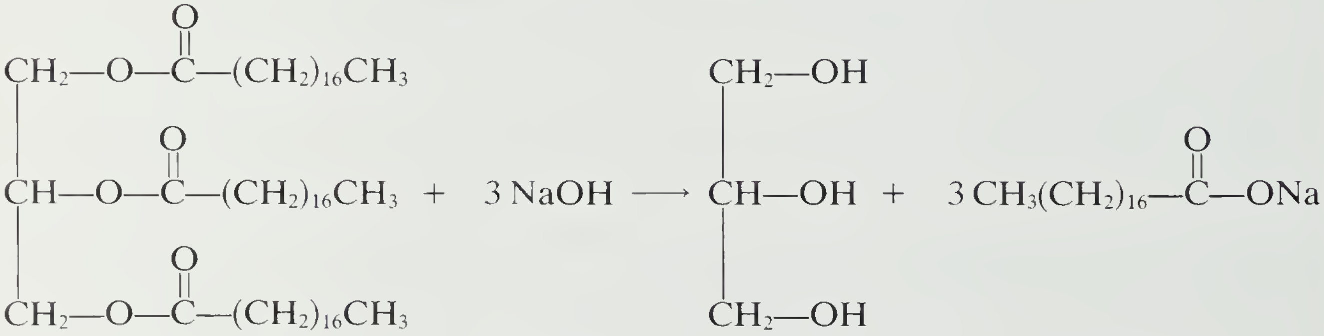
$$\begin{array}{l}
\mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_7{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}(CH_2)_7CH_3} \\
| \\
\mathrm{CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_7{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}(CH_2)_7CH_3} \\
| \\
\mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_7{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}(CH_2)_7CH_3}
\end{array}$$

glyceryl trioleate

Oils obtained from natural sources are not normally pure compounds but are mixtures of various unsaturated esters of glycerol. Vegetable oils have double bonds, and they are said to be *unsaturated.* In recent years it has been claimed that polyunsaturated oils are nutritionally preferable to saturated fats. Some researchers believe that high intakes of saturated fats are associated with such problems as heart disease and hardening of the arteries.

When vegetable oils such as corn oil are treated with hydrogen gas in the presence of a nickel catalyst, hydrogen atoms are added at the double bonds in their structures; the carbon-carbon double bond remains as one single bond, and the hydrogen atoms are linked to the carbon atoms by other single bonds. This is an example of **hydrogenation,** and it is a common method of reducing the degree of unsaturation in fats and oils. Shortening and margarine are useful products obtained by the partial hydrogenation of vegetable oils.

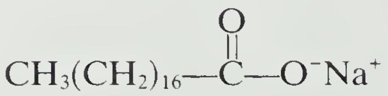
Fats and oils will react with sodium hydroxide to reform glycerol and produce the sodium salt of the carboxylic acid. For example, glyceryl tristearate reacts with sodium hydroxide to form glycerol and sodium stearate:



glyceryl tristearate + *sodium hydroxide* ⟶ *glycerol* + *sodium stearate*

Sodium salts of long chain carboxylic acids are often used as laundry soaps. Potassium salts of these acids are used as bath soaps because of their greater lathering ability and kindness to the skin.

A molecule of a typical soap has a long, nonpolar "tail" and a very polar, water-soluble "head." The tail should be easily soluble in nonpolar materials, and the head should be quite soluble in water:



$$CH_3(CH_2)_{16}\text{—}\overset{\overset{O}{\|}}{C}\text{—}O^-Na^+$$

nonpolar end (covalent bonds) *polar end (ionic bond)*

When soapy water comes in contact with a soiled object such as a grease spot on a sweater, the tails of the soap molecules tend to dissolve in the grease layer. The polar heads will remain in the polar solution. A little agitation will loosen the film and cause it to break up into tiny globules which remain suspended in the solution (Fig. 14-1).

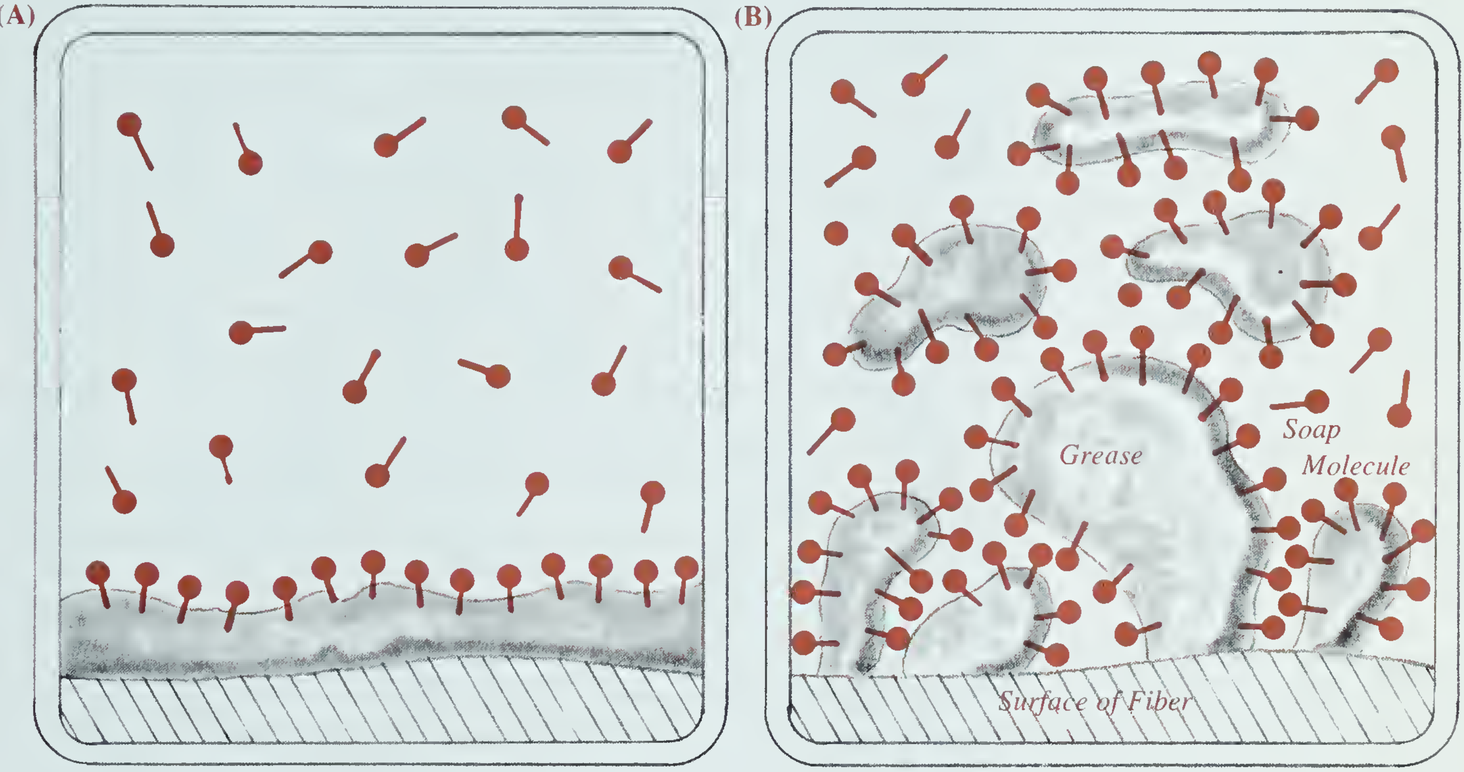


Fig. 14-1 Detergent Action **(A)** *Nonpolar tails of soap molecules become embedded in the grease layer.* **(B)** *Polar heads of soap molecules assist in breaking up the grease layer, removing it from the surface of the fiber, and keeping the droplets suspended in the solution.*

14-2/CARBOHYDRATES

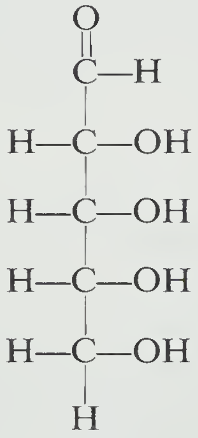
Sugars, starch, and cellulose are members of the carbohydrate family. Carbohydrates are especially common in plants where they are products of photosynthesis. The sugars and starch are vital foods, and their metabolism in our bodies provides much of the energy necessary for life.

The word **carbohydrate** arises from the observations that in many of the molecules in this family, hydrogen and oxygen are present in a two-to-one ratio as in water. Glucose has the formula $C_6H_{12}O_6$ and sucrose is $C_{12}H_{22}O_{11}$. These formulas can be rewritten as $C_6(H_2O)_6$ and $C_{12}(H_2O)_{11}$. Because of this it was once thought that these compounds were hydrates of carbon formed by the addition of water to carbon. Today we know that this is not so; however, the term "carbohydrate" remains.

Simple carbohydrates are either *polyhydroxyaldehydes* or *polyhydroxyketones.* That is, their molecules consist of chains of carbon atoms, all but one of which have a hydroxyl group attached. This remaining carbon atom forms part of either an aldehyde or a ketone group.

Almost all carbohydrates have names ending in "-ose." If the molecule contains an aldehyde group, it is called an aldose; if a ketone group is present, the molecule is called a ketose. Carbohydrates can also be classified according to the number of carbon atoms they contain. A carbohydrate containing five carbon atoms is called a pentose. A six-carbon carbohydrate is called a hexose. These two methods of classification can be combined. Thus, a five-carbon sugar containing an aldehyde group is called an aldopentose. A six-carbon sugar containing a ketone is called a ketohexose.

Ribose is an aldopentose. It is an important constituent of nucleic acids in living cells. RNA, or ribonucleic acid, is involved in carrying genetic information from the cell nucleus* to other locations in the cell where molecules such as proteins are actually synthesized.



$$\begin{array}{ccccc} & & \mathrm{O} & & \\ & & \| & & \\ & & \mathrm{C} & - & \mathrm{H} \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

ribose

Glucose (dextrose) is an aldohexose which is found in fruit juices, especially grape juice. Glucose is also present in blood and is metabolized by living cells, releasing energy as needed by the body. Glucose exists in two forms. One form is a chain and the other is a ring. In solutions the ring form prevails:

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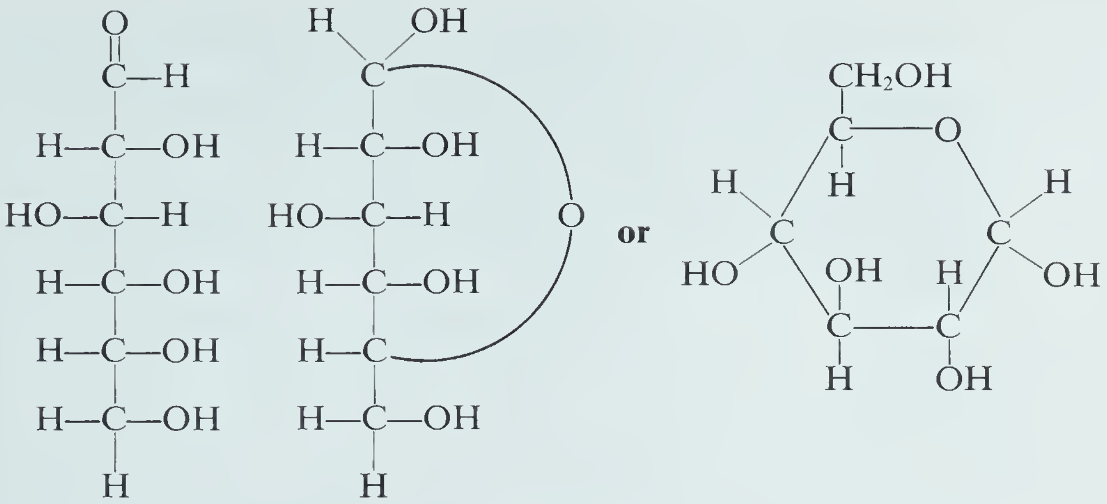
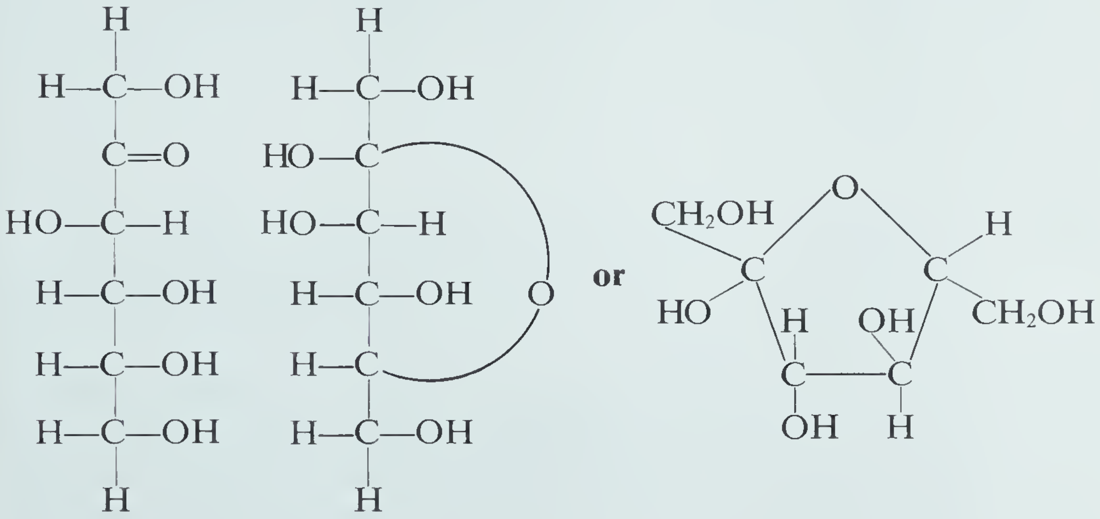
* Do not confuse the cell nucleus with the nucleus of an atom.



glucose

Much of the glucose produced commercially is used by the candy industry though it is used to sweeten a variety of other foodstuffs as well. Glucose tastes somewhat less sweet than ordinary table sugar. Dilute solutions of glucose are fed intravenously to hospital patients who are unable to take nourishment in the usual way.

Fructose is another important carbohydrate. Fructose is a ketohexose, that is, a six-carbon sugar with a ketone carbonyl group in place of an aldehyde carbonyl group:

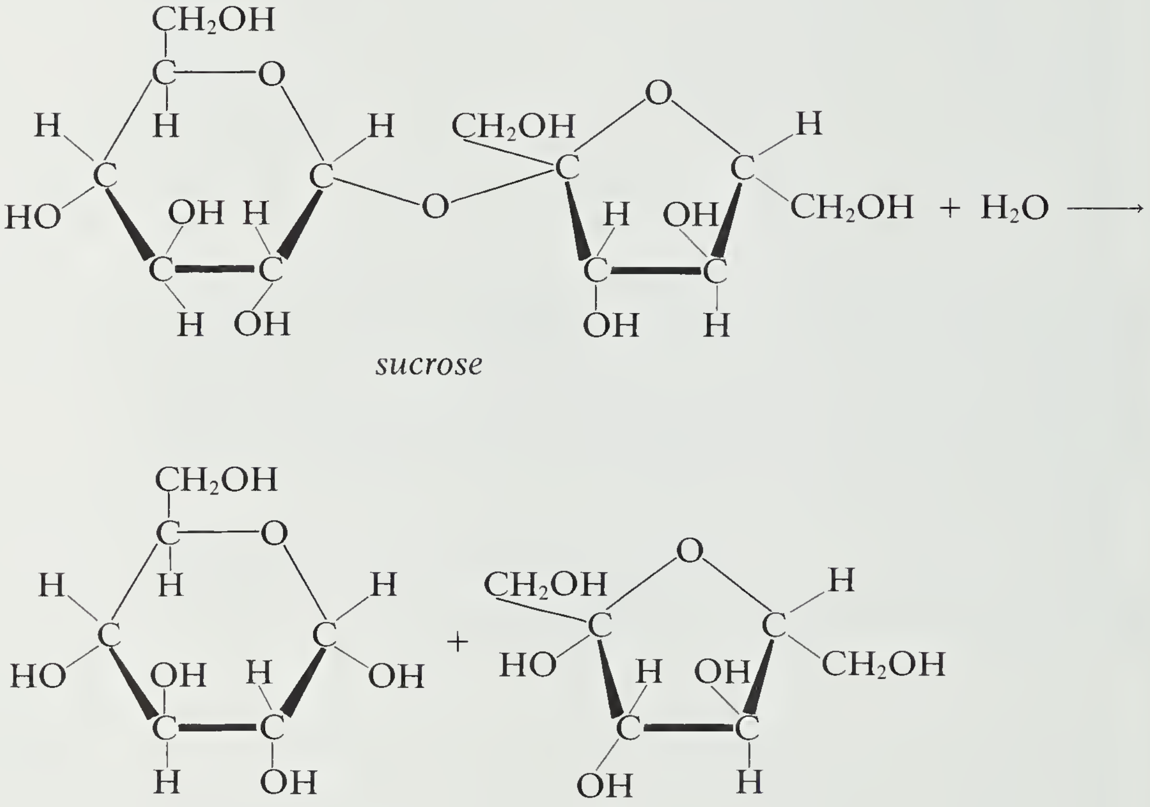


fructose

Fructose is sometimes called fruit sugar. It is the sweetest of the sugars. Honey is an approximately 50:50 mixture of glucose and fructose.

If a carbohydrate cannot be hydrolyzed (caused to react with water) to give simpler carbohydrates, it is called a **monosaccharide.** There are many monosaccharides. Ribose, glucose, and fructose are monosaccharides.

Sucrose, on the other hand, can be hydrolyzed to give two monosaccharides, fructose and glucose. It is called a **disaccharide:**



sucrose

glucose *fructose*

Sucrose, the "sugar" we use in the home, is the most abundant and commerically important of all the sugars. On a world-wide basis, more sucrose is produced than any other pure organic chemical.

Starch is a naturally occurring polymer consisting of many glucose units joined together in much the same way that glucose joins to fructose in the sucrose molecule. Because starch is a polymer of a simple saccharide, it is called a **polysaccharide.** Starch is found in most plants, but corn and potatoes are its principal commercial sources. The presence of starch may be tested for by treating a sample with a solution of iodine dissolved in potassium iodide solution. A characteristic dark blue color results if starch is present.

Cellulose, like starch, is a polysaccharide composed of glucose units. However, the glucose units in cellulose are joined together differently from the way in which they are joined in starch. Cellulose therefore has properties which are very different from those of starch. Cellulose is a fibrous material which is insoluble in water as well as in almost every other solvent. Starch exists as tiny granules which dissolve in hot water to form a turbid suspension.

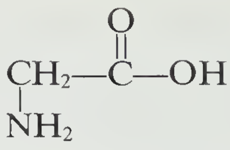
Starch is an important foodstuff for man. The human digestive system, however, does not have the ability to hydrolyze cellulose to glucose at a rate fast enough to be useful. The digestive tracts of horses, sheep, goats, and cattle, however, contain the bacteria necessary to convert cellulose to glucose. That is why these animals can obtain nourishment from grass and twigs.

Cellulose forms the cell membranes of some higher plants. Wood typically consists of about 50 percent cellulose, and cotton is almost pure cellulose. The paper on which these words are printed is made of cellulose fibers plus small amounts of special additives.

Glycogen is similar to starch in structure, except that its individual chains are shorter. Glycogen or "animal starch" is the form in which glucose is stored in animal tissues (usually in the liver and the muscles). Under the control of enzymes, some of which are in turn controlled by hormones, glucose molecules can be released from these glycogen reserves to supply energy for the body.

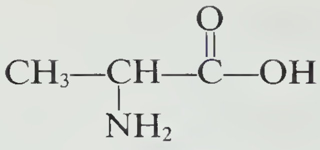
14-3/AMINO ACIDS AND PROTEINS

Amino acids are compounds which contain one or more amino groups and one or more carboxylic acid groups in the same molecule. In *alpha-amino acids* the amino group is attached to the carbon atom next to the carboxyl group (the so-called *alpha carbon*). Alpha-amino acids are the building blocks or monomers for the construction of **proteins,** which are polymers found in all plant and animal tissues. There are about 20 commonly occurring amino acids. Four of them are shown:



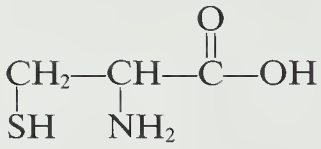
$\underset{NH_2}{\underset{|}{CH_2}}-\overset{O}{\overset{\|}{C}}-OH$

glycine



$CH_3-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$

alanine



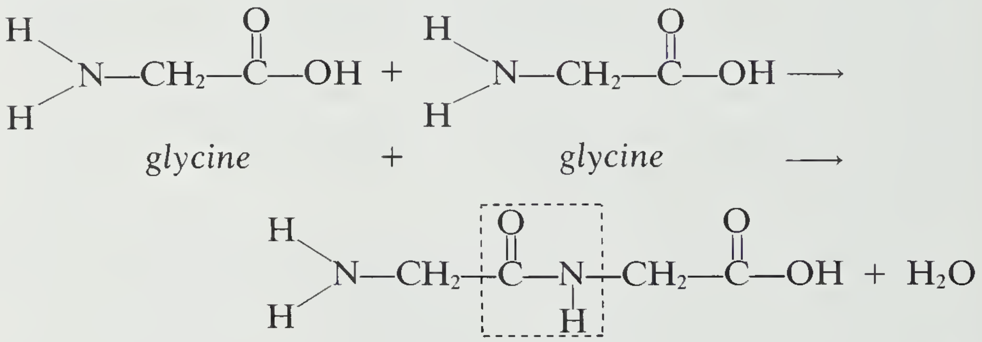
$\underset{SH}{\underset{|}{CH_2}}-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$

cysteine

$HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$

glutamic acid

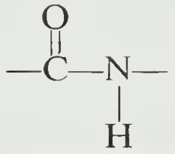
Two amino acids will react together to form a **dipeptide.**
0510 Two molecules of glycine will react to form the dipeptide,
0520 glycylglycine:



$$H_2N-CH_2-\overset{O}{\overset{\|}{C}}-OH + H_2N-CH_2-\overset{O}{\overset{\|}{C}}-OH \longrightarrow H_2N-CH_2-\boxed{\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}}-CH_2-\overset{O}{\overset{\|}{C}}-OH + H_2O$$

glycine + *glycine* ⟶

glycylglycine + *water*



The $-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-$ unit shown in glycylglycine is called an **amide,** or a **peptide, linkage.**

In the preceding example, two amino acids unite to form a dipeptide; however, it is possible for hundreds or thousands of amino acids to join together to form polymers. These polymers have large molecular masses and are called **polypeptides.** Naturally occurring polypeptides are called **proteins.**

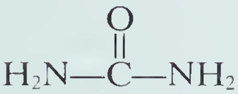
Proteins are found in all plant and animal tissue; however, they make up a higher percentage of the mass of animals than of plants. Despite the large number of proteins known, only 20 different alpha-amino acids have been found. These 20 acids can be arranged in protein chains in an incredibly large number of ways.

The molecular masses of proteins can vary a great deal depending on the type of protein. Insulin has a reasonably small molecular mass of around 5700 u. The molecular mass of the albumin found in egg white is around 45 000 u. The influenza virus is one of the largest, if not the largest protein molecule. It has a molecular mass of about 322 million atomic mass units!

There are two categories of proteins: simple proteins and conjugated proteins. Simple proteins such as egg albumin and keratin (found in hair) contain only alpha-amino acids. Conjugated proteins such as mucus and hemoglobin (found in blood) contain alpha-amino acids plus substances that are not amino acids.

When protein is treated with concentrated nitric acid, a yellow color is produced. This is called the *xanthoproteic* reaction. If one were to accidentally get nitric acid on one's fingers, a yellow stain, which would take several days to disappear, would develop where the nitric acid reacted with the protein in the skin.

When protein is consumed as food, it is hydrolyzed to amino acids in the digestive tract. These amino acids pass through the walls of the intestines and enter the bloodstream. They are transported to the cells which make up body tissues, and three things can happen to them: (1) They can be re-formed into protein which serves to build up muscles and other body tissues. (2) They can be used as sources of energy. In this case, the amino acids are converted to H_2O, CO_2, and NH_3. The CO_2 and NH_3 are then converted to urea



$$H_2N\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2$$

which is eliminated from the body as part of the urine. (3) The amino acids can be used in the cells for building enzymes, which in turn control the production of hormones, nucleic acids, and other substances which are vital to body functions.

14-4/WHAT IS LIFE?

Living organisms are composed of mixtures of carbohydrates, fats, proteins, nucleic acids, inorganic salts, and water. However, would life result if we were to mix the right amounts of each of these kinds of materials in a test tube? It would not. Life depends on more than these substances being mixed together. These materials must be present together in a very carefully defined manner which man has not yet been able to duplicate in the laboratory. What is the difference between a mixture of chemicals and living matter? In general, living things are capable of the following functions which nonliving matter cannot carry out:

(1) They can absorb or ingest materials from their environment as nourishment.
(2) They can excrete waste products.
(3) They can reproduce themselves.
(4) They can respond to a stimulus from their environment. (A man who covers his ears in the presence of a loud noise is responding to a stimulus.)
(5) They can move from one location to another (locomotion).

Not all living organisms possess every one of these attributes; however, all living organisms do possess the majority of them.

A borderline case is the class made up of the viruses. Are viruses living or nonliving? Viruses are composed of a conjugated protein called nucleoprotein. Nucleoprotein is made up of a polypeptide chain chemically joined to a nucleic acid chain. Viruses are like living organisms in that they reproduce themselves, but they can do so only in the living cells of a "host" organism where they disrupt the normal chemical processes of the host cell and induce the cell contents to reproduce the virus structure. The virus by itself possesses neither the smaller molecules nor the enzymes required to reproduce itself. Viruses can be crystallized and stored in a bottle like any lifeless chemical compound. However, once they are put back into solution after months or years and injected back into a living organism, they begin to reproduce as before.

14-5/PHOTOSYNTHESIS

Living organisms take in nourishment, transform it chemically into other substances, and eliminate waste products. The organism may use an ingested substance to build tissue, or it may use the substance as a source of energy. In this second case, the substance is chemically broken down into simple materials. Generally, organisms ingest carbohydrates to be used as sources of energy. Proteins and fats serve to build up tissue. However, all three classes of substances can play both roles.

In the digestion and metabolism process within a living organism, fats and proteins are usually first transformed into simpler substances which are later rebuilt as proteins and fats within the organism. Carbohydrates are transformed by a long series of chemical reactions into carbon dioxide, water, and energy. Carbon dioxide and water are eliminated as waste products, and energy is used by the organism for its life processes.

Carbohydrates are constantly being used up by organisms which require them as sources of energy. If carbohydrate supplies were not restocked, it would be only a matter of time before the world's carbohydrate supply was exhausted. The resupply of carbohydrates is achieved by means of **photosynthesis** in plants. In this process, water and carbon dioxide are made to recombine to give back carbohydrates and oxygen:

$$6\,CO_2 + 6\,H_2O \xrightarrow[\text{energy from sun}]{\text{chlorophyll}} C_6H_{12}O_6 + 6\,O_2$$

The $C_6H_{12}O_6$ is glucose or some other simple sugar which may further react to produce more complex carbohydrates such as starch or cellulose. In this reaction, energy from the sun is required. One could say that this energy is stored in the carbohydrate molecule. The catalyst for this reaction is chlorophyll, a green-colored substance contained in all green plants. Chlorophyll is a complex compound containing a metal, magnesium, bonded to an organic molecule. This type of complex substance is called an organometallic molecule.

The glucose and other carbohydrates formed in the photosynthesis process are stored within plants. When plants are eaten by animals, the plant carbohydrates are used by the animals as sources of energy. In the final analysis, this energy is derived from the sunlight necessary for photosynthesis. The oxygen produced by photosynthesis is released into the air, and it is believed that all the oxygen in the air comes from this source.

14-6/ENZYMES

To be carried out efficiently, almost all of the chemical processes which take place in living organisms require the presence of enzymes. **Enzymes** are organic catalysts which promote biochemical reactions without themselves becoming permanently altered.

An example of an enzyme in action is the conversion of the starch in a soda cracker to a sugar, maltose. If you chew a soda cracker and retain it in your mouth for a few minutes, you will notice that the taste gradually becomes sweet. The starch in the soda cracker reacts with water in the saliva in the presence of the enzyme amylase to produce maltose. The amylase is also present in the saliva and is not changed chemically in this reaction.

Starch consists of many glucose units joined together. The starch, an enzyme (amylase), and water form an unstable complex which breaks down into the disaccharide maltose, regenerating the amylase. Maltose is a disaccharide which consists of two glucose units joined together.

It has been found that all the enzymes so far isolated are either simple or conjugated proteins. Many enzymes consist of a protein chain chemically associated with a nonprotein or coenzyme portion. Many vitamins function as coenzymes in various enzyme systems. The vitamin and polypeptide parts of these enzyme systems together catalyze reactions within the living cell that are necessary to life and good health. If we can find out what these reactions are, we can see exactly how certain vitamins are important to us.

Several points have been noted regarding enzymes. First, enzymes can operate as catalysts inside or outside of living tissues. Pepsin is an enzyme found in the digestive juices of the stomach which causes proteins to break down into smaller polypeptide fragments. Pepsin can also break down protein in a laboratory flask. Second, enzymes are extremely effective as catalysts. Only a small quantity of an enzyme is necessary to catalyze a biochemical reaction. Third, enzymes are very specific in the reactions which they will catalyze. For example, one enzyme, catalase, will catalyze only one reaction even though it has been tried in hundreds of reaction systems.

Fermentation is a general term referring to enzyme-catalyzed chemical transformations which take place anaerobically (in the absence of oxygen). A particularly important fermentation is the transformation of sugars to ethyl alcohol and carbon dioxide with the use of yeast. At least a dozen enzymes in yeast are involved in the change.

14-7/SOME WORDS FOR JOULE JUGGLERS

Respiration is the process whereby energy is extracted from nutrients by living cells. There are two types of respiration: aerobic and anaerobic. **Aerobic respiration** requires oxygen. In this process nutrients such as carbohydrates are transformed in the cell to carbon dioxide, water, and energy. This energy is used by the organism for various life processes. The reaction is aided by enzymes which are found in living cells. **Anaerobic respiration** does not require atmospheric oxygen. This type of respiration is called fermentation. The anaerobic respiration of glucose results in the formation of ethyl alcohol, carbon dioxide, and a relatively low yield of energy. In muscles it results in the formation of lactic acid.

Aerobic respiration is an important part of the *metabolism* of all higher plants and animals. How does the atmospheric oxygen get to the cells so that aerobic respiration can take place? When air enters the lungs, its oxygen passes into tiny blood capillaries and forms a weak bond with the iron in the hemoglobin of red blood cells. The product is called an oxyhemoglobin complex. The oxyhemoglobin complex is carried to the various cells of the body, where the bond is broken, and the oxygen is released to be used in respiration.

The aerobic respiration of glucose which takes place in living cells can be represented by the following equation which shows only the reactants and products:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{Energy}$$

The energy yields of nutrients can be measured in terms of joules. One joule is approximately the amount of work required to lift two golf balls through a height of one metre. If a girl (mass 50 kg) climbs a stairway with a height of 3 m, she expends 1.5 kJ (kilojoules) of energy. If she had previously eaten a piece of apple pie, she would have absorbed about 1200 kJ of energy. Thus the pie would have given her plenty of energy to spare.

One might wonder how much energy is required to keep the human body operating. This depends on a number of factors. Age, sex, state of health, and work habits all influence the amount of energy a person requires. A young adult remaining in bed for 24 h without eating or moving needs 6700 kJ to keep alive. The 6700 kJ is his so-called basal metabolic rate. An office worker who sits at a desk all day might use about 10 500 kJ. Someone engaged in heavy labor could use as much as 25 000 kJ a day.

Thus, what determines a person's tendency to gain or lose mass? It seems that the key factor is the number of kilojoules taken in as food versus the number of kilojoules used up by the body. If a person takes in more kilojoules than he uses, he will gain mass in the form of deposits of fatty tissue. Various metabolic processes in the body allow for the conversion of unused carbohydrates and proteins into fats. An excess of only 40 kJ per day of food intake over energy requirements would lead to a gain in mass of about a kilogram in a year's time.

When the intake of food is less than the body's energy requirements, the body draws upon its own substance in order to make up the difference. If a person wants to lose mass, he cuts down on the amount of food and changes the type of food he eats. Increasing the amount of exercise he does will also help him lose mass. The first of the body's stored materials to be used up in the absence of food are the carbohydrates. Carbohydrates are stored in the liver and muscles as glycogen. The glycogen deposits are used rather rapidly. The fat deposits are the next to be drawn upon. These fat deposits are usually enough to supply the energy requirements of the body for several weeks. In cases of advanced starvation, the body consumes its own proteins, first of its muscles and then of its vital organs until death occurs.

The desired rate of mass loss for most people ranges from about 500 to 1000 g per week. For most women, diets ranging from 5000 to 6500 kJ a day are satisfactory. For men, the range is between 6500 and 8500 kJ a day. An intake of less than 5000 kJ a day is generally not a wise practice unless it is done under medical supervision.

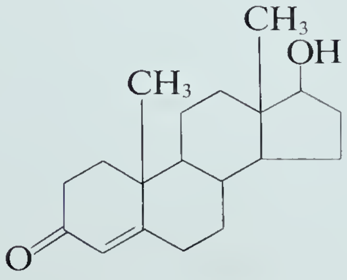
Five basic types of nutrients are required by the human body. These are protein, fat, carbohydrate, vitamins, and certain minerals. These must all be included in a diet for normal health. The body suffers if any one category is neglected. A balanced diet, featuring a reduction in the total food intake, is recommended for anyone who seriously wants to lose mass.

Many individuals have difficulty staying on a diet, and they must be highly motivated in order to maintain a food intake low enough to bring on a loss of mass. Appetite-depressing drugs have been used by some doctors to curb the appetite. The ingredients of these pills include amphetamines (which suppress the appetite), digitalis (which affects the heart), various diuretics (which increase the amount of urine), and other substances. Some of these drugs are potentially addictive; others tax the heart. Reliance on these drugs, rather than on a proper diet, will lead to an unsuccessful mass-reduction plan, and there are indications that their unsupervised use may be harmful.

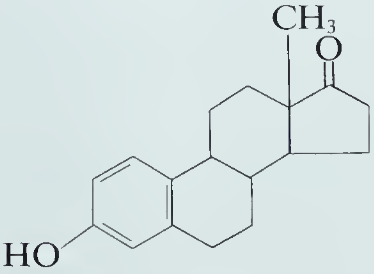
14-8/HORMONES

A number of organs in the body produce substances which are secreted directly into the bloodstream. These substances, which play vital roles in regulating body functions, are called **hormones.** Hormones influence our emotions, regulate our metabolic rate, and even determine whether we will be short or tall.

The reproductive organs manufacture hormones which belong to the steroid class of compounds. Steroid compounds have four rings. Testosterone is a male sex hormone or androgen. Androgens are responsible for the changes which take place in boys during adolescence such as the deepening of the voice or the growth of the beard. Estrone is one of the female sex hormones or estrogens:



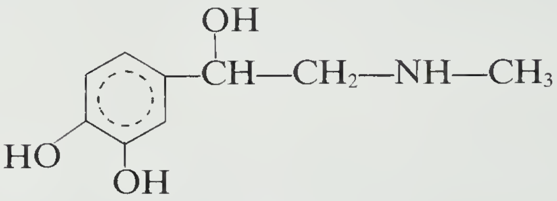
testosterone



estrone

The adrenal glands secrete several hormones. Several of these hormones are essential to life and removal of both of the adrenal glands results in death in about ten days unless the necessary hormones are medically provided. One of the best known adrenal hormones is the steroid, cortisone. Cortisone extracted from the adrenals of slaughtered cattle is used as a medication for those who suffer from rheumatoid arthritis.

The adrenals also produce a nonsteroidal hormone called **adrenalin** which is a very powerful stimulant. When a person is frightened or angry, the adrenal glands introduce adrenalin into the blood stream causing increased blood pressure and an increased heartbeat. Furthermore, the glucose level in the blood rises, which provides extra energy for the muscles and enables the individual to survive the emergency:



adrenalin

The organs that secrete hormones are called the endocrine glands. The pituitary gland (found at the base of the brain) is the master gland of the body. It secretes hormones which control the activity of the other endocrine glands and regulates the growth process. The growth hormone appears to be a protein. Production of too much of this hormone causes gigantism and production of too little causes dwarfism.

The pancreas is a vital organ which secretes pancreatic juice into the small intestine. This juice is essential in the digestion of proteins and starches. The pancreas also secretes a hormone, insulin, into the blood stream. Insulin is a protein hormone which is necessary for the proper metabolism of sugars and fats in the body. If insufficient insulin is produced, diabetes results. In diabetes, the level of glucose in the blood stream becomes abnormally high because lack of insulin prevents the glucose from being oxidized in the normal manner.

Thirst, hunger, and frequent urination are the first symptoms of diabetes. Glucose in the blood stream is not normally removed by the kidneys and passed into the urine. However, in uncontrolled diabetes, the blood-sugar level rises to such a point that the kidney has to take on a regulatory function and remove glucose from the blood. Glucose in the urine is therefore a sign of diabetes. In some severe cases of diabetes, the formation of carboxylic acids from the improper metabolism of fats causes the blood to become too acid. In this condition, called acidosis, the blood loses its ability to transport oxygen. In addition to carboxylic acids, acetone is produced in abnormal quantities in the body of a diabetic to the point where its odor may be detected in the breath.

Prior to 1922, the only treatment for the diabetic was a low carbohydrate diet, but this was effective only in mild cases. In 1922 the Canadian physician, Dr. Frederick Banting, was able to extract a crude insulin from the pancreas of dogs. He showed that injection of this insulin into a person suffering from diabetes lowered the blood sugar level and caused a remission in the symptoms of the disease.

Because this remission of symptoms is only temporary, the insulin must be injected at regular intervals. In past years this meant three or four times a day; however, modification of the insulin extract now makes one injection a day sufficient in most cases. Almost all of the insulin used today is extracted from the pancreas of hogs and cattle killed in slaughterhouses.

14-9/WHAT IS A DRUG?

Any chemical substance which can bring about a change in the function of living tissue is called a **drug.** This definition can encompass poisons as well as medicines. Most drugs are both medicines and poisons. Many very useful drugs will produce undesirable side effects if they are administered improperly. Thus, they should be given only under a physician's close supervision. That is why a prescription signed by a doctor is required for the purchase of many drugs. For example, penicillin, which has been so successful in combatting bacterial infections, causes allergic reactions in some patients. This small percentage of patients develops reactions to penicillin ranging from skin rashes to death. Even aspirin, one of the safest drugs, can be dangerous for some people. Of course, like many drugs, aspirin is very dangerous if consumed in large quantity.

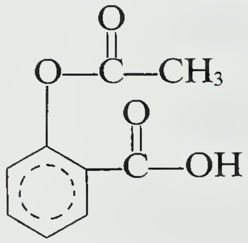
Today a large array of medicinal chemicals is available. Heading any list of drugs are the ones that reduce fever, relieve pain, or fight infections. In the following sections we will take a look at some types of medicinal chemicals.

14-10/ANALGESICS—PAIN-RELIEVING DRUGS

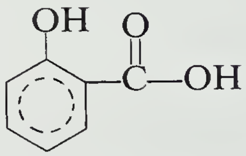
Headaches are caused by emotional problems (tension), heredity (migraine—also associated with tension), and occasionally, eye strain, acute sinus conditions, inflammation of the brain lining, infection of a cranial nerve, carbon monoxide poisoning, or poorly positioned teeth.

In tension headaches, muscles are strained and tightened. These overworked head muscles ache the same way that an overworked arm or leg muscle would ache. The tight muscle may also squeeze arteries and reduce the flow of blood through the muscle which adds to the pain.

Aspirin (acetylsalicylic acid) is a very common painkiller (analgesic) and fever-reducing (antipyretic) drug:



acetylsalicylic acid



salicylic acid

Aspirin is slowly converted to salicylic acid in the body. Because salicylic acid is poisonous, it is not safe to take it directly. The slow conversion of aspirin to salicylic acid in the body prevents a harmful amount of the salicylic acid from building up in the body at any given time. Salicylic acid acts on the central nervous system to reduce the pain of a headache. The hypothalamus gland, attached to the pituitary gland near the center of the brain, is the body's thermostat. When the white cells engulf bacteria, they secrete a chemical which migrates to the brain and resets the thermostat to raise the body temperature. This produces fever. In some way, aspirin readjusts the body temperature to normal.

The pain of a migraine headache is caused by a constriction of one or more arteries in the brain (which is painless) followed by an expansion of the arteries (which is painful), and by a headache fluid. Each time the heart pumps, the arteries expand further and a throbbing pain results. The headache fluid makes the nerves more sensitive to pain. Ergotamine tartrate (usually combined with caffeine), taken early enough, will relieve a migraine headache. It acts by constricting the muscles of the blood vessels, preventing painful stretching. Once a migraine headache establishes itself, only an analgesic will relieve the pain. Migraine headaches are hereditary and are often associated with a state of tension.

14-11/ANTISEPTICS

An **antiseptic** is a compound which prevents the growth of microorganisms. Because these compounds are poisonous, they are suitable only for external use. Examples of antiseptics are iodine, alcohol, hydrogen peroxide, mercurochrome, and hexachlorophene. Some of these compounds are oxidizing agents and can oxidize any cells including human cells. Often they are used as disinfectants for destroying the germs on nonliving objects.

Many of us have felt the sting of iodine because of the alcohol in which it is dissolved. Water-soluble polymers have been developed which contain iodine. These iodophors, as they are called, are efficient and painless disinfectants and are the active ingredient in a popular mouthwash. They are also used to disinfect a patient's skin prior to surgery.

Antiseptics are toxic to all living matter. They may help to prevent the spread of disease, but they are useless in treatment of disease because they act against all cells. Antibiotics, on the other hand, act preferentially against infecting bacteria and have a mild effect on body cells.

14-12/ANTIBIOTICS

Antibiotics have been so effective in combatting disease that they have been called "miracle drugs." They aid the white blood cells by stopping bacteria from multiplying. When a person is sick with an infectious disease, the bacteria have multiplied faster than the white cells can devour them, and bacterial toxins have increased faster than the antibodies can neutralize them. The action of the white blood cells and antibodies plus an antibiotic is generally enough to repel the attack of germs.

Penicillin was the first antibiotic to be discovered. In 1928 Alexander Flemming, a bacteriologist at the University of London, was examining some culture plates on which he was growing staphylococcus bacteria. One of the plates had been contaminated with mold. Many people would have thrown the contaminated plate away, but Flemming noticed that the staphylococcus would not grow within a considerable distance of the mold. Further study showed that the mold had a lethal effect against many harmful organisms. The mold was *Penicillium notatum*, so called because the spores sprout and branch out in pencil shapes. Flemming found that the broth from this mold was effective against pneumonia in mice. The active principle, penicillin, was difficult to isolate in pure form, and Flemming turned to other work. Later two Oxford researchers, Florey and Chain, were able to develop the knowledge regarding penicillin to the point where the drug could be manufactured on a large scale. By 1945, most of the problems associated with the production of penicillin had been overcome, and there was enough penicillin for everyone.

After penicillin came streptomycin, aureomycin, chloromycetin, and terramycin. Antibiotics owe their success to the fact that they kill bacterial cells and not human cells. Only a few antibiotics are relatively nontoxic. Even penicillin is toxic to some people, and streptomycin has been removed from the market because it is more toxic than some equally effective, newer antibiotics.

14-13/ANTIHISTAMINES

An **allergy** is an adverse reaction of the body to a foreign substance that produces no obvious ill effects in most other organisms. An allergen is a substance that initiates the allergic reaction. What is the cause of an allergy such as hay fever?

For a patient with a pollen allergy, the pollen grains enter his nose and cling to the mucous membranes. The nasal secretions release the grains' allergens. The allergens come in contact with special cells in the nose and react with antibodies present in these cells. Allergen-antibody complexes are formed, and the formation of these complexes causes the release of the compound, histamine, by the cell. Histamine accounts for many of the symptoms of hay fever and other allergies. It can produce skin swelling and stimulate the glands that secrete watery nasal fluids, mucus, tears, and saliva.

Antihistamines occupy the sites on cells normally occupied by histamine. This blocks the action of histamine. Efforts are being made to find drugs with less troublesome side effects than antihistamines. The most troublesome side effects are drowsiness, dizziness, headache, nervousness, nausea, and depression. There is no proven drug which will relieve the allergy and completely avoid the side effects. A new drug, however, which has been quite successful in treatment of many asthma cases, apparently acts by blocking the release of histamine in the first place.

14-14/ANTACIDS

The human stomach contains hydrochloric acid which acts directly on ingested food and activates the enzyme pepsin for digesting proteins. Occasionally people suffer from excess acidity. Antacids are compounds that reduce the amount of acid in the stomach.

Magnesium hydroxide (milk of magnesia) neutralizes the hydrochloric acid to form water and magnesium chloride:

$$Mg(OH)_2 + 2\ HCl \rightarrow MgCl_2 + 2\ H_2O$$

A combination of aluminum hydroxide and sodium carbonate, dihydroxyaluminum sodium carbonate, is the active ingredient in a common antacid. The reaction is:

$$NaAl(OH)_2CO_3 + 4\ HCl \rightarrow NaCl + AlCl_3 + 3\ H_2O + CO_2$$

The best antacids are the ones that do not reduce stomach acidity too much. If the reduction of acidity is too great, the stomach secretes an excess of acid (acid rebound). Antacids treat the symptoms of excess acidity, and not the causes, and they should be used with caution.

14-15/DRUGS IN COMBINATION

Some drug combinations can be very harmful. For example, an ageing business executive took an antidepressant and then ate a meal that included wine and cheese. The antidepressant inhibits the enzyme that helps to control blood pressure. Both the cheese and the wine contain amines which raise blood pressure. Without the controlling effect of the enzyme, these amines caused his blood pressure to skyrocket, and he had a stroke. The combination of the antidepressant and the amines caused the stroke.

Alcohol combined with many antihistamines or tranquilizers is dangerous. In fact, it is better to stay away from most alcohol-drug combinations, but that is not as easy as it may seem. Many people, for example, do not even realize that cough syrup contains an appreciable amount of alcohol. The best advice is to take drugs only when one is sick, and to make sure that the doctor knows all of the drugs you are taking.

14-16/TOXIC SUBSTANCES

Some chemicals, present in small amounts, upset the biochemical reactions of the body. These substances are toxic. Lethal doses are expressed in milligrams of substance per kilogram of mass of the subject. How do we measure toxicity? Various dosages of substances to be tested are injected into laboratory animals such as rats. The dosage that is lethal to 50 percent of a large number of the animals under controlled conditions is called the LD_{50}. Thus, if the data show that a dosage of 1 mg/kg kills 50 percent of a large population of rats, the LD_{50} for this poison would be 1 mg/kg. Different animals have different LD_{50}'s for the same poison so we cannot extrapolate these data to humans with positive assurance. However, a substance that has a low LD_{50} value for several animal species is likely to be quite toxic to humans.

An incredibly poisonous substance is produced by the botulinus bacillus. This microorganism multiplies in spoiled food and secretes a toxin which is the most powerful food poison yet known. This toxin is so poisonous that its lethal dose is estimated to be only eight molecules per nerve cell. One milligram would be enough to kill over 20 million mice, and 200 g would destroy all the human beings on earth.

14-17/CORROSIVE POISONS

Substances such as acids and alkalies which destroy the tissue they come in contact with are called corrosive poisons. Sulfuric acid (used in car batteries), hydrochloric acid (muriatic acid), and sodium hydroxide (lye, the active ingredient of most drain cleaners) are all highly corrosive. These materials first dehydrate cellular structures. After the cell dies, its protein structures are destroyed. Both acids and alkalies catalyze the breaking of the peptide links in protein. As more and more peptide links are broken the tissue disintegrates.

14-18/CARBON MONOXIDE

Carbon monoxide is an insidious poison which is present in auto exhausts, smoldering leaves, and charcoal burners (e.g., in hibachi stoves). Carbon monoxide inhibits the ability of hemoglobin to carry oxygen to the cells of the body. As you recall, oxygen combines with hemoglobin to form oxyhemoglobin, which carries oxygen to the cells. Carbon monoxide also reacts with hemoglobin to form carboxyhemoglobin, a complex which is much more stable than oxyhemoglobin. In addition, the presence of the carboxyhemoglobin interferes with the normal oxygen release by oxyhemoglobin. The carbon monoxide ties up some hemoglobin, and it prevents still more from supplying oxygen to the cells. Breathing air which is 0.1 percent carbon monoxide for four hours converts about 60 percent of the hemoglobin of an average adult to useless carboxyhemoglobin. Thus, the carbon monoxide competes with oxygen in bonding to hemoglobin. The best way to help a victim of carbon monoxide poisoning is to administer fresh air, or better still, pure oxygen. In this way, the oxygen has a better chance of bonding to the hemoglobin, because there is much more oxygen present than carbon monoxide. Charcoal-burning stoves should *never* be used indoors.

14-19/CYANIDE

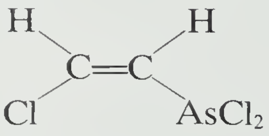
Cyanide compounds such as hydrogen cyanide are among the most rapidly working poisons. Lethal doses taken orally act in minutes. Cyanide does not prevent the cells from getting oxygen; it interferes with the enzymes which catalyze the reaction between carbohydrates (such as glucose) and oxygen. Thus, plenty of oxygen gets to the cells, but the process by which this oxygen is used in the biochemistry of life is stopped.

14-20/HEAVY METALS

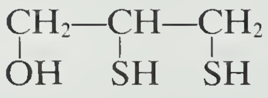
Poisonous heavy metals include lead and mercury as well as cadmium, chromium, and thallium. The metalloid, arsenic, is also a toxic substance.

Metals are toxic primarily because of their ability to react with and inhibit sulfhydryl (—S–H) enzymes such as the ones involved in the production of cellular energy. The metal replaces the hydrogen on the sulfhydryl group.

In World War I, the arsenic-containing gas, Lewisite, was used as a poisonous gas. Once the sulfhydryl interaction was understood, British scientists set out to find a compound that contained very reactive sulfhydryl groups to combine with the arsenic and render the poison harmless. A compound called British Anti-Lewisite (BAL) was the result:

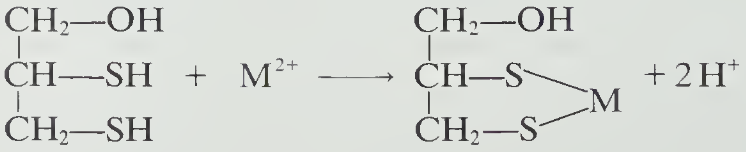


Lewisite



$$\begin{array}{ccccc} CH_2 & — & CH & — & CH_2 \\ | & & | & & | \\ OH & & SH & & SH \end{array}$$

BAL



With the arsenic or other heavy metal tied up by BAL, the sulfhydryl groups in vital enzymes are free to perform their normal functions.

Mercury is a liquid metal which fascinates some people, especially children, who love to touch it and coat coins with it. It is poisonous in itself and it gives off toxic mercury vapor. It also builds up in the body because the body has no quick way of getting rid of it. While mercury is rather unreactive compared to other metals, it is easily absorbed through the skin. Mercury poisoning is a hazard to people who work with it. Dentists use it in making amalgams for fillings; scientific laboratory personnel use mercury compounds and mercury pressure gauges; some agricultural workers use mercury salts as fungicides.

Lead is another poisonous metal. We constantly ingest lead compounds but the human body can rid itself of about 2 mg of lead a day through the kidneys and the intestinal tract. The daily intake is normally less than this. However, if intake exceeds this amount, accumulation and storage results. Lead behaves like the other heavy metals in its poisoning process. In addition, lead, like mercury and arsenic, can affect the central nervous system.

Lead salts, unless they are very insoluble, are always toxic. Their toxicity is related to the solubility of the salt. One common lead compound, tetraethyl lead (found in leaded gasoline), is readily absorbed through the skin. Even metallic lead can be absorbed through the skin. Cases of lead poisoning have resulted from frequent handling of lead foil and bullets.

14-21/NEUROTOXINS

Some poisons limit their actions to the nervous system. These include strychnine, curare, and the nerve gases. The exact modes of action of most neurotoxins are not known for certain but we do have an idea of how some of them work.

A nerve impulse is transmitted along a nerve fiber by electrical impulses. The nerve fiber connects with either another nerve fiber or with another cell which is capable of being stimulated by the impulse. When the impulse reaches the end of certain nerves, a small quantity of a compound called acetylcholine is liberated. This activates a receptor on an adjacent nerve.

Neurotoxins often act at the point where two nerve fibers come together. This point is called the synapse. Neurotoxins, such as atropine and curare, occupy the receptor sites on nerve endings of organs which are normally occupied by acetylcholine. When atropine or curare occupies the receptor site, no stimulus is transmitted to the organ.

A well-known organic compound that blocks receptor sites, similar to curare and atropine, is nicotine. This is a powerful poison which first causes stimulation and then depression of the central nervous system. Pure nicotine was first extracted from tobacco, and its toxic effect was observed only after smoking was established as a common habit.

14-22/HALLUCINOGENS

The hallucinogens produce temporary changes in perception, mood, and thought. They include mescaline, lysergic acid diethylamide (LSD), tetrahydrocannabinol (marijuana), and more than 50 other substances. They are mentioned because they can be toxic in relatively small doses.

Each of the hallucinogens is capable of disturbing the mind and producing bizarre interpretations of external stimuli. One of the oldest known hallucinogens is mescaline which was isolated from the peyote plant in 1896. However, as early as 1560 the Mexican Indians who ate or drank the peyote experienced visions and inebriation which lasted for two or three days.

Hundreds of scientists are studying the effects of hallucinogens like LSD. They are probing its effects on chromosomes, nerve and brain function, tissue structure, and the body in general. There is no consensus on the toxic effects that LSD can cause. Getting good data is difficult for several reasons. Users do not have accurate records of the amount of LSD they have used; the purity is often in question; and some users take other drugs in addition to LSD. There are conflicting studies and conflicting evidence as there was in the days of Lavoisier and Priestley.

The debate over the dangers of LSD is continuing and will not likely be resolved for some time. However, some dangers in the use of LSD are well documented, including the fact that

LSD destroys one's sense of judgment. Such things as height, heat, or a moving truck may seem to hold no danger for a person under its influence. Excessive or prolonged use of LSD can cause brain damage. After one "trip" a user can experience another "trip" later, unexpectedly, without taking any more drug.

How does LSD cause a trip? One theory will be outlined here. Serotonin and norepinephrine are thought to carry messages from one end of a brain cell to the end of another brain cell across the gap or synapse. LSD releases, in a chemical way, experiences that are hidden away or chemically stored in the lower midbrain or brain stem. Serotonin or norepinephrine, or both, inhibit the escape of these experiences into consciousness. LSD interacts with the serotonin or norepinephrine and nullifies their blocking effect. Thus these stored, previously rejected experiences enter the conscious part of the brain and the imaginary "trip" occurs.

QUESTIONS

1. What is the main difference between animal fats and vegetable oils?
2. How does the molecular structure of a soap help remove a grease stain from a piece of cloth?
3. What is a ketopentose? An aldohexose?
4. How do we know that sucrose is a disaccharide?
5. What carbohydrate is found in starch, table sugar, cellulose, and grape sugar?
6. What is the main function of the carbohydrates that are ingested by living organisms?
7. For which polymers found in plant and animal tissue are the alpha-amino acids used as monomers or building blocks?
8. What is an enzyme?
9. To which group of substances present in humans do adrenalin, testosterone, and insulin belong?
10. What is the main effect of a lack of insulin on the human body?
11. What is an analgesic? Which drug is the best known analgesic?

12. What is the scientific definition of an allergy?
13. What is the difference between an antibiotic and an antiseptic?
14. How does carbon monoxide kill humans?
15. Why is mercury such a dangerous metal?
16. If you were told that the LD_{50} for a certain substance is 0.001 mg/kg, what would you know about the substance?

QUESTIONS TO THINK ABOUT

17. Why do you suppose that the polar heads of the soap molecules prevent the suspended droplets of grease or oil from coalescing into larger droplets?
18. Why do you suppose that polyunsaturated fats are preferred over saturated fats for human consumption?
19. How many different tripeptides can be formed from glycine, alanine, and cysteine?
20. In analytical chemistry dimethylglyoxime (DMG) is used to precipitate nickel ions (similar to the reaction of BAL with heavy metals). Look up the structure of dimethylglyoxime and find out how it reacts with nickel. Like DMG, BAL is a chelating agent. What is a chelating agent?

15

CHEMISTRY AND THE ENVIRONMENT

In the 1970s, mankind became more aware of its effect on the environment and of the interrelatedness of all living things as they exist in nature. During the centuries that human beings have occupied this earth, the human population and technological advances have increased together. This has been especially true during the last several decades. To many people technology seems to be the main factor responsible for our problems with pollution. Some may regard technology and progress as demons responsible for the destruction of the environment. However, we should recall that technology is merely the application of scientific knowledge by people. People have misused technology to despoil the environment. Therefore people must use technology to clean up the environment.

One other point should be made. One cannot lay all the blame for our environmental problems at the feet of technologists. One should also consider the effect of the increasing human population. Living things have always had an effect on nature. Because of the sheer size of the global environment, nature has been able to adjust its balance. However, the disrupting effect of a highly concentrated population in a particular area may so alter the environment of that area that the balance of nature can never be achieved. The concentration of humanity in certain areas means the concentration of humanity's effects on the environment in those areas. This is true regardless of the state of the technology. Would Toronto be more habitable if horses were used instead of automobiles? Even if there were room for the horses, the accumulated animal refuse would probably make the streets of Toronto unacceptable.

In this chapter, we shall consider some of the information dealing with air and water pollution. We shall also consider the problems of pesticides and solid wastes.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Define pollutant, biochemical oxygen demand, biodegradable detergents, eutrophication.
2. Describe and explain the effects of solid particles in the atmosphere.
3. Describe the nature and effects of the London-type smog and the Los Angeles-type smog.
4. List ways by which atmospheric pollution can be diminished.
5. Name and describe the types of water pollution.
6. List the ways by which polluted water is purified.
7. Describe the environmental problems associated with the use of pesticides and with solid waste disposal.

15-1/CHANGES IN THE AIR ENVIRONMENT

Air is a mixture of gases such as oxygen, nitrogen, argon, carbon dioxide, and others. The atmosphere consists of air plus droplets of liquid, mainly water, and finely divided solid particles. The gaseous part of the atmospheric mixture is quite uniform near the earth's surface. The gas molecules are constantly in random motion and tend to mix evenly. Wind aids this mixing process. Thus, the atmosphere is a dynamic system in which the molecules are in continuous random motion. Chemical reactions occur among the substances present in the atmospheric mixture, and physical changes also take place. These physical changes include the settling out of solid and liquid particles.

The earth has been in a stable orbit for eons. Over the period of the earth's history natural balances have slowly been established in the atmosphere and a wide variety of equilibria have been reached. What is an equilibrium? To learn about equilibria in general, we shall consider the cycles by which the amount of carbon dioxide in the atmosphere has been limited to a concentration of about 0.03 percent.

Natural events such as forest fires, animal respiration, and volcanic eruptions pour carbon dioxide into the atmosphere. Some of this carbon dioxide is used by plants for photosynthesis. When animals eat the plants and breathe, the carbon dioxide returns to the atmosphere to complete the cycle. Other carbon dioxide dissolves in the water present in the atmosphere:

$$CO_2 + H_2O \rightarrow \underset{\textit{carbonic acid}}{H_2CO_3}$$

The carbonic acid reacts with minerals to form limestone, $CaCO_3$. Carbon dioxide also dissolves in the oceans and some of it ends up as $CaCO_3$ in the shells of ocean creatures.

Thus, carbon dioxide is involved in an equilibrium process. The amount of carbon dioxide entering the atmosphere from forest fires, volcanic activity, and animal and plant respiration is equal to the amount of carbon dioxide leaving the atmosphere by photosynthesis and carbonic acid formation. An equilibrium like this takes years to be reached and can be destroyed if another factor enters the picture.

The other factor is mankind's need for heat. Mankind has increased the carbon dioxide content of the atmosphere by the massive burning of fossil fuels such as coal and petroleum. The natural processes by which carbon dioxide is removed from the atmosphere cannot keep pace with this increase in carbon dioxide content. Mankind has destroyed nature's carbon dioxide balance. It now appears that the carbon dioxide content of the atmosphere is increasing.

Other gases such as carbon monoxide (CO), sulfur oxides (SO_2 and SO_3), nitrogen oxides (NO and NO_2), and hydrocarbons have always been present in the atmosphere. Volcanic action has produced sulfur oxides, and lightning produces nitrogen oxides from nitrogen and oxygen. However, mankind has added to the concentration of these noxious gases. In some areas of the world, people have been forced to regret high concentrations of these pollutants as we shall later see.

A **pollutant** is a substance that is present in high enough concentration to produce adverse effects on the things that man values. What man values must include not only his own health, safety, and property, but also acceptable conditions for all plants and animals. Man cannot control the amount of pollutants injected into the atmosphere by natural processes. However, the balancing mechanisms of nature normally act to prevent these quantities of pollutant molecules from rising to dangerous levels. What man must control is the quantity of pollutant molecules that enter the atmosphere as a result of his own actions. In the next sections, a number of substances that are known air pollutants will be discussed.

15-2/THE EFFECTS OF SOLID PARTICLES IN THE ATMOSPHERE

The presence of particles of dust and smoke has a great effect on the ability of the atmosphere to transmit radiation from the sun. The earth is warmed by infrared radiation from the sun. Any change in the amount of infrared radiation reaching the earth would change the temperature of the earth. Blocking the infrared light reaching the earth's surface would prevent the earth from reaching its normal temperature. Most atmospheric particles have a size ranging from 0.0001 to 0.01 mm in diameter. Larger particles are too heavy to remain in the atmosphere. The smaller particles are bounced about by collisions with gas molecules and tend to remain airborne for long times. These particles create a hazy atmosphere which allows less infrared light to reach the surface of the earth. Evidence actually exists that the average global temperature has fallen 0.2°C between 1940 and 1967. This may be due to a larger number of particles in the air. Continued temperature decreases would change the climate of portions of the globe.

Some solid particles, such as those in the smoke of metal smelters, contain poisons which are harmful to animals. The harmful effects of filling the lungs with soot, silica, arsenic oxides, or lead are well known. Studies suggest that respiratory diseases can be caused by breathing air which contains large quantities of particles.

Nature removes particles from the atmosphere by gravitational settling, rain, and snow. Mankind already has the technology which can aid nature in removing particles from the atmosphere. Taller smoke stacks are not the answer since they merely disperse the particles higher into the atmosphere. Filter bags made of glass fiber, cotton, nylon, wool, or felt can be used to filter particles from gases. Centrifugal separators whirl gases and throw particles to the walls of the apparatus where they can be collected.

Cottrell electrostatic precipitators (Fig. 15-1) can remove dust particles from plant exhaust gases. The dust particles pass through a strong electric field (about 50 000 V). If the particles are not already charged, they become charged. The charged particles are quickly attracted to oppositely charged plates where they are neutralized and fall to the bottom of the precipitator to be collected.

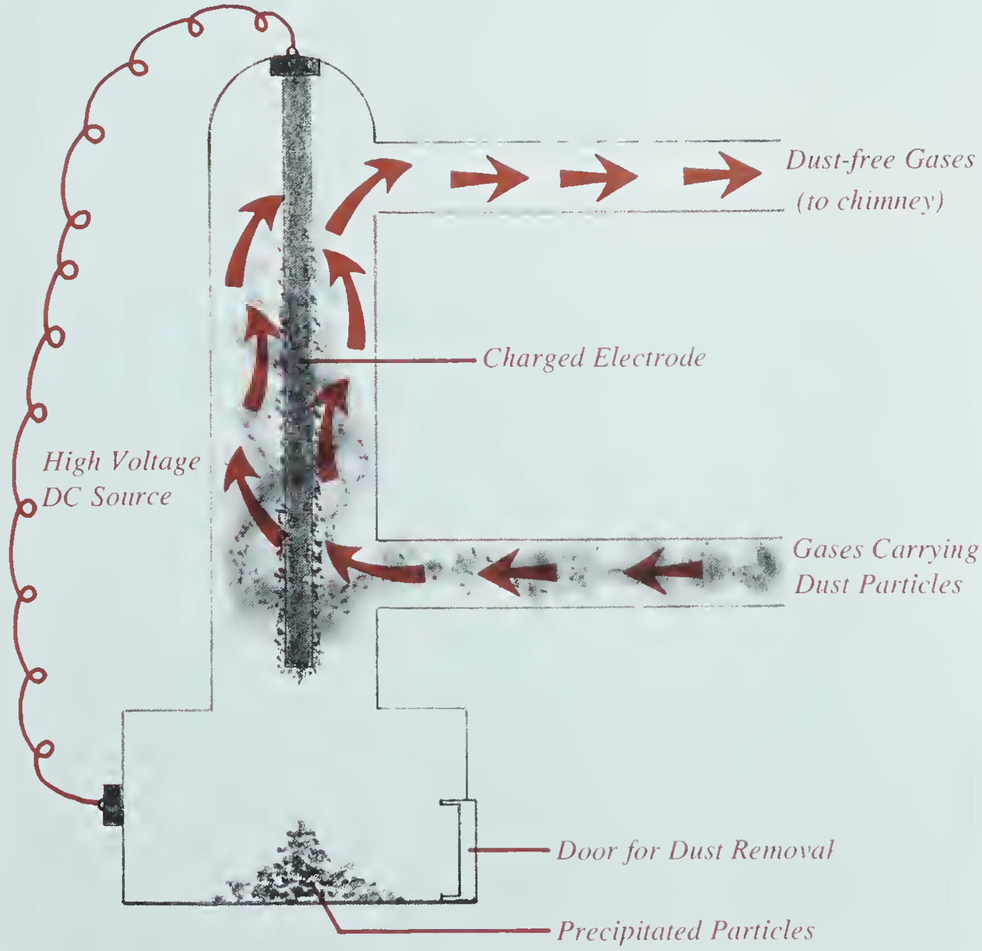


Fig. 15-1 Cottrell Electrostatic Precipitator

Equipment like the Cottrell precipitator can remove more than 99 percent of the dust particles from power plant exhaust gases.

Another control consists of better regulation of the combustion process. If enough air is used to burn carbon-containing compounds, more carbon dioxide and less carbon soot is produced.

15-3/CARBON DIOXIDE AND THE GREENHOUSE EFFECT

The carbon dioxide content of the atmosphere is increasing. Carbon dioxide is not a poisonous gas, nor is it very corrosive; however, it is interesting to observe that even carbon dioxide can cause environmental problems if its concentration in the atmosphere becomes too great.

Light from the visible and ultraviolet regions of the spectrum passes through carbon dioxide molecules without being absorbed. However, infrared light (the source of heat energy) causes the CO_2 molecules to vibrate more vigorously. Thus, the carbon dioxide molecules absorb and later reemit infrared light.

When the surface of the earth cools at night or under a cloud layer, the infrared energy which the earth gives off is trapped by the carbon dioxide in the atmosphere, and part of this infrared energy is re-emitted back to the earth. This leads to what is called the **greenhouse effect.** The glass roof of a greenhouse allows light and heat in, but it reflects back into the greenhouse some of the heat that tries to escape. The temperature inside a greenhouse is higher than the temperature outside it.

It has been estimated that an increase of 10 percent in the atmospheric CO_2 content would raise the average global temperature by 0.5°C. It is estimated that between 1890 and 1940, the global temperature rose by 0.4°C. Since 1940 the increase in the amount of particles in the atmosphere has caused the earth to cool down more than the increase in CO_2 has caused it to warm up. Thus, since 1940, the cooling effect due to an increased number of particles has dominated the warming effect due to an increase in the amount of CO_2.

However, if humans take steps to eliminate much of the particle pollution in the atmosphere, and at the same time continue to increase its CO_2 concentration, the world will begin to warm up again. This could cause a melting of the polar ice caps and result in the flooding of many coastal cities. The time may come when CO_2 will have to be regarded as a serious pollutant. We may have to remove CO_2 from the exhaust of all fossil-fuel burning energy converters such as home furnaces and thermal electric generating stations.

15-4/SULFUR DIOXIDE—LONDON-TYPE SMOG

Air pollution damage near Copperhill, Tennessee, is as dramatic in magnitude as the damage caused by an earthquake or a tidal wave. Copper ore has been mined and smelted there since 1847. In the smelting process copper ore containing copper(I) sulfide is converted to copper and sulfur dioxide:

$$\underset{\substack{copper(I)\\ sulfide}}{Cu_2S} + O_2 \xrightarrow{\Delta} 2\,Cu + SO_2$$

Fig. 15-2 Sudbury, Ontario *Sulphur dioxide is the major pollutant that has contributed to the devastation of large areas of vegetation in this mining community. (Photo courtesy of Dr. T. C. Hutchinson)*

The sulfur dioxide was discharged into the air until 1917. After 1917, the sulfur dioxide was used to make sulfuric acid. During the period from 1847 to 1917, the sulfur dioxide simply killed all vegetation in the area of Copperhill. Similar damage is being done at Sudbury (Fig. 15-2).

The mixing of moist air from above the nearby warm Gulf Stream and air from above the frigid Arctic currents frequently causes fogs in London. However, the fog of December 1952 was different. It was especially thick and cold. Because it was so cold, Londoners fired their coal heaters hotter and hotter. Because of the thick fog conditions, the smoke did not vanish into the upper atmosphere. The smoke mixed with the fog and became thicker and thicker. For five days, 12 million people filled their lungs with this smog (smoke+fog). A state of concern resulted as deaths from bronchitis jumped to nine times the usual rate. Deaths from pneumonia increased fourfold. Over 4000 deaths were attributed to the effects of this smog. Those fatally affected were usually 45 a old or older, but the mortality rate of infants under one year also rose.

What was the killer, and how did it attack people? The killer was sulfur dioxide and its source was coal. Both fossil fuels, coal and petroleum, were formed from once-living plant material. Along with the plant carbohydrates, there was sulfur-containing protein material. Thus sulfur is a contaminant in fossil fuels. Low-grade coal contains about 8 percent of the sulfur impurity. When such fuel is burned, the sulfur also undergoes combustion. Typical reactions are:

$$S + O_2 \rightarrow SO_2$$

$$2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$$

Much of the sulfur dioxide is converted in the atmosphere to sulfur trioxide:

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

This sulfur trioxide can then dissolve in the water vapor of a fog or in the water in the human body to form sulfuric acid:

$$H_2O + SO_3 \rightarrow H_2SO_4$$

The Londoners in 1952 were actually breathing a mist of dilute sulfuric acid! This sulfuric acid irritated the lungs, resulting in oxygen starvation and heart failure.

Today, we recognize the danger to human life caused by sulfur dioxide, sulfur trioxide, and sulfuric acid. Breathing air containing fine droplets of sulfuric acid irritates the whole respiratory tract from the mucous membranes in the nose and throat to the lung tissue. The presence of sulfur dioxide and sulfuric acid in the atmosphere is especially destructive to vegetation. An acidic atmosphere has harmful effects on most materials, especially paper, cloth, or leather. These airborne acid molecules usually attack buildings, monuments, statues, and everything else they contact causing unsightly pitting and corrosion.

The answer to the problem of sulfur dioxide is to eliminate its source. Several parts of the world have required the use of coal and fuel oil with low sulfur content in power-generating stations. This has appreciably abated the threat of sulfur dioxide. Oil refineries already possess the technology required to remove sulfur from sulfur-containing crude oil. Thus, little sulfur gets into gasoline. However, the cost of applying this technology to fuel oil adds to the cost of heating and electric power.

The tremendous power needs of the future will mean that we will eventually have to start burning coal with a higher sulfur content. Procedures will have to be developed to remove the sulfur dioxide from exhaust gases. One process which may be very useful involves the introduction of limestone ($CaCO_3$) into the combustion chamber. In the combustion chamber it decomposes into lime (CaO) which reacts with SO_2 or SO_3 to form solid particles. The reactions are:

$$CaCO_3 \rightarrow CaO + CO_2(g)$$

$$CaO + SO_2 \rightarrow \underset{\textit{calcium sulfite}}{CaSO_3(s)}$$

$$CaO + SO_3 \rightarrow \underset{\textit{calcium sulfate}}{CaSO_4(s)}$$

The solid calcium sulfite and calcium sulfate particles can be removed as the gas moves up the smokestack. Note that in the process more CO_2 is produced as the SO_2 and SO_3 are removed. In a sense we are trading one bad pollutant (SO_2) for a more subtle pollutant (CO_2). We may be solving one problem and creating another.

Another process is being developed which scrubs the emerging gases to remove SO_2 by a similar set of reactions with an alkaline material. The alkaline material can be regenerated and reused. The sulfur dioxide is eventually converted to sulfur. This sulfur can be sold—which helps to offset the cost of installing the scrubbing equipment.

15-5/PHOTOCHEMICAL OR LOS ANGELES-TYPE SMOG

There are two general types of smog. We have already studied the London type which is largely caused by the combustion of coal and oil. This type of smog contains sulfur dioxide mixed with soot, fly ash, smoke, and some organic compounds. The second type of smog is photochemical smog, or Los Angeles-type smog. It is called photochemical smog because light from the sun is important in starting the chemical process. This second type of smog is practically free of sulfur dioxide but it contains large amounts of nitrogen oxides, ozone, ozonated hydrocarbons, organic peroxides, and hydrocarbons of varying complexities. As we shall see, the smog for which Los Angeles is so famous (and which most cities have in varying degrees) is caused primarily by the automobile.

Los Angeles had almost no air pollution problem until around 1940 when population growth and industrial expansion in the area suddenly accelerated. It was at this time that the air pollution problem began to manifest itself. The previously clean atmosphere became frequently transformed into smog—a brown haze of smoke and offensive odors. Several factors were responsible for this: the sudden increase in the number of automobiles in Southern California and the peculiar natural climatic conditions in and around Los Angeles (including the legendary California sunshine) combined with the fact that the city lies in a mountain-rimmed depression.

Before the anti-pollution laws controlling automobile emissions were enacted, the thousands of cars around Los Angeles daily poured out enormous quantities of pollutants consisting mainly of nitrogen oxides and hydrocarbons (crankcase oil vapors and unburnt gasoline). These were the starting materials in the smog formation process. Because of its unusual geography, the city often experiences an abnormal meteorological phenomenon known as **thermal inversion** which prevents any pollutants from moving to the upper atmosphere where they can be dispersed. Normally, a layer of warmer, less dense air first forms near the earth and then rises carrying with it pollutants such as smoke, gases, dust, and others. The colder, more dense air from the upper atmosphere moves downward to replace it and the cycle is repeated. When thermal inversion occurs, a layer of warm air is *already* resting on top of a layer of cooler, more dense air near the earth. This lower layer cannot move upward; nor can it move sideways because of the mountains ringing Los Angeles. So a stagnant layer of polluted air used to remain trapped in and over the city. The abundant solar radiation acted on the trapped nitrogen oxides and hydrocarbons and the resultant photochemical reaction produced the smog (Fig. 15-3).

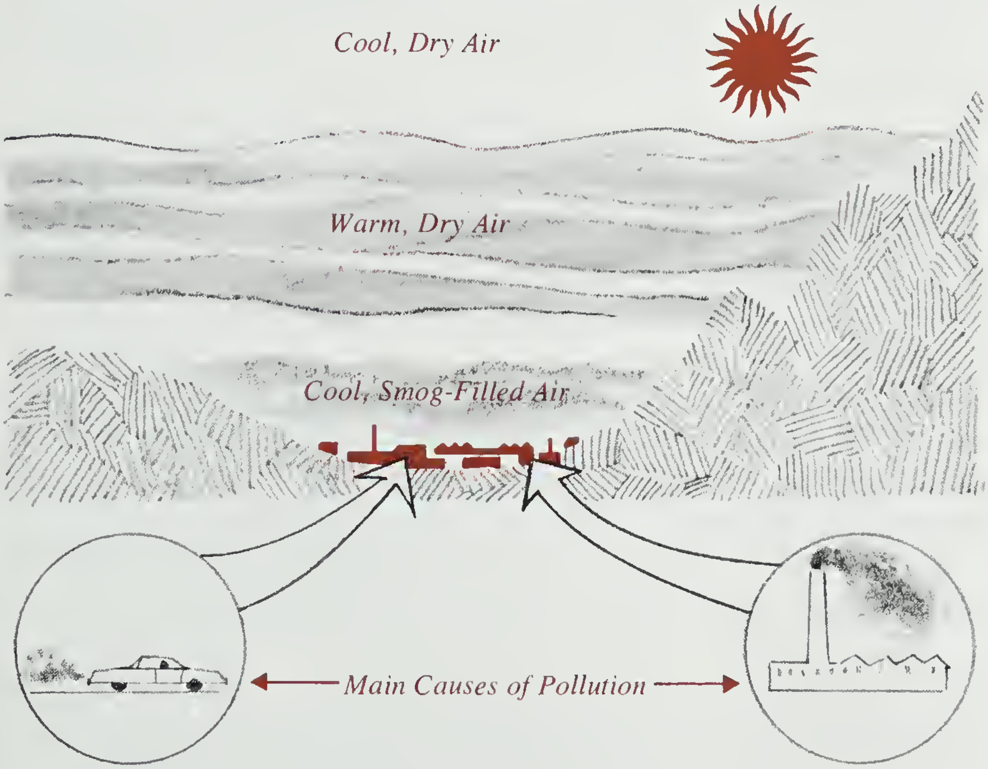


Fig. 15-3 A Thermal Inversion
The cool, smog-filled air is trapped by a layer of warm, dry air.

Thus, when nature supplies sunshine and a thermal inversion, and man supplies the killing ingredients by gasoline combustion and evaporation in automobiles, a photochemical smog results. Nature supplies the reaction vessel—the energy in the form of sunlight—and man supplies the chemicals. When suitable meteorological conditions prevail, the concentrations of contaminants in Los Angeles are enough to produce an objectionable smog during a one- or two-hour exposure to bright sunlight.

Research into the series of photochemical reactions that produce smog has added to our understanding of the process. Nitrogen(II) oxide (NO) arises from a direct combination of nitrogen and oxygen which is produced by the high temperature inside the automobile engine cylinders during the ignition stroke:

$$N_2 + O_2 + \text{heat} \rightarrow 2\,NO$$

This nitrogen(II) oxide immediately reacts with oxygen to form nitrogen(IV) oxide:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

At this point, the photochemical process is thought to begin. Ultraviolet light from the sun breaks up the nitrogen(IV) oxide molecule:

$$NO_2 + \text{UV light} \rightarrow NO + O$$

The oxygen atom has only six outer electrons, and it is a highly reactive species. It can react with oxygen to form ozone:

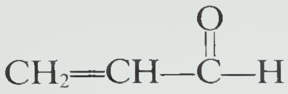
$$O + O_2 \rightarrow O_3$$

Ozone is a form of oxygen which has three atoms of oxygen per molecule. Ozone is called an allotrope of oxygen, and it is toxic and corrosive to tissue. Even at low concentrations ozone can kill plants.

Some ozone reacts with nitrogen(II) oxide to reform nitrogen(IV) oxide:

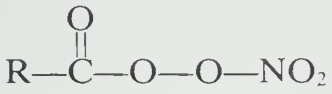
$$NO + O_3 \rightarrow NO_2 + O_2$$

Some of the reactive oxygen atoms follow another path. They can react with hydrocarbon molecules to produce organic free radicals. Free radicals are organic fragments in which unpaired electrons impart a great reactivity to the species. These free radicals can react with molecular oxygen to produce even more reactive free radicals, which can then react to form secondary pollutants such as aldehydes (formaldehyde, acetaldehyde, acrolein), ketones, and peroxyacyl nitrates (PAN):



$CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$

acrolein



$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}NO_2$

a peroxyacyl nitrate

It is known that formaldehyde, acrolein, and PAN are all lachrymators (tear producers). These three substances cause most of the physical discomfort produced by smog. Smog, however, contains hundreds of different molecules as a result of these free radical reactions.

15-6/EFFECTS OF PHOTOCHEMICAL SMOG

What is it like to be in Los Angeles when a combination of thermal inversion, low winds, bright sunlight, and hundreds of thousands of automobiles bring on the smog? Consider the possibilities.

The day begins clear and sunny. As traffic increases, the air begins gradually to become a yellow-brown haze. The odor is sharp and pungent. The shroud of pollution obscures prominent landmarks and limits visibility. The intensity of the smog increases during the day. Around noon the pollution becomes intense. People complain of eye irritation, and many find it difficult to breathe.

At street level, the carbon monoxide emitted from automobile exhausts reaches 50 parts per million, and traffic policemen complain of headaches. The carbon monoxide is combining with hemoglobin in their blood and is starving their bodies of oxygen.

The smog worsens, and school children are not allowed to have outdoor recreation classes. The ozone level has exceeded 0.35 parts per million, and at that level fifteen minutes in the outdoors can cause respiratory irritation accompanied by choking, coughing, and severe fatigue.

The smog grows thicker. The air mass is still held stationary by the thermal inversion and by the mountains. There is no wind—not even a breeze. The people of Los Angeles live in an atmospheric sewer, each person breathing 25 000 ℓ of this polluted air every day, 300 days a year. The air contains more than 50 pollutants. More than 2 million Californians (one person in eight) have some kind of respiratory problem such as emphysema, bronchitis, or asthma. There is more lung disease in California than in any other state.

Through this sewage drives John Citizen. He wonders if he should have his wife's car tuned up. He wishes that the emission control devices did not mean such low gasoline mileage. He wonders if his daughter's car has been safety-checked this year. He wonders what kind of automobile he will get for his 17-year-old son. Above all, he wonders when someone is going to do something about all this smog.

Although Los Angeles remains the chief center for photochemical smog, this phenomenon has been detected in varying degrees in most major metropolitan areas. Unless pollutant emissions are controlled, the sun, which has made life on this planet possible, could make city life unbearable.

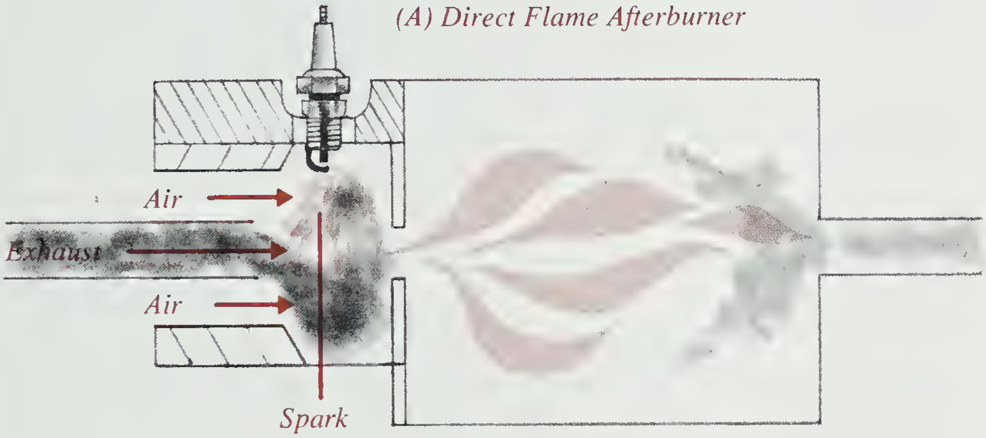
15-7/WHAT CAN BE DONE ABOUT AIR POLLUTION?

The previous sections have included discussions concerning some (but not all) of the possible air pollutants. The question is, what should be done about air pollution?

The first step is to pass laws to regulate the introduction of pollutants into the atmosphere. One city has banned the use of soft coal for heating purposes. Soft coal has a high sulfur content, and when it burns, it releases large quantities of sulfur dioxide into the air. Other cities have forbidden the burning of rubbish and the construction of private incinerators. New York is attempting to obtain more natural gas, which burns cleanly to produce mostly CO_2 and H_2O, for electric generating plants. Atomic energy would cut down air pollution. Smokestacks should have Cottrell precipitators to cut down on the amount of particles they produce. Eventually we will require national and international air standards. As the world population grows, we will require tougher air standards. However, with a combination of common sense, necessity, and research, there is no reason to believe that we will not be successful.

For example, because we know that the automobile produces hydrocarbons, nitrogen(II) oxide, and carbon monoxide, we will try to cut down the emission of these pollutants from automobile exhaust. Hydrocarbons and carbon monoxide will perhaps be burned more efficiently to produce carbon dioxide. A direct flame afterburner (Fig. 15-4) would mix unburned pollutants from the engine exhaust with additional fresh air, and then ignite the mixture with a spark or a flame.

(A) Direct Flame Afterburner



(B) Catalytic Device

Fig. 15-4 Devices for Controlling Automobile Exhaust Pollution

A catalytic device (Fig. 15-4) would consume these same pollutants by passing them together with additional air over a bed of mixed catalysts. We will also require catalysts capable of converting nitrogen(II) oxide to nitrogen and oxygen. This will be done while the gases are still in the engine or in the exhaust system. Tetraethyl lead has to be left out of gasoline used in automobiles equipped with catalytic devices because the lead renders the catalyst ineffective.

15-8/WATER POLLUTION

The cause of water pollution is negligence rather than ignorance. A community which dumps its raw sewage into a body of water is not ignorant of the effect of this action. Those who are unwilling to pay the cost of sewage treatment facilities can no longer use as an excuse the claim that the body of water is big enough to handle raw sewage. We are finding more and more that even huge lakes such as Lake Erie cannot absorb an unending flow of household and industrial waste. Dilution is no solution for pollution.

Surely every manufacturing plant administrator knows that the liquid which carries off his plant's wastes, when joined by the effluents of hundreds of plants, will overtax the natural processes by which even the largest rivers are cleaned of pollutants.

The existing technology of today could be applied to eliminate most water pollution if everyone were willing to pay the costs. The initial attack on the problem would be the removal of pollutants at the source.

We must also be ready to pay for further research. We must be able to analyze for insidious pollutants in minute concentrations. We must learn more about methods which nature uses for slowly cleaning polluted water. We must learn methods for purifying water efficiently.

15-9/BACTERIOLOGICAL CONTAMINATION

Bacteriological contamination is the form of water pollution which is most dangerous to human health. Most municipalities in Europe, North America, and Japan have adequate water treatment facilities, and water-carried diseases are at a minimum. In the past, outbreaks of cholera and typhoid fever killed thousands of people. Occasionally, cases of typhoid fever occur in areas where wells are located too close to septic tanks.

15-10/INDUSTRIAL WASTES

Industrial wastes tend to affect aquatic life rather than cause human illness. Compounds of lead and copper, certain phenol derivatives, and hydrogen sulfide can destroy life in streams where these substances are dumped. Acids from coal mines and chemical plants may greatly increase the acidity of rivers and lakes and make it impossible for plants or fish to live.

Mercury pollution is an insidious form of water pollution. The mercury is eventually absorbed by fish which in turn may be eaten by humans. Mercury poisoning and several deaths have been reported in Japan where contaminated fish were consumed.

15-11/THERMAL POLLUTION

Thermal pollution results when water is used for cooling purposes and in the process is heated up. Water is an ideal cooling fluid for thermal generating stations, nuclear generators, and industrial plants. The Thames River in England has been warmed up three degrees in 20 a from an average temperature of 12°C to 15°C.

The increased temperature means that less oxygen can dissolve in the water since gases dissolve more readily in cold liquids. The problem of oxygen depletion will be discussed more fully in the next section. However, thermal pollution aggravates the problems of oxygen supply in water, and a significant rise in the temperature of a body of water can destroy entire biological populations.

15-12/OXYGEN DEPLETION

When waste material from paper mills, coal-tar residues from dyestuff factories, or certain other organic materials (e.g., sewage) are dumped into streams, they react with the oxygen dissolved in water. Most of the degradation (breaking down) of organic molecules is accomplished by the action of microorganisms which use organic molecules as food by metabolizing them with oxygen dissolved in the water. This dissolved oxygen is breathed by fish and is as vital to them as atmospheric oxygen is to us. If large amounts of the dissolved oxygen are used up by the oxidation of wastes, the fish will not survive. The term **biochemical oxygen demand** (BOD) is used to describe the oxygen take-up by organic matter present in water. If the BOD is large, the water is considered to be polluted.

15-13/HOUSEHOLD DETERGENTS

The enormous quantities of detergents used in homes and dishwashing operations have presented another pollution problem. Flocks of ducks have drowned after landing on detergent-filled ponds (Fig. 15-5). The detergents washed off the oil on their feathers. This oil allowed the ducks to remain afloat, and when it was removed the ducks sank.

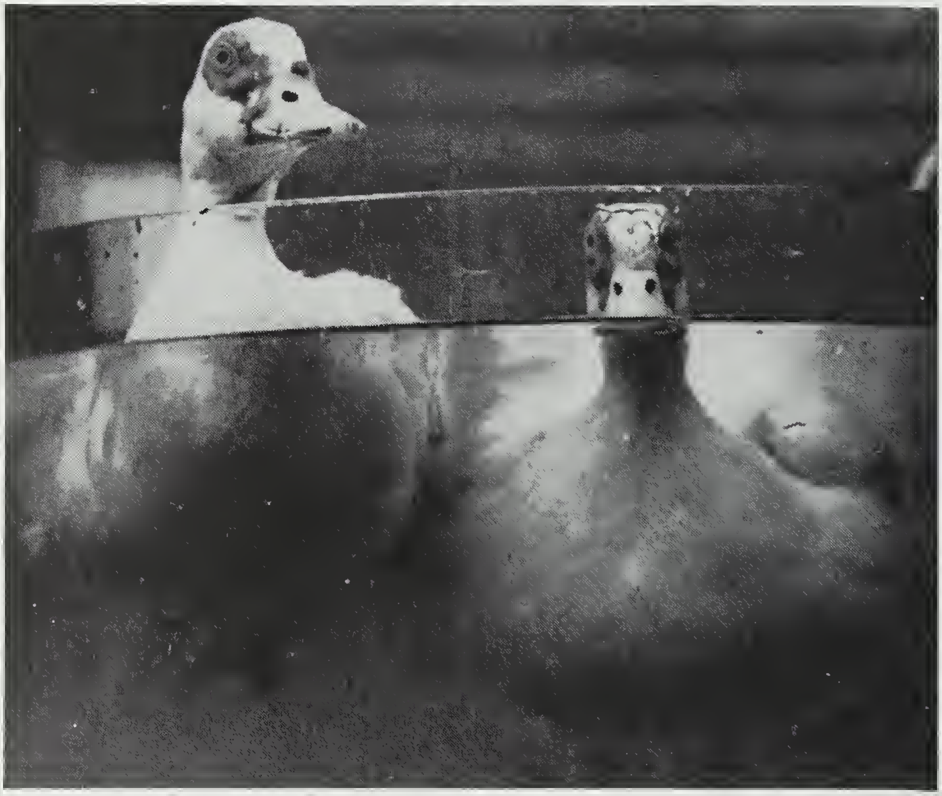


Fig. 15-5 This duck lost the ability to float because of the presence of a detergent in the water. *(Photo courtesy of the Litton Educational Publishing)*

The basic cause of detergent pollution lies in the fact that many commercial detergents have had chemical compositions which resist degradation by microorganisms. Municipal systems traditionally deal with sewage by relying on microorganisms for its degradation. The sewage is normally concentrated into a sludge which is then activated with microorganisms to hasten decay. When detergents were first introduced as replacements for soaps, many sewage treatment plants found themselves overwhelmed with foam. In recent years, detergents with structures that are easily attacked by microorganisms have been developed. These are called **biodegradable detergents.**

15-14/EUTROPHICATION

Eutrophication occurs when a nutrient substance (e.g., a nitrogen or a phosphorus compound) becomes a water pollutant in a lake or pond causing the removal of dissolved oxygen from the water. When the nutrient substances are present in abnormally high concentration, algae and plants grow profusely. While growing they photosynthesize plant tissue and generate some oxygen, most of which goes into the air. When the plant dies, the carbohydrate material of which it was made decays or is degraded by microorganisms. This bacterial decomposition consumes oxygen. When the quantity of decaying matter becomes large enough, the sequence of processes uses up so much dissolved oxygen that aquatic life cannot survive.

In many eutrophication studies compounds of phosphorus seem to be the most important nutrient pollutants. The evidence in the case of Lake Erie points to domestic sewage as the greatest source of phosphorus compounds. Most of the sewage entering this lake is treated to remove degradable organic compounds, but large amounts of phosphate additives from detergents go into the lake. Another source of nutrients, especially nitrates, would be fertilizer runoff from farms. Some studies indicate that CO_2 rather than phosphates or nitrates is the controlling nutrient in eutrophication. In waters where there are large amounts of degradable organic pollutants, algae seem to grow, even with little phosphate present. Microorganisms metabolize the organic molecules and supply large amounts of CO_2. This CO_2 is used by the algae for photosynthesis, and they grow fast enough to begin the process of eutrophication.

15-15/PURIFYING POLLUTED WATER

Municipal water supplies require treatment before the water can be used for human consumption. Sediment and suspended matter must be removed. Bacteria must be destroyed and industrial wastes must be neutralized or destroyed.

Much of the water which comes from lakes or streams contains particles of clay, sand, or organic matter. The larger particles are allowed to settle out of their own accord in reservoirs. The smaller particles are too small to settle out on their own. The water is treated with aluminum sulfate and calcium hydrogen carbonate. The two compounds form aluminum hydroxide which comes out of solution as a white gelatinous precipitate:

$$Al_2(SO_4)_3 + 3\ Ca(HCO_3)_2 \rightarrow 2\ Al(OH)_3(s) + 6\ CO_2 + 3\ CaSO_4$$

The aluminum hydroxide traps the small particles and carries them to the bottom of the tank. Water is drawn off from the top and any $Al(OH)_3$ particles are removed by filtration through a bed of sand. These chemicals also neutralize any acidic or alkaline water created by pollutants.

Organic compounds which cause objectionable taste or odors are removed by passage of the water through a bed of finely divided charcoal. The organic molecules are removed by attraction to the surfaces of the charcoal particles (adsorption).

Harmful bacteria are destroyed by adding a chemical disinfectant such as chlorine. Chlorine reacts with water to form hypochlorous acid (HClO):

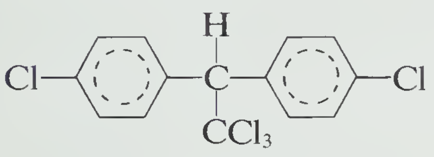
$$Cl_2 + H_2O \rightarrow HClO + HCl$$

Both the dissolved chlorine and the hypochlorous acid are highly toxic to bacteria. Iodine and ozone can also be used in place of chlorine. One advantage of ozone is that it decomposes rapidly in the water and does not leave an unpleasant taste as does chlorine.

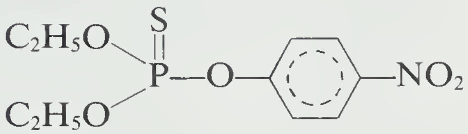
15-16/PESTICIDES

Pesticides are an important part of the interface between man and his environment. Pesticide is a general term used to cover insecticides, herbicides, fungicides, and rodenticides.

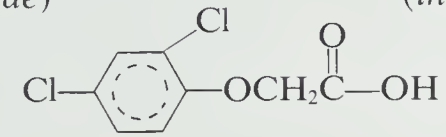
Insecticides include the chlorinated hydrocarbons, DDT, aldrin, and dieldrin. Malathion and parathion are organophosphorus insectides. Herbicides include 2,4-D and 2,4,5-T. A common rodenticide is warfarin (a potent anticoagulant) which is used to kill rats. Formulas for some of these products are shown below.



DDT
(*insecticide*)



parathion
(*insecticide*)



2,4-D
(*herbicide*)

The pesticide DDT (**d**ichloro**d**iphenyl**t**richloroethane) came into prominence in 1942 when U.S. and British authorities used it to control typhus in the war zones. It was used in Naples in January 1944 when a total of 1 300 000 civilians were dusted with DDT. DDT controls typhus by killing the body lice which transmit the disease.

DDT has been used in India to drastically decrease the incidence of malaria (spread by the anopheles mosquito) which, before DDT, was killing 2 million Indians every year. The "green revolution" in India, producing 100 billion kg of food annually, was also made possible. Modern agriculture owes much of its efficient use of land to the effective control of crop-destroying insects made possible by the use of insecticides.

On the other hand, the indiscriminate use of pesticides is contaminating water and soil and even destroying beneficial plants and animals. In the early years of pesticide use, the advantages outweighed any undefined potential dangers.

However, today a more careful study of pesticide use is under way.

Undesirable effects of pesticides may occur if human exposure to more than an acceptable minimum amount occurs. Two potential dangers of pesticides must be carefully studied for each pesticide in use. First, some pesticides, such as DDT and aldrin, do not degrade rapidly in the soil. For example, it takes two months for half the aldrin used in any field to degrade. Second, some pesticides degrade rapidly, but they break down into compounds that are also dangerous to the environment.

The harmful effects of DDT have been well studied. DDT is persistent. It may become part of the "food chain." DDT is taken up by plankton, which are eaten by small fishes, then trout, then man. Another sequence involves leaves, to compost, to earthworms, to birds. DDT is fat soluble and accumulates year after year in the fat and in the liver cells of the body. This makes the uncontrolled and improper use of DDT potentially very dangerous. This accumulation may cause liver damage and perhaps other illness. Because of these dangers, the use of DDT has been limited.

Nonetheless, it is necessary to use pesticides. They are needed in agriculture. They are needed to control diseases such as cholera, amoebic dysentery, and many parasitic diseases. What must be done is to improve the nature and use of pesticides so that minimum harm comes to man and to the environment.

The need of an exploding population for more food requires the development of safer and more effective pesticides. Ideally, these pesticides should affect only the harmful life form. This aim is difficult to achieve. Pests tend to adapt to a poison. The anopheles mosquito, which transmits malaria, has developed a resistance to DDT. In Great Britain, rats are beginning to develop a resistance to warfarin. New pesticides must be developed continually to meet the challenges of the pests that are not killed by old pesticides.

15-17/SOLID WASTE DISPOSAL

As the human population grows, the problem of increasing amounts of solid trash also grows. There is little specific chemistry to discuss; however, any plans for alleviating the problems of solid waste must be based on general chemical considerations.

In addition to handling the safe destruction of many types of trash, methods for recovery of reusable materials must be developed. The dwindling supplies of metal ores demand the recovery and reuse of aluminum, iron, zinc, tungsten, and other metals.

The need for increasing amounts of thermal energy for conversion into other forms of energy suggests that waste incinerators be designed to utilize the fuel value presently being wasted. Undoubtedly, these new facilities will add to the cost of living, but some of these facilities will at least partially pay their way by reclaiming useful products and providing energy in the form of heat.

Today, too many municipalities get rid of trash in open dumps. Noxious fumes from decaying refuse and the inevitable open fires contribute to smog-producing atmospheric conditions. Drainage water from these open dumps carries pollutants into streams and lakes.

Sanitary landfill techniques alternate layers of compacted trash and earth so that microorganisms can degrade organic materials. This procedure minimizes atmospheric pollution, but it does have possible hazards. About three quarters of typical municipal waste is a mixture of paper, plastics, wood, textiles, and garbage. Seldom is there enough air permeating the compacted material to allow oxygen-using microorganisms to complete the decay process. The decay is taken over by microorganisms that do not require oxygen. These organisms degrade the organic materials to methane, CH_4. It is safe to use landfill areas for parks, but it is not safe to construct buildings on landfill areas since the methane would be an explosion hazard if trapped by these buildings. A problem of the sanitary landfill technique is the cost of hauling trash to a proper landfill site. It is not likely that sanitary landfill will ever be the best method for trash disposal.

The most likely methods will probably be incineration procedures which recover heat and other useful products and which are designed to eliminate atmospheric pollutants. A high-temperature incinerator may be the answer. Typical municipal trash is burned at a temperature in excess of 1500°C. At that temperature, the organic matter is completely burned. No soot or carbon monoxide would likely form. The heat from burning the organic material can be used to generate electric power. This temperature is high enough to cause glass and most metals to melt. The molten glass and metals separate into layers which can be separated. All of these products have an economic value which will help to make up for the capital and operating costs of the high-temperature incinerator.

QUESTIONS

1. What are two main causes of the increase in pollution in recent years?
2. The carbon dioxide content in the atmosphere at one time was kept constant because the amount of carbon dioxide entering the atmosphere was equal to the amount of carbon dioxide leaving the atmosphere. What process injected carbon dioxide into the atmosphere, and what processes removed carbon dioxide from the atmosphere? What fairly recent factor has disturbed this carbon dioxide balance?
3. What is a good definition of a pollutant?
4. Evidence exists that the average global temperature has fallen 0.2°C between 1940 and 1967. To what do we attribute this temperature decrease?
5. What is the main effect of an increasing amount of carbon dioxide in the atmosphere?
6. To what source can the SO_2, SO_3, and H_2SO_4 in London-type smog be traced? What are the effects of an increase of SO_2 in the atmosphere? How can we cut down on the amount of SO_2 getting into the atmosphere?
7. What is a thermal inversion?
8. What is the main cause of photochemical smog?
9. Describe the factors that operate to give Los Angeles such a severe photochemical smog problem.
10. What is meant by the term *biochemical oxygen demand* (BOD)?

11. Name two of the things that must be done to polluted water before it is suitable for drinking.
12. What effect does eutrophication have on the amount of oxygen dissolved in a body of water? Why?
13. What factors should be considered when selecting a new pesticide?
14. Free radicals are involved in the production of photochemical smog. What feature of the structure of free radicals makes them so reactive?
15. Write a balanced equation for the burning of FeS_2 in coal to produce SO_2 and Fe_2O_3.
16. What are the major sources of the following air pollutants?
    (a) Oxides of nitrogen
    (b) Sulfur dioxide
    (c) Ozone
    (d) Carbon monoxide
17. Of the air pollutants (particulates, sulfur dioxide, carbon monoxide, carbon dioxide, ozone, and oxides of nitrogen):
    (a) Which is associated with London-type smog?
    (b) Which is not normally harmful to people?
    (c) Which can be removed by Cottrell precipitators?
    (d) Which affects the hemoglobin of the blood?

QUESTIONS TO THINK ABOUT

18. If you were a legislator attempting to construct a bill to regulate water pollution, what facts would you try to gather?
19. Who should be responsible for the removal of pollutants from used water?
20. What is the most effective method of garbage disposal, in your opinion?
21. In one study in Long Island Sound where the marshes were sprayed with DDT to kill mosquitoes, the following concentrations of DDT were found: plankton, 0.04 ppm (parts per million); minnows, 0.5 ppm; cormorants, mergansers and ospreys, 25 ppm. The data illustrate the increasing concentration of DDT as it moves up the food

chain from plankton to fish to birds. Do the data suggest that the increases are constant, accelerating, or decelerating? Can you suggest a reason for this?

22. Suppose you are disturbed by the odor of some small animals you keep in a cage in your room. Comment on each of the possible solutions to your problem:
    (a) Place a fan in the window to blow out the bad air.
    (b) Spray a pleasant scent into the room to make it smell better.
    (c) Clean the cage every day.
    (d) Spray a disinfectant into the room to kill the germs.
    (e) Install a device to pass the room air through activated charcoal.
    (f) Install an air conditioner to cool and recirculate the room air.
23. Our intestines contain bacteria to aid our digestive processes, and we live in harmony with these bacteria. Then why are digestive bacteria such serious pollutants of drinking water?
24. Incineration and recycling both have advantages and disadvantages as means of solid waste disposal. Discuss the economic and ecological trade-offs involved in each process.

16

NUCLEAR CHEMISTRY

Up to this point, we have almost completely ignored the nucleus of the atom. This chapter is devoted to introducing nuclear chemistry.

When you have finished studying this chapter, you should be able to attain the following objectives:

1. Define and where appropriate, give an example of: radioactivity, mass defect, binding energy, p/n ratio, even-odd rule, alpha decay, transmutation, half-life, beta decay, heavy water, transuranium element, fission, fusion, critical mass, nuclear reactor, moderator.
2. Describe the properties of radioactive substances such as compounds of radium.
3. Predict the relative stability of a given nucleus.
4. List the properties of alpha, beta, and gamma rays.
5. List the four types of nuclear reaction and give an example of each.
6. Balance nuclear equations.
7. Explain the principles of carbon-dating, and given the number of disintegrations of $^{14}_{6}C$ per minute, calculate the approximate age of a carbon-containing sample.
8. Describe the operation of a cyclotron and of a linear accelerator.
9. Write nuclear equations for the reactions occurring in a nuclear reactor.
10. Describe the ZEEP, NRX, and CANDU nuclear reactors.
11. Explain the principles of operation of a breeder reactor.

16-1/RADIOACTIVITY

The discovery of radioactivity was made by the French physicist Henri Becquerel in 1896. He had been studying the properties of metals and was especially interested in those metals that fluoresce (emit light). Accidentally, he found that exposure to a uranium ore caused a covered photographic plate to become fogged. He wrapped photographic plates in thin sheets of copper and aluminum and placed uranium salts on the covered plates. Again the photographic plates were blackened when they were developed. Becquerel decided that uranium salts emit rays which are capable of penetrating black paper and thin sheets of metal. The elements which give off these invisible rays are said to be **radioactive.** The property of giving off these rays is called **radioactivity.**

The French wife and husband team, Marie and Pierre Curie, took up Becquerel's research. They found that pitchblende, an ore which was partially made up of uranium, was more radioactive than uranium itself. The Curies believed that this ore contained a new element which was more radioactive than uranium.

The Curies obtained several tonnes of pitchblende and attempted to concentrate the material. For the next two years they labored. The work was tedious, painstaking, and unexpectedly dangerous since they were ignorant of the detrimental effects of exposure to radioactive materials. The Curies were nearly killed by fumes from the boiling vats in the laboratory, so they had the vats moved outside and worked there. As a result, during one severe winter, Marie caught pneumonia. Later she became pregnant but even then she continued the heavy manual labor required by the refining process. Most of the time, during the later stages of their research, both Curies were continually ill. Nevertheless, in spite of such spirit-breaking strain, they finally succeeded in concentrating the sources of the radioactivity. One of the sources was a substance which Marie Curie (Fig. 16-1) called *polonium*, in honor of her native land, Poland. Polonium was many times more radioactive than uranium.

Fig. 16-1 Marie Curie (1867-1934) *(Photo courtesy of The Bettmann Archive)*

They continued the tedious separation process and isolated a new element which was even more radioactive than polonium. This new metal was named *radium*. They separated only a few milligrams of radium chloride from the large quantity of pitchblende. However, radium is about a million times more radioactive than uranium. Marie Curie isolated pure radium from radium chloride. She found that it had the same chemical properties as the Group II element, calcium. However, it also possessed a new set of properties due to its strong radioactivity.

16-2/PROPERTIES OF A RADIOACTIVE ELEMENT—RADIUM

The invisible rays given off from radioactive elements affect the light-sensitive emulsion on a photographic plate in the same way that ordinary light affects a photographic plate. These rays from a radioactive element are able to penetrate paper, wood, flesh, and thin metal sheets.

The invisible rays from a radioactive element will also discharge a charged electroscope (Fig. 16-2).

When a charged rod touches the metal disc of the electroscope, the charge is distributed throughout the electroscope, including the two pieces of metal foil. The pieces of foil separate because like charges repel each other. This is a charged electroscope. The rays from a radioactive source ionize the gas (air) molecules in the electroscope by knocking off the outer electrons of the gas molecules. These charged ions are able to conduct electricity, and thus the charge is removed from the foil pieces which then fall back together.

The invisible rays also affect a Geiger-Müller tube (Fig. 16-3). The radiation ionizes the gas present in the Geiger-Müller tube. Thus, the temporarily ionized gas molecules allow an electric current to pass through the tube. This current can be measured with a Geiger counter.

Radium compounds, mixed with some other compound such as zinc sulfide, cause the latter to glow in the dark. This type of mixture has been used in making the luminous paint for instrument dials. Most manufacturers have stopped making this type of paint because of the radiation hazard to the workers who prepare and apply the paint.

Radium exhibits a number of physiological effects. Its radioactivity causes burns and destroys skin tissue. It kills

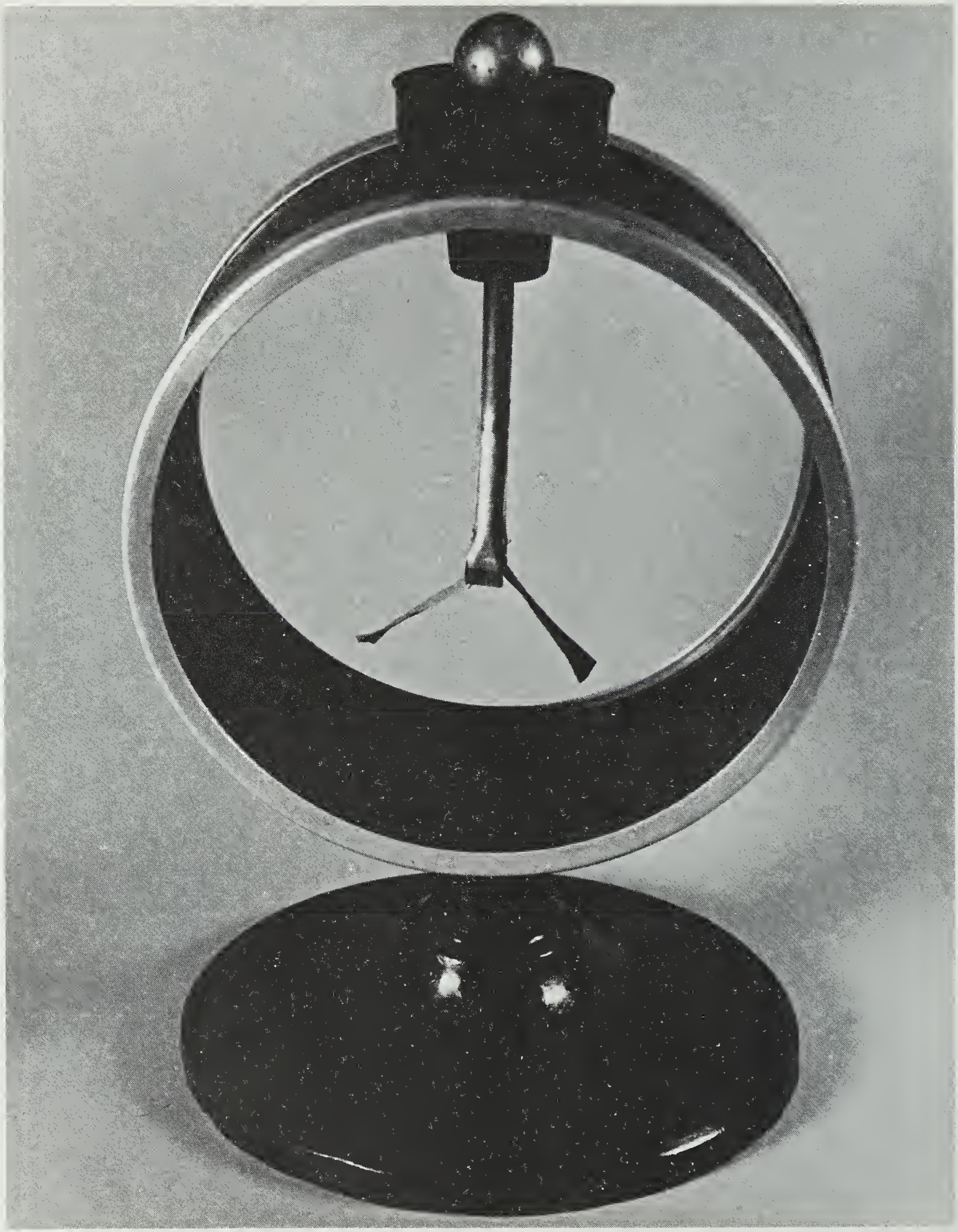


Fig. 16-2 A Charged Electroscope

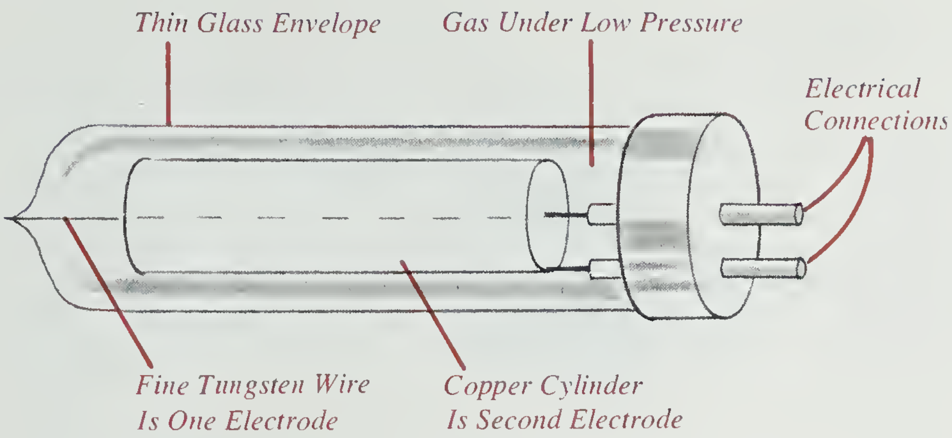


Fig. 16-3 Geiger-Müller Tube

bacteria or small animals, and it prevents seeds from germinating.

Radium salts are constantly emitting energy. Part of this energy is in the form of light. Radium salts glow in the dark; however, they do not give off enough light to be seen in daylight. Radium salts also give off heat energy. In one hour radium gives off enough heat to melt 1.5 times its own mass of ice.

16-3/THE LEAD BLOCK EXPERIMENT

The British scientist Lord Rutherford (Fig. 16-4) placed a few grains of radium salts in the bottom of a hole in a block of lead (Fig. 16-5). The radiation escaped from the hole and was allowed to strike a zinc sulfide screen. Zinc sulfide flashed when it was bombarded with the radiation, and Rutherford observed a small luminous patch on the screen. By placing a magnet near the path of the rays, Rutherford found that three patches of light were produced. Some rays were bent in one direction, some in the opposite direction, while others were not bent at all. From the direction in which the rays were bent, Rutherford concluded that some were positively charged, some were negatively charged, and others were uncharged. He named these **alpha, beta,** and **gamma rays** (Fig. 16-5).

Alpha particles were found (after Rutherford's experiment) to be helium nuclei. They have two protons and two neutrons.

Fig. 16-4 Lord Rutherford (1871-1937)
This British scientist was at one time the head of the physics department at McGill University. (Photo courtesy of The Bettmann Archive)

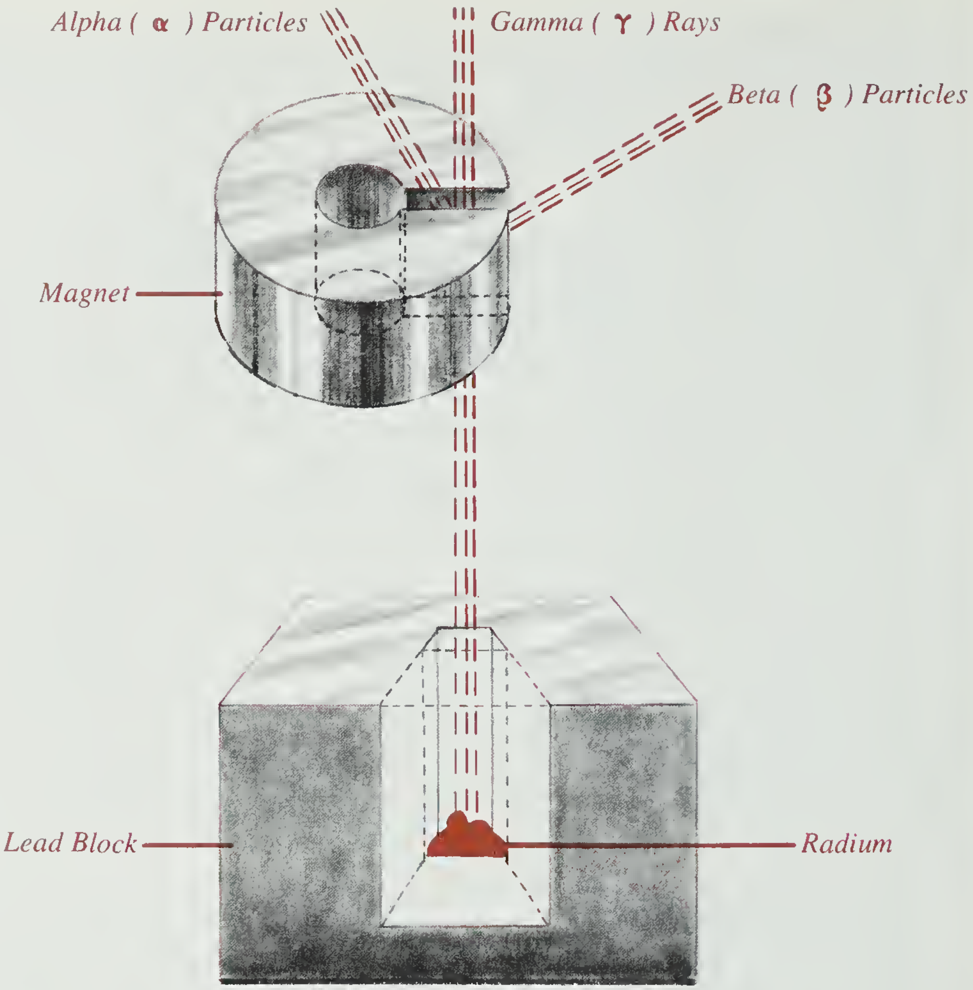


Fig. 16-5 Lead Block Experiment

Their positive charge is two units, and they have a mass number of 4 u. They travel at high speeds (around 0.05 times the speed of light), but they have weak penetrating power. They have a range of only a few centimetres in air, and they are stopped by thin sheets of aluminum or even paper. However, they do ionize the molecules of any gas through which they pass.

Beta particles are high-energy electrons, and they are negatively charged. They travel at speeds which approach the speed of light (around 0.3 to 0.99 times the speed of light) and have a greater penetrating power than alpha particles. They can pass through several millimetres of aluminum. They do not ionize a gas through which they pass as well as the alpha particles do.

Gamma rays are not deflected by a magnet. They are not charged particles. In fact, they are not particles at all. Gamma rays are high-energy, high-frequency electromagnetic radiations, similar to X-rays. They travel at the speed of light and are very penetrating. They can pass through 5 cm of lead or 30 cm of steel. They have little ionizing effect on gases.

In experiments like the one described above, the alpha particles are too heavy to be deflected very much. The beta particles are light and negatively charged. They are deflected in the opposite direction and to a greater extent than alpha particles. Because they have no charge, the gamma rays are not deflected at all.

16-4/STABILITY OF THE NUCLEUS

In order for an atom to be radioactive, its nucleus must be unstable. Thus, certain unstable nuclei spontaneously break down into more stable nuclei, emitting particles and rays as they do so. Three factors can be considered when one is trying to decide whether a nucleus is stable or not.

(*a*) *Mass*

The atomic mass of a helium nucleus is 4.0015 u. This nucleus is made up of two protons (1.0073 u) and two neutrons (1.0087 u). The sum of the masses of the two protons and the masses of the two neutrons is 4.0320 u:

$$2(1.0073)+2(1.0087)=4.0320\text{ u}$$

Apparently, 0.0305 atomic mass units were lost when two protons and two neutrons combined to form a helium nucleus. This is called the mass defect. The **mass defect** is the mass converted into energy when the helium nucleus is made from its components. This energy is called **binding energy.** Whenever the binding energy is large, the nucleus will be stable. However, it has been found that the binding energy is smaller for the very heavy and very light nuclei than it is for nuclei of intermediate mass. Thus, the nuclei of the very light and the very heavy atoms are least stable because they have the smallest binding energies. In fact, all nuclei heavier than bismuth (mass, 209 u) are unstable.

(*b*) *p/n Ratio*

The stability of a nucleus also depends on the proton to neutron ratio. For any given number of protons, there is a small range of numbers of neutrons that permits a stable nucleus. In the case of the first 20 elements of the periodic table, the preferred ratio is one proton to every one neutron.

(*c*) *Even-Odd Rule*

One can also predict the stability of a nucleus by looking at the number of protons and neutrons in it. A nucleus with an even number of protons and an even number of neutrons has a better chance of being stable than a nucleus with an odd number of protons and an even number of neutrons, or a nucleus with an even number of protons and an odd number of neutrons. There are very few stable nuclei that have both an odd number of neutrons and an odd number of protons:

Protons	*Neutrons*	*Number of Stable Nuclei*
Even	Even	165
Odd	Even	50
Even	Odd	51
Odd	Odd	4

The known number of stable nuclei decreases if the number of either protons or neutrons is odd.

These three factors (mass, p/n ratio, and the even-odd rule) can be used to predict the stability of a nucleus. However, in some cases prediction is difficult because the rules contradict one another. In the case of nitrogen (seven protons and seven neutrons), the p/n ratio is 1/1 but the nucleus has odd numbers of protons and neutrons. In the case of boron (five protons and six neutrons), the p/n ratio is not 1/1, but there is an even number of neutrons. However, in the case of carbon (six protons and six neutrons), both rules are satisfied. One would readily predict that the nucleus is stable and, in fact, it is.

16-5/TYPES OF NUCLEAR REACTIONS

There are four types of nuclear reactions. The first type is **radioactive decomposition.** If a nucleus is altered by the loss of an alpha particle or a beta particle, the reaction is a radioactive decomposition.

If a nucleus is bombarded by alpha particles, protons, or neutrons, an unstable nucleus may result. The unstable nucleus can emit a proton or a neutron in order to gain stability. This process is called **nuclear disintegration.**

If a heavy nucleus splits to form nuclei of intermediate mass, the process is called **fission.**

If two light nuclei combine to form heavier, more stable nuclei, the process is called **fusion.**

Examples of these types of nuclear reactions appear in the following pages of this chapter.

16-6/BALANCING NUCLEAR EQUATIONS

Before one can study nuclear reactions, it is necessary to learn how to balance a nuclear equation. There are a number of concepts to be remembered.

First, only nuclei are represented. The carbon isotope, having six protons and six neutrons, is represented by the symbol: $^{12}_{6}C$. The subscript (6) is the number of protons in the nucleus (atomic number). The superscript (12) represents the total number of protons and neutrons in the nucleus (mass number). Thus, $^{80}_{35}Br$ indicates that bromine has 35 protons and 45 $(80-35=45)$ neutrons. The symbols for some important particles are shown below.

Name of Particle	*Symbol*
Alpha	$^{4}_{2}He$ or α
Beta	$^{0}_{-1}e$ or β^-
Proton	$^{1}_{1}H$ or p
Neutron	$^{1}_{0}n$ or n
Deuteron	$^{2}_{1}H$

Notice that the beta particle is ${}_{-1}^{0}e$ because its charge is -1 and its mass number is 0. The deuteron is the deuterium nucleus. Deuterium is an isotope of hydrogen. It has one proton and one neutron, and its mass number is two. It is often called heavy hydrogen.

When one attempts to balance a nuclear equation, one must remember to make sure that the sum of the superscripts on the left equals the sum of the superscripts on the right (conservation of mass). One must also ensure that the sum of the subscripts on the left equals the sum of the subscripts on the right (conservation of charge):

$$\text{e.g.,}\qquad {}_{92}^{238}\mathrm{U} \rightarrow {}_{90}^{234}\mathrm{Th} + {}_{2}^{4}\mathrm{He}$$

$$238 = 234 + 4$$

$$92 = 90 + 2$$

$${}_{7}^{13}\mathrm{N} + {}_{-1}^{0}\mathrm{e} \rightarrow {}_{6}^{13}\mathrm{C}$$

$$13 + 0 = 13$$

$$7 + (-1) = 6$$

$${}_{11}^{24}\mathrm{Na} \rightarrow {}_{12}^{24}\mathrm{Mg} + {}_{-1}^{0}\mathrm{e}$$

$$24 = 24 + 0$$

$$11 = 12 + (-1)$$

$${}_{92}^{235}\mathrm{U} + {}_{0}^{1}\mathrm{n} \rightarrow {}_{38}^{90}\mathrm{Sr} + {}_{54}^{143}\mathrm{Xe} + 3\ {}_{0}^{1}\mathrm{n}$$

$$235 + 1 = 236 = 90 + 143 + 3 \times 1$$

$$92 + 0 = 92 = 38 + 54 + 3 \times 0$$

The total positive charge of the reacting nuclei must equal the total positive charge of the product nuclei. The mass of the reactants must equal the mass of the products.

16-7/RADIOACTIVE DECOMPOSITION

(*a*) *Alpha Decay*

Certain heavy nuclei break down into lighter nuclei spontaneously. Alpha particles (helium nuclei) are emitted. This is known as alpha decay:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

The uranium nucleus has been changed to a thorium nucleus because two protons have left the uranium nucleus. A **transmutation** is a change in the identity of a nucleus because of a change in the number of protons in the nucleus. Uranium has been transmuted to thorium.

When uranium is transmuted to thorium, the above equation describes 77 percent of the decay events. However, for 23 percent of the decay events, the following reaction is more correct:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th}^{*} + {}^{4}_{2}\mathrm{He}$$

$$\textbf{then} \quad {}^{234}_{90}\mathrm{Th}^{*} \rightarrow {}^{234}_{90}\mathrm{Th} + \text{Gamma Rays}$$

The $^{234}_{90}\mathrm{Th}^{*}$ is an excited (high energy) thorium nucleus which loses its extra energy by giving off gamma rays.

If a sample initially contained a certain number of nuclei, then after a period of time called the **half-life** ($t_{1/2}$), only half of the original number of nuclei will remain. The half-life for uranium-238 is 4.6×10^{9} a (years). After 4.6×10^{9} a, only one half of the original uranium will be left.

(*b*) *Beta Decay*

The emission of a negatively charged electron (beta particle) from a nucleus causes the positive nuclear charge to increase by 1 [since $-(-1)$ is equal to $+1$]. Since the mass of an electron is very small, loss of one electron causes no change in the mass number. The thorium-234 nucleus formed during the alpha decay of a uranium-238 is itself unstable and is transmuted to a protactinium-234 nucleus by beta decay:

$$^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$

Since nuclei are supposed to contain only protons and neutrons, one wonders where the electron (beta particle) originated. The Italian nuclear scientist Enrico Fermi suggested that an electron is created at the moment of beta decay. A neutron is believed to be transformed into a proton and an electron at the moment of decay:

$$^{1}_{0}\mathrm{n} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}\mathrm{e}$$

Just as in alpha decay, some beta decays produce an excited state of protactinium-234, and gamma rays are produced as the excited protactinium decays.

The half-life of thorium-234 is 24 d (days). Thus, as the uranium slowly decays to thorium by alpha decay, the thorium more rapidly decays to protactinium by beta decay.

This radioactive decay series began with uranium-238, decaying to thorium-234, which in turn decayed to protactinium-234. The protactinium-234 decays by beta decay:

$$^{234}_{91}\mathrm{Pa} \rightarrow {}^{234}_{92}\mathrm{U} + {}^{0}_{-1}\mathrm{e}$$

The uranium-234 then decays by five alpha decays in a row to $^{214}_{82}\mathrm{Pb}$. The lead-214 decays by two beta, then one alpha, then two more beta, and finally one alpha decay to $^{206}_{82}\mathrm{Pb}$. Lead-206 is a stable nucleus and the series ends. This series is one of three naturally occurring radioactive decay series. All naturally occurring radioactive elements belong to one of the three series.

Alpha decays produce more stable nuclei by decreasing the mass of a heavy nucleus. The loss of an alpha particle lowers the mass of a heavy nucleus by four mass units. You will recall that nuclei of intermediate mass have more stability than heavy nuclei.

Beta decays produce more stable nuclei by converting a neutron into a proton. Since many nuclei have more neutrons than protons, the conversion of a neutron into a proton brings the proton-to-neutron ratio closer to one-to-one.

16-8/APPLICATIONS OF NATURAL RADIOACTIVITY

A reliable method of determining the age of an old object depends on the presence of natural radioactivity. Consider the chemical composition of a very old crystal of pitchblende (U_3O_8). We may presume that it precipitated from molten rock during cooling. The resulting crystal would tend to be pure U_3O_8. However, analysis shows that every deposit of pitchblende contains some lead. Scientists assume that this lead came from uranium by natural radioactive decay. The quantity of lead is proportional to the length of time from the solidification of the rock to the present. The rate at which uranium disintegrates is known, and the age of the rock can be calculated from the amounts of lead and uranium in the rock. Minerals dated this way have been found to be at least 5×10^9 a old.

Another type of dating is called **carbon-dating.** Radioactive carbon-14 is produced from the bombardment of atmospheric nitrogen by neutrons from cosmic rays:

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \rightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

The concentration of radioactive $^{14}CO_2$ in the atmosphere is kept in balance by the constant production of carbon-14 and decay of carbon-14 back to nitrogen-14.

Living plants and animals establish a balance with the atmospheric $^{14}CO_2$, and thus they contain a constant amount of carbon-14. When these plants and animals die, the balance is upset as the carbon-14 decays without being replaced. Carbon-14 has a half-life of 5570 a, and measurement of the carbon-14 radioactivity in a specimen allows the calculation of how long ago death took place. Carbon-dating has shown that the Dead Sea Scrolls are about 2000 a old.

16-9/NUCLEAR DISINTEGRATION

Rutherford produced the first nuclear disintegration in 1919. He allowed alpha particles from a radium source to bombard nitrogen atoms. Protons and an isotope of oxygen were produced:

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \rightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$$

Rutherford repeated this experiment with other elements. Nearly all the light elements behaved like nitrogen and emitted protons. However, for some reason the alpha particles would not penetrate the nuclei of elements heavier than potassium.

Since alpha particles have two positive charges each, they are repelled by the positively charged nuclei. A fast-moving alpha particle can overcome the reasonably small repulsive forces of the light elements. However, the repulsive force is greater when heavier elements with more protons in their nuclei are used as targets, and the alpha particles are repelled by these heavier nuclei.

If one wishes to use a more efficient "bullet," a particle with a smaller positive charge should be used. A proton has only one half of the positive charge of an alpha particle. Therefore, protons should be able to enter the nucleus of an element more readily than alpha particles can.

In 1932, two English scientists, Cockcroft and Walton, bombarded a target of lithium with high-energy protons, obtained by ionizing hydrogen gas and accelerating the protons with a voltage of 250 000 V. Alpha particles were obtained:

$$^{7}_{3}\mathrm{Li} + ^{1}_{1}\mathrm{H} \rightarrow ^{4}_{2}\mathrm{He} + ^{4}_{2}\mathrm{He} + \text{energy}$$

Also in 1932, the English scientist Chadwick bombarded beryllium with alpha particles. A particle with no charge and a mass of 1 u was obtained. This particle was called the neutron:

$$^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \rightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}\mathrm{n}$$

16-10/PARTICLE ACCELERATORS

There are several kinds of particle accelerators. Two, the cyclotron and the linear accelerator, will be described here.

The **cyclotron** was invented by the American scientist E. O. Lawrence in 1931. It consists of two flat, hollow D-shaped electrodes called dees (Fig. 16-6). They resemble a circular pillbox cut vertically in half. The dees are placed in an evacuated metal container situated between the poles of a

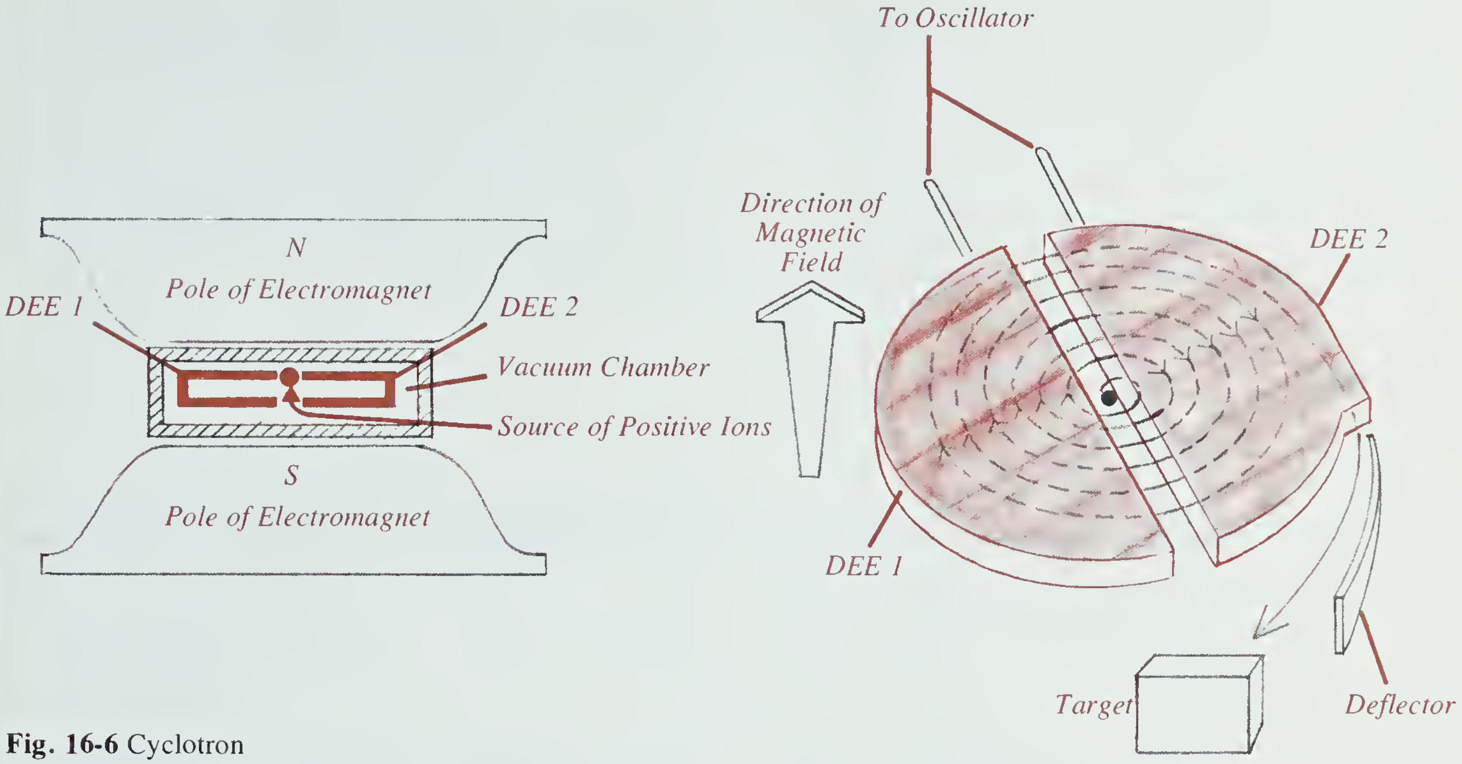


Fig. 16-6 Cyclotron

powerful electromagnet. The dees are connected to an electrical oscillator (100 000 V). The poles of the electromagnet force the charged particles (protons, deuterons, or alpha particles) to follow a circular path.

Suppose that a positive ion is produced by the ion source located between the two dees. If the right dee is negative at that moment, the ion will be accelerated towards that dee, and the magnetic field will force it to move in a curved path. Once inside the dee the ion experiences no further electrical forces. It continues to move in a circular path until it reaches the gap between the dees. At that moment the dees reverse charge (i.e., the positive dee becomes negative and vice versa). The ion moves across the gap to the left dee and is accelerated by the high voltage. Again the ion follows a semicircular path and returns to the gap where it is again accelerated. At each crossing of the dee gap, the energy of the ion increases. The path of particles in a cyclotron is a spiral of gradually increasing radius. When the ion has reached a radius which is almost as large as the radius of the dees, it is pulled from its path by a negatively charged deflector electrode. In large cyclotrons, the ions approach the speed of light. Lawrence was able to transmute sodium into magnesium by bombarding sodium with deuterons from a cyclotron:

$$^{23}_{11}\text{Na} + ^{2}_{1}\text{H} \rightarrow ^{24}_{12}\text{Mg} + ^{1}_{1}\text{H} + ^{0}_{-1}\text{e}$$

The *linear accelerator* uses no magnets, and the particles travel in straight lines. A large number of electrodes is required (Fig. 16-7).

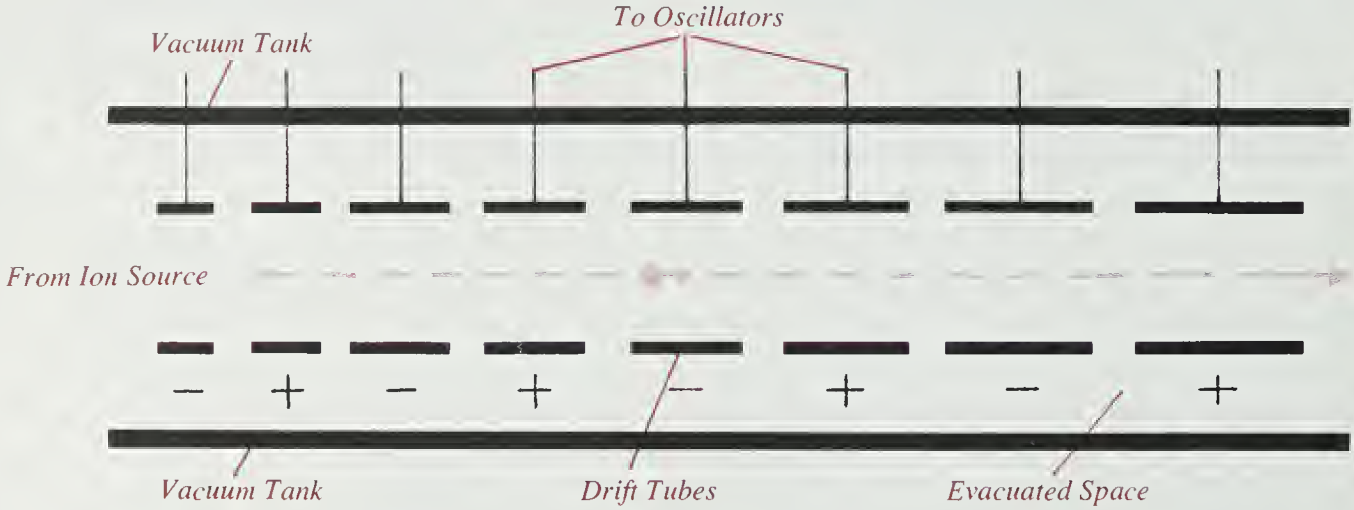


Fig. 16-7 Linear Accelerator

The apparatus consists of a large tank in the center of which are suspended many metal tubes called drift tubes. The drift tubes are connected to a high-frequency oscillator. If a positive ion enters the tank when the first drift tube is negatively charged, it will be accelerated. Once the ion is in the first drift tube, it experiences no further forces, and the oscillator can switch the charge on this tube from negative to positive. At the same instant, the second drift tube changes from positive to negative, and the ion is further accelerated as it travels all the way down the linear accelerator. As the velocity of the particle increases, the length of the drift tubes must also increase so that the particle will arrive at each gap at the same time as the charge on the drift tubes is about to change.

The *heavy ion linear accelerator* or Hilac at the University of California at Berkeley has been used to make man-made elements. For example, boron-11 was accelerated in the Hilac, and was shot at californium. The man-made element lawrencium was prepared:

$$^{252}_{98}\mathrm{Cf} + {}^{11}_{5}\mathrm{B} \rightarrow {}^{257}_{103}\mathrm{Lw} + 6\,{}^{1}_{0}\mathrm{n}$$

16-11/NEUTRONS ARE BETTER BULLETS

Before the discovery of neutrons in 1932, alpha particles, deuterons, and protons were used for studying atomic nuclei. These positively charged particles must be hurled against nuclear targets at tremendous speeds because they are repelled by the positive nuclear targets. However, neutrons have no charge, and they are more readily able to penetrate the nuclei of target atoms.

Fast neutrons can either go through the atoms without causing change or they can disintegrate the nuclei. Slow neutrons, on the other hand, can become trapped in a target nucleus. This may cause the target nucleus to become unstable and to disintegrate.

Fast neutrons can be slowed down by allowing them to pass through elements of low atomic mass such as the hydrogen in water, deuterium in heavy water, or carbon (graphite). Deuterium ($^{2}_{1}\mathrm{H}$) is the isotope of hydrogen which has one proton and one neutron. It is called heavy hydrogen. If water (H_2O) is made with the deuterium isotope rather than the regular hydrogen isotope, the water is called deuterium oxide or **heavy water** and has the formula D_2O.

A convenient laboratory source of neutrons is obtained by bombarding beryllium with alpha particles:

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$$

Neutron bombardment may produce man-made elements. When slow neutrons strike uranium-238 the product uranium-239 is unstable. This nucleus undergoes beta decay and is converted to a man-made element, neptunium-239. The neptunium is also unstable and undergoes beta decay to form another man-made element, plutonium-239.

$${}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{239}_{92}\text{U}$$

$${}^{239}_{92}\text{U} \rightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e}$$

$${}^{239}_{93}\text{Np} \rightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e}$$

Neptunium and plutonium are two **transuranium elements.** That is, they have more than 92 protons in their nuclei.

Stable nuclei can be made artificially radioactive by neutron bombardment. Cobalt-59 is not radioactive, but it can be converted to radioactive cobalt-60:

$${}^{59}_{27}\text{Co} + {}^{1}_{0}\text{n} \rightarrow {}^{60}_{27}\text{Co}$$

Sulfur-32 is not radioactive but can be converted to radioactive phosphorus-32:

$${}^{32}_{16}\text{S} + {}^{1}_{0}\text{n} \rightarrow {}^{32}_{15}\text{P} + {}^{1}_{1}\text{H}$$

It has been possible to prepare radioactive isotopes of all the elements. Many of the radioactive isotopes are useful, as we shall see later.

16-12/FISSION

At the time that Enrico Fermi was demonstrating that uranium-238 could be transmuted to neptunium and plutonium, a number of unexplained results indicated that occasionally a process which released tremendous energy took place. In 1939 two Germans, Hahn and Strassman, proved that whenever this large energy release occurred, atoms of intermediate atomic number were produced. Lise Meitner, a refugee from Hitler's Germany, suggested that the uranium nucleus absorbed a neutron and then split into two roughly equal fragments. The smaller masses associated with these fragments allow for a great release of energy. In fact, as the uranium nucleus splits, about 0.1 percent of its mass is converted into a huge amount of energy. Meitner passed her idea to Bohr who was on his way to the United States. This idea caused great excitement.

The splitting of a uranium nucleus into two smaller nuclei was called **fission.** It was found that uranium-235 was responsible for most of the fission, and that in the process, two or three neutrons were set free:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{141}_{56}\mathrm{Ba} + ^{92}_{36}\mathrm{Kr} + 3\,^{1}_{0}\mathrm{n} + \mathrm{Energy}$$

The fact that neutrons were released in the reaction meant that if these neutrons encountered other uranium-235 nuclei, they would cause additional fissions. A rapidly growing chain reaction would occur (Fig. 16-8). Since nuclear reactions are very fast, the almost instantaneous release of huge quantities of energy with every fission could produce an explosion of unprecedented size.

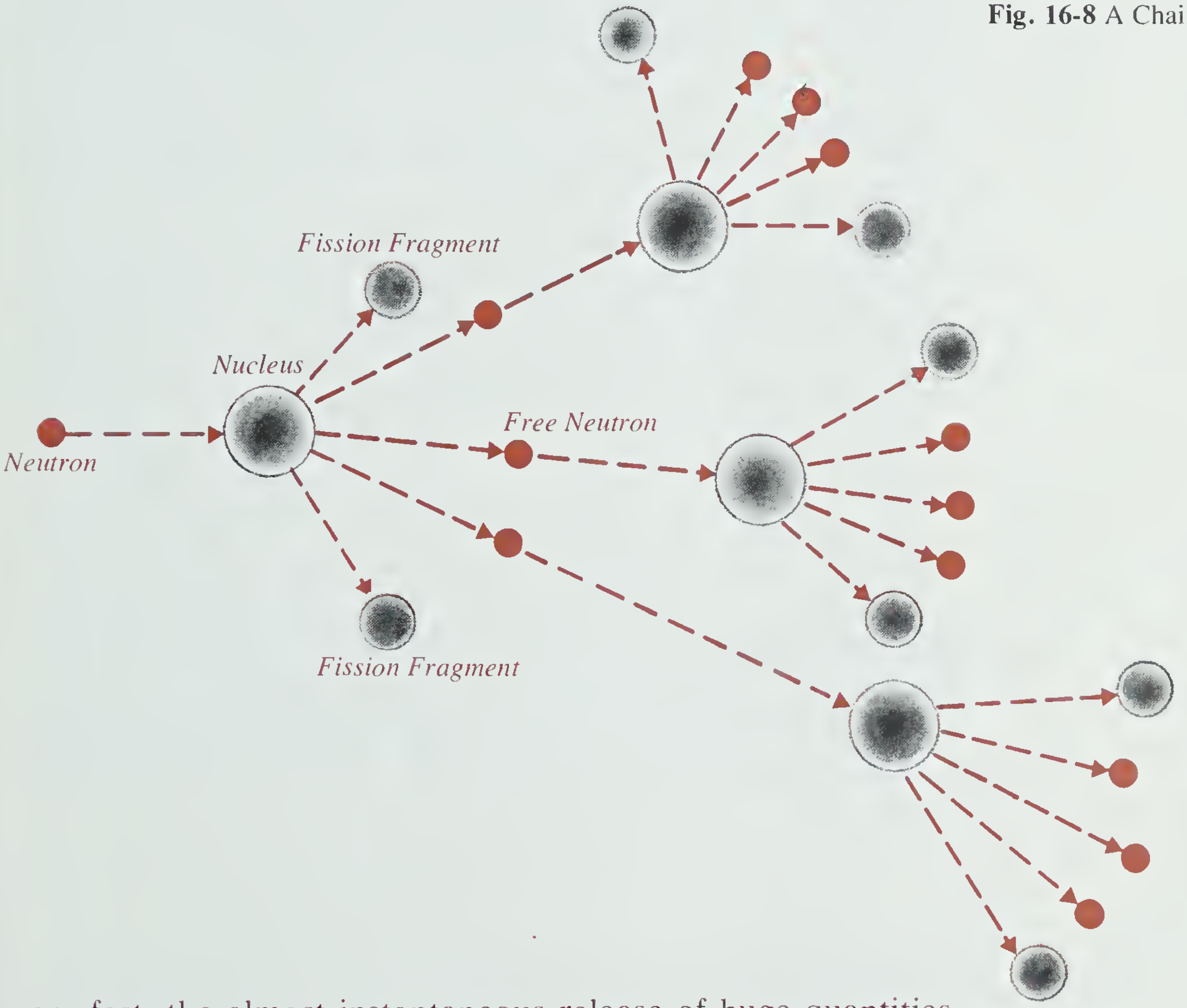


Fig. 16-8 A Chain Reaction

Scientists in the United States could easily foresee a weapon of incredible destructiveness. The fact that German scientists knew as much about fission as Americans did was very upsetting to the American scientists. In 1939, Albert Einstein urged President Roosevelt to increase research in the area of nuclear fission. The atomic bomb was developed from a research effort (the Manhattan Project) which cost 2.2 billion dollars.

16-13/THE ATOMIC BOMB

Natural uranium is 99.3 percent uranium-238 and 0.7 percent uranium-235. Uranium-235 is fissionable when it is struck by neutrons. The fission of uranium-235 produces a variety of pairs of fission products such as barium and krypton. Uranium-238 does not split. It absorbs slow neutrons without fission. To isolate enough uranium-235 or plutonium (which will also undergo rapid fission in a chain reaction) is one of the difficult tasks in making an atomic bomb.

In order for it to explode, the bomb must contain a certain minimum quantity of fissionable material. This minimum quantity is called the **critical mass.** If the amount of fissionable material is too small, too many neutrons leave the mass without striking other nuclei. Neutrons from nuclei on the surface escape into space. The bomb, in the safety position, consists of two or more separate quantities of fissionable material, all of which contains less than the critical mass. If such masses are jammed together to form a larger mass which has less surface area per unit volume, the critical mass is exceeded and an explosive chain reaction results.

The explosion of an atomic bomb produces extremely high temperatures, a severe shock wave, and dangerous gamma rays.

16-14/NUCLEAR REACTORS

In 1942, in a converted squash court at the University of Chicago, a group of scientists led by Fermi showed that a chain reaction could be controlled in a device called a **nuclear reactor.** Their reactor was called an atomic pile. Most of the pile was made of graphite blocks in which uranium fuel rods were embedded. The graphite acts as a **moderator** on the neutrons of the chain reaction. When they are first thrown out of a fissioning nucleus, the neutrons have enormously high speeds. Fermi believed that since uranium-235 is present in such small proportions in natural uranium the neutrons must be slowed down so that they can be more easily captured by the uranium-235 nuclei that are present. The neutrons can be slowed down by bouncing them off the carbon atoms in the graphite blocks. The original pile also contained control rods of cadmium metal. When these rods were inserted in the reactor, they absorbed neutrons and slowed down the chain reaction. The first pile contained more than the amount of uranium needed to maintain the chain reaction. The control rods were in place, and as they were removed, fissions were able to occur. At the critical point, the pile operated on its own. The pile could be shut down by replacing the control rods.

There are two types of reactions in a reactor which is fueled with natural uranium (99.3 percent uranium-238 and 0.7 percent uranium-235): the fission reaction and a neutron capture reaction. The fission reaction involves the splitting of uranium-235 into smaller products. An example of the fission reaction is:

$$^{235}_{92}\text{U} + \underset{\text{slow}}{^{1}_{0}\text{n}} \rightarrow {}^{90}_{38}\text{Sr} + {}^{143}_{54}\text{Xe} + 3\,\underset{\text{fast}}{^{1}_{0}\text{n}} + \text{Energy}$$

The fast neutrons that are produced are slowed down by a moderator so that they can bombard other uranium-235 nuclei efficiently. The neutron capture reaction involves the conversion of uranium-238 to plutonium-239:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{239}_{92}\text{U} \rightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e}$$

then $^{239}_{93}\text{Np} \rightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e}$

Notice that the fission reaction is a chain reaction because neutrons are used up and they are also produced. The neutron capture reaction uses up neutrons, but it does not produce them.

Fermi's pile was cooled by allowing air to circulate between the graphite blocks. All reactors have a fuel, a moderator, a control, and a cooling system.

16-15/CANADA AND NUCLEAR CHEMISTRY

Much of the fundamental research on radioactivity has been done in Canada, and it is appropriate that Canadians are very interested in the peaceful uses of nuclear energy. The Atomic Energy Research Laboratories at Chalk River, Ontario, began operation in the summer of 1944. In 1947, they were taken over as a division of the National Research Council. In 1952, the crown corporation, Atomic Energy of Canada Limited (AECL) took over the job of running the Chalk River Laboratories. Today, besides the nuclear research laboratories at Chalk River, AECL has a reactor design group in the Sheridan Park Laboratories, Toronto, a group with a reactor at Whiteshell, Manitoba, and a commercial products group in Ottawa.

Canadian scientists have concentrated on using natural uranium as fuel and heavy water as moderator in their reactors. Canadians made the first reactor built outside the United States. In 1945, the ZEEP (Zero Energy Experimental Pile) was made operational at Chalk River. ZEEP is an aluminum tank (2.4 m in diameter and 3.0 m deep) which is filled with heavy water and surrounded with a graphite layer (0.9 m thick) which tends to reflect departing neutrons back into the heavy water. Movable rods of uranium cased in aluminum are hung in the heavy water. The distance, which gives the best thickness of heavy water between rods, is found experimentally. If the rods are too close together, the fast neutrons are not slowed down enough to cause sufficient fission reactions. If the rods are too far apart, the neutrons are scattered without causing fission reactions. The ZEEP is used to find the best distances between fuel rods for various fuels. The distance differs for metallic uranium, uranium oxide, and uranium carbide. The best distance between fuel rods also depends on the kind of metal container in which the fuel is placed.

The heavy water NRX reactor (Fig. 16-9) began operation at Chalk River in 1947. It is now operating, releasing 42 MW (megawatts) of power. NRX consists of an aluminum tank or calandria, 3.0 m deep and 2.4 m in diameter, through which pass vertically 200 aluminum tubes. Through 176 of these tubes pass natural uranium rods, 3.3 cm in diameter and 3.0 m long. Each of these rods is sheathed in aluminum and is

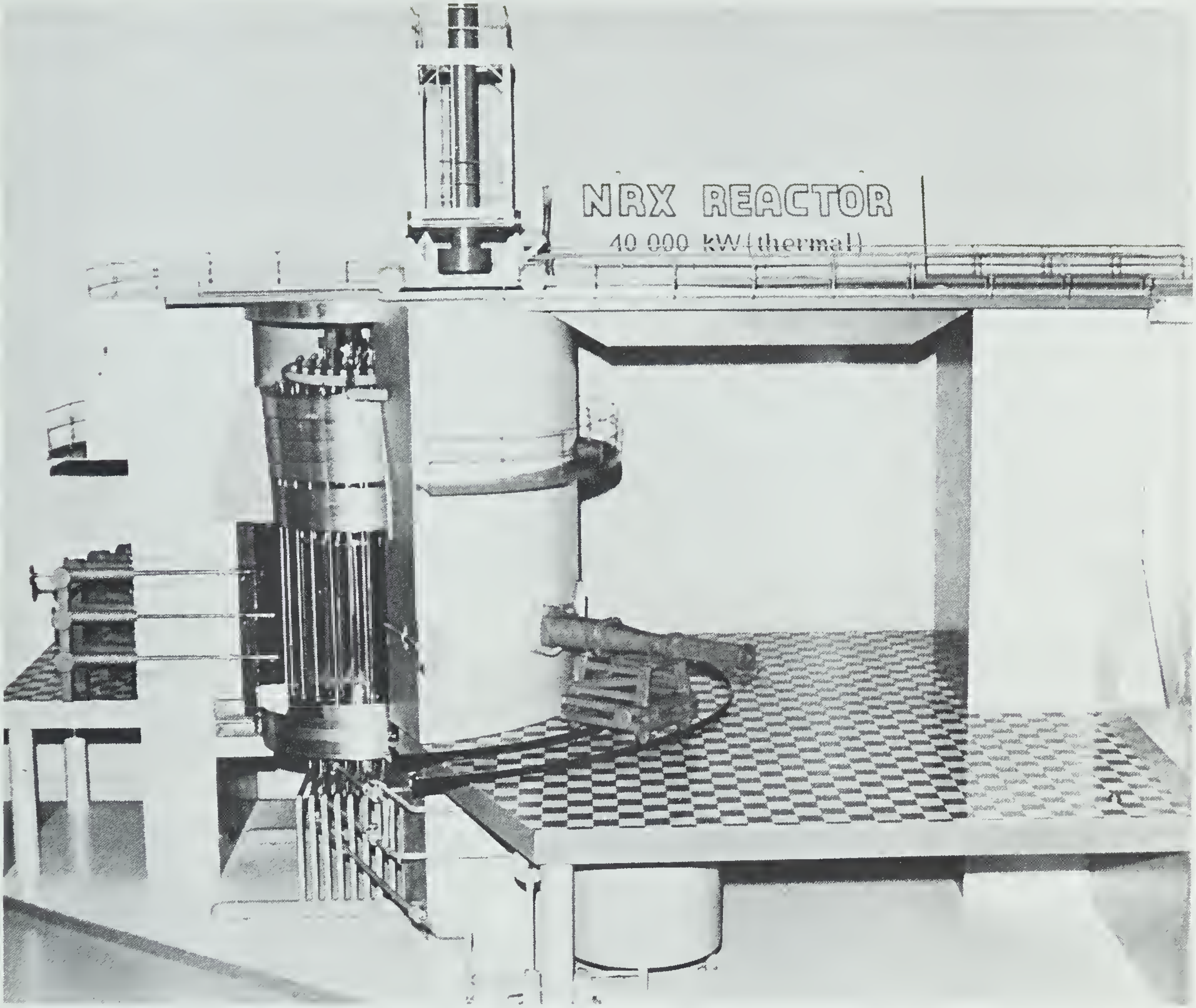


Fig. 16-9 NRX Reactor

surrounded by a second aluminum cylinder leaving a small annulus (ring-like space) through which cooling light water passes. This ordinary water removes the heat generated by fission. The space between the 200 aluminum tubes is filled to a definite height with the moderator, heavy water. This heavy water can be raised or lowered in the calandria. If the calandria is half-full of heavy water, the reactor works at less than full power. This is because the neutrons are slowed down properly only in that part of the calandria that contains the heavy water. Thus, the power output of NRX is controlled by the depth of the heavy water. The calandria is surrounded by a layer of graphite 1 m thick which reflects neutrons back into the reactor. This in turn is surrounded by steel plates which stop some radiation, and then by 2.4 m or more of concrete to protect the workers from the neutrons and the intense gamma radiation.

Reactors have three main functions. They produce radioactive isotopes which have many applications; they release vast amounts of energy in the form of heat from the fission of small quantities of matter; and they produce new nuclear fuels from nonfissionable elements.

NRX has automatic means of irradiating materials for the production of isotopes. NRX produces a great quantity of neutrons from the fission of uranium-235. Any element placed in NRX is subjected to high neutron bombardment and will become a radioactive isotope of the same or some other element. For example,

$$\underset{\text{nonradioactive}}{{}^{59}_{27}\text{Co}} + {}^{1}_{0}\text{n} \rightarrow \underset{\text{radioactive}}{{}^{60}_{27}\text{Co}}$$

The cobalt nucleus has picked up a neutron and has become unstable.

NRX has openings out of which beams of neutrons emerge; these are used for fundamental research purposes. NRX can also be used to test various fuel assemblies.

NRX was unsurpassed as a research and fuel testing reactor until the construction of the 200 MW reactor, NRU. NRU began operation in 1957. It has the finest research facilities of any reactor. NRU is similar to NRX except that it is cooled with heavy water instead of ordinary water. It is fueled with natural uranium and moderated with heavy water. It can operate continuously as the fuel is changed, and it was the first reactor in the world in which the fuel was changed while the reactor was operating at full power.

16-16/AECL POWER PROJECTS

The AECL Power Projects group is responsible for the design of nuclear power plants and for the project management of nuclear power stations built by AECL. Since the fission of 1 kg of a nuclear fuel such as uranium-235 releases as much heat as the burning of 2 700 000 kg of coal, or 2 600 000 ℓ of fuel oil, it is natural that scientists should be interested in using this source of energy for the production of electric power.

The Canadian nuclear power program is based on experience with the heavy water-moderated, natural uranium type of reactors which have been so successful at Chalk River. Canadian scientists have had more experience with this type of reactor than any other group. Southern Ontario requires more electricity than can be supplied by hydro stations. Thus, in the past coal-burning stations were built. It was decided to develop a nuclear power system in order to see if it could compete with a coal-burning system.

A 20 MW nuclear power demonstration plant (NPD) was built in 1962 at Rolphton, Ontario. The NPD reactor (Fig. 16-10) is an aluminum tank, 4.6 m long and 5.2 m in diameter, pierced by 132 horizontal pressure tubes. Eighteen tonnes of natural uranium fuel are placed in the pressure tubes.

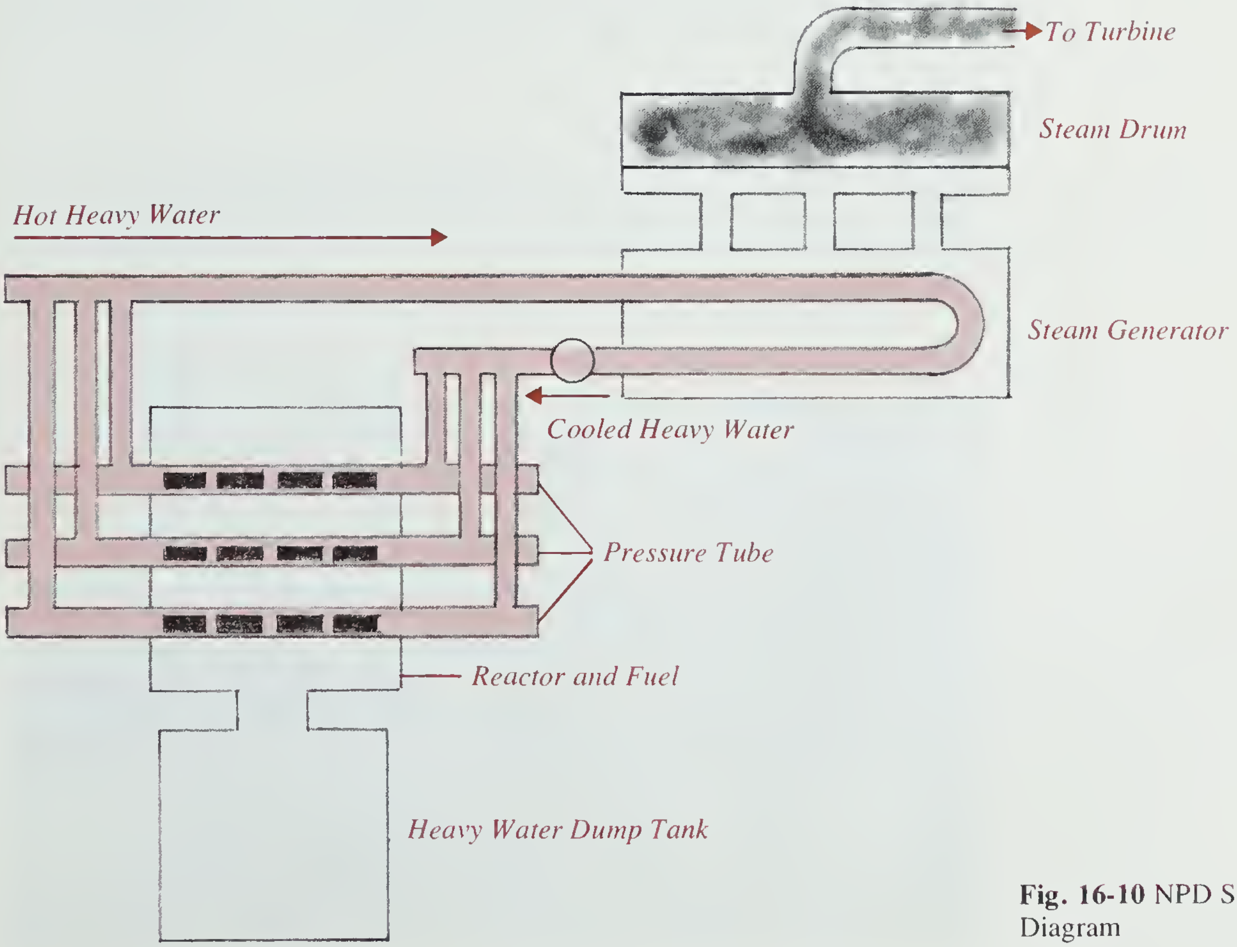


Fig. 16-10 NPD Schematic Diagram

These pressure tubes are surrounded by the heavy water moderator. About 55 t (tonnes) of heavy water are used as moderator.

If the height of the heavy water moderator in the reactor tank is raised, more neutrons are slowed down to the speed required to split additional uranium-235 nuclei. This produces heat in the uranium fuel as the fission products fly apart jostling neighboring atoms. The heat output of NPD is controlled by raising or lowering the height of the heavy water. Heavy water moderator can be released into or pumped out of a dump tank located below the reactor tank.

The heavy water coolant in a separate system (containing 12 t of coolant) is pumped through the pressure tubes to transfer heat from the hot fuel to a steam generator. As the hot heavy water heats up the ordinary water, the steam produced is fed to conventional steam turbines which drive electrical generators. Two automatic fueling machines, one at each end of the tank, insert fresh fuel rods and remove used rods.

NPD was successful and a full-size plant was constructed at Douglas Point, Ontario, in 1967. The Douglas Point Power

Fig. 16-11 Douglas Point Nuclear Power Station

Reactor (Fig. 16-11) is a bigger reactor and similar to NPD except that it produces 200 MW. This reactor was built by AECL and is operated by Ontario Hydro. It is a CANDU (Canadian Deuterium Uranium) reactor. Another plant operated by Ontario Hydro is located at Pickering about 30 km east of Toronto. It produces about 2000 MW and is made up of four CANDU reactors. A nuclear power station at Gentilly, Québec, is operated by Hydro Québec. Again a CANDU reactor is being used. However, this reactor uses boiling light water instead of heavy water as a coolant. The Gentilly nuclear reactor is a 250 MW station. The Bruce Nuclear Generating Station at Douglas Point has a potential capacity of 3200 MW (Fig. 16-12).

CANDU-type reactors have been built abroad. A nuclear power plant similar to the one at Douglas Point has been built by the Indian Government at Rajasthan. Canadian General Electric has built a 137 MW CANDU plant near Karachi for the Pakistan government.

Heavy water is by far the best moderating material. It is about 70 times more efficient than graphite. The efficiency of heavy water as a moderator makes it possible to carry natural

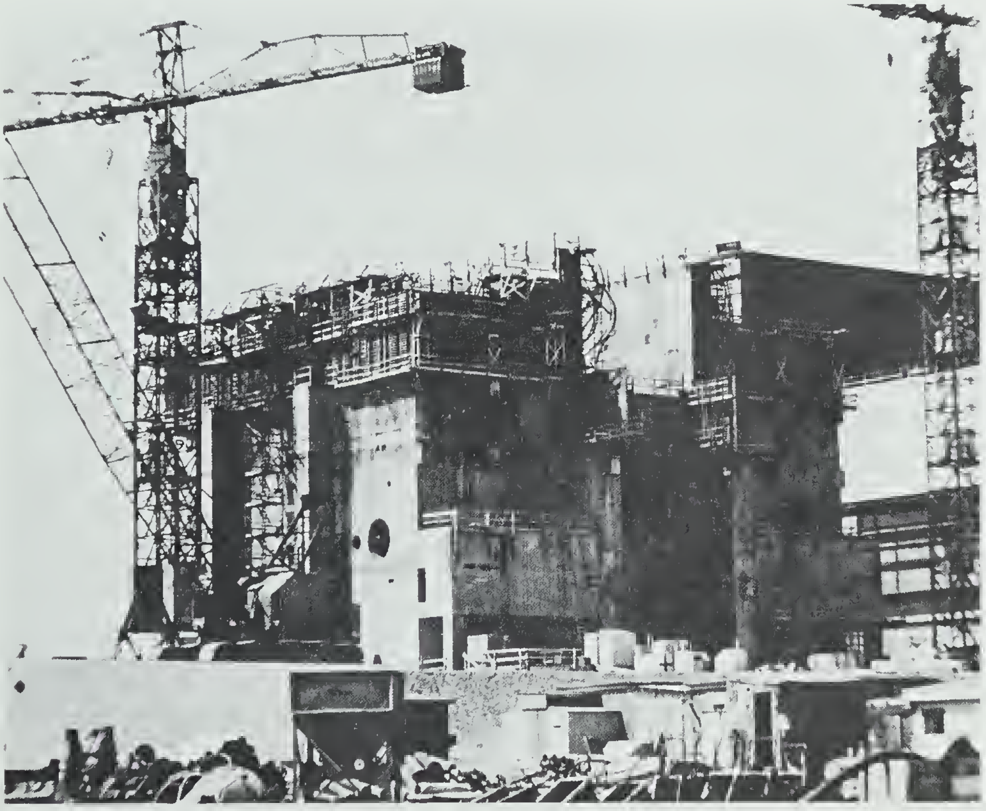


Fig. 16-12 Construction at Bruce Nuclear Power Station

uranium to a very high value of burn-up. Burn-up indicates the amount of energy extracted from the fuel during its stay in the reactor (about 2 a). One obtains a higher power output from a smaller amount of fuel when the burn-up is high.

The disadvantage of heavy water is its high cost. Heavy water costs more than sixty dollars per kilogram, and the Douglas Point unit alone uses a total of 190 000 kg of heavy water.

16-17/AECL COMMERCIAL PRODUCTS

The Commercial Products group of AECL is responsible for the processing and distribution of radioactive isotopes and for the design and manufacture of associated equipment. It is a unique organization, being the only one of its kind in the world to offer a complete "package" comprising the preparation and supply of radioisotopes, manufacture and installation of equipment, and the provision of a variety of consulting and technical services.

Radioactive isotopes have application in medical therapy. Canadians and Canadian reactors have played an important role in this field. Through the effort of Dr. Cipriani at Chalk River, the first radioactive cobalt-60 sources were made for the treatment of malignant tumors. These cobalt-60 sources produce intense beams of gamma rays which destroy tumors. In addition to the cobalt-60 cancer therapy machines (*cobalt bombs*), cesium-137 *Caesatrons* have been made and sold by AECL Commercial Products. Over 700 cancer therapy units have been made by the Commercial Products group of AECL and shipped to 51 different countries.

The gamma radiation from cobalt-60 is used to sterilize vegetables, fruit, and grain, as well as medical supplies and wool. Potatoes sterilized by the radiation from cobalt-60 will not sprout, fruit can have a longer shelf life in stores, and medical instruments can be put in packages and sterilized by gamma radiation, ready for use when unpacked. Commercial Products supplied the first commercial units for this type of sterilization to companies in Canada, the United States, India, and New Zealand.

Radioisotopes are used in industry to study the wearing of machine parts. For example, the efficiency of lubricants to diminish wear on moving parts of machines is determined by incorporating radioisotopes into the metal surfaces. After even the slightest amount of metal wear, radioactive atoms will be detected in the lubricants. Radioactive isotopes may be added to a liquid flowing in a pipeline. By means of a Geiger counter, one can determine the position of a leak or obstruction in the pipeline.

16-18/BREEDER REACTORS

In addition to the fission of uranium-235 in a reactor, a second reaction takes place:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e}$$

$$\textbf{then} \quad {}^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e}$$

In fact, nonfissionable uranium-238 is converted to fissionable plutonium-239. Since an average of 2.5 neutrons are released during each fission of a uranium-235 nucleus (2 neutrons are produced in some fissions, and 3 are produced in others; the average is 2.5), it appears possible to make a reactor that produces more fuel than it burns.

Suppose we have 100 fissions of uranium-235. Then 250 neutrons are released. It requires 100 of these to maintain the chain reaction at the same power level. There is a surplus of 150 neutrons. Some of these will be lost. Suppose, however, that the reactor is designed so that 110 neutrons are captured by uranium-238 to form 110 atoms of plutonium-239. We have used 100 uranium-235 atoms to get the 100 fissions, but we have produced 110 plutonium-239 atoms. This is a 10 percent increase in fuel. Such reactors have been constructed. The largest breeder is at Dounreay in the north of Scotland. This reactor also produces electricity.

16-19/FUSION

Energy is released when the light atoms combine to form heavier atoms. These reactions are called **fusion reactions.** A simple fusion is the combination of hydrogen nuclei (protons) to form helium nuclei:

$$4\,{}^{1}_{1}\mathrm{H} + 2\,{}^{0}_{-1}\mathrm{e} \rightarrow {}^{4}_{2}\mathrm{He} + \mathrm{Energy}$$

This is the type of reaction that occurs in the sun. The reactants have more mass than the products. Thus, some mass has been converted into a tremendous amount of energy. In fact, a fusion reaction liberates more energy than a fission reaction.

The fusion of light elements is a difficult operation. All nuclei are positively charged. To make them combine, they must be shot at one another with high enough speeds to overcome their mutual repulsion. Because of this, fusion will take place only at high temperatures. The fusion of hydrogen nuclei to form helium nuclei takes place only in the sun and other stars where the interior temperatures are around 20 million degrees.

16-20/THE HYDROGEN BOMB

The heavier isotopes of hydrogen, deuterium, and tritium fuse more rapidly than ordinary hydrogen and at a lower temperature and can be used to construct a new type of bomb. Hydrogen bombs have already been tested. The main reaction is the fusion of deuterium and tritium. Tritium is prepared from lithium-6, and the compound lithium deuteride supplies both the tritium and deuterium. An A-bomb is the detonator for an H-bomb. The A-bomb produces the high temperature necessary for the fusion to take place.

There are probably three different reactions in the hydrogen bomb. The explosion of the fission bomb or A-bomb is the first. In addition to the high temperature, it also liberates neutrons.

The lithium-6 is split into tritium and helium by the neutrons:

$$^{6}_{3}\text{Li} + ^{1}_{0}\text{n} \rightarrow ^{3}_{1}\text{H} + ^{4}_{2}\text{He} + \text{Energy}$$

The tritium fuses with the deuterium:

$$^{3}_{1}\text{H} + ^{2}_{1}\text{H} \rightarrow ^{4}_{2}\text{He} + ^{1}_{0}\text{n} + \text{Energy}$$

The hydrogen bomb releases much more energy than the atomic bomb.

16-21/PROBLEMS OF THE NUCLEAR AGE

The first problem of the nuclear age is what to do with the radioactive wastes from a reactor. Some of these radioactive wastes have short half-lives and "cool off" rapidly. However, some of the radioactive wastes, such as strontium-90 and cesium-137, have long half-lives.

These wastes must be stored in safe places for many years. Strontium-90 and cesium-137 have half-lives of about 30 a. It has been suggested that it takes 20 half-lives before a decaying isotope is safe. Thus, it would require 600 a for cesium-137 and strontium-90 to decay to a safe radiation level. This means that the storage facilities for radioactive wastes must be safe and impervious to geological action for up to a thousand years.

The total problem of radioactive waste disposal, not only of fission products but also of the slightly contaminated water or even trash from reactor plants, is one on which no compromises can be allowed. This is one area where neither industry nor government agencies should be allowed to take shortcuts.

A second problem is the fallout from the explosion of atomic and hydrogen bombs. The actual explosions of these bombs blow radioactive materials such as strontium-90 high into the stratosphere. Eventually these radioactive particles fall back to earth. A shower of intensely radioactive particles can produce severe burns. These particles can also contaminate our food. Strontium-90 gets into plants and then into animals where it accumulates. People consume animal products and may take in a sizable dose of strontium-90. Because strontium-90 is chemically similar to calcium, it collects in our bones. There it can cause cancer; it can destroy skin tissue; and it can ultimately cause death.

The last and probably the greatest problem of the nuclear age is the fact that several countries have at their disposal a large number of atomic and hydrogen bombs. Ironically, the prospect of an all-out nuclear war is so terrifying it has been an effective deterrent against even the use of smaller tactical atomic weapons. Still the threat remains and "conventional" wars continue. The problems of international conflict will be solved only when their primary causes are eradicated by upgrading the quality of life on a global scale. The contributions which the world's scientists can make are obvious.

QUESTIONS

1. What evidence caused Marie Curie to suspect that there were radioactive elements other than uranium in pitchblende?
2. How does the presence of a radioactive material affect the speed of discharge of an electroscope?
3. What information regarding radioactivity was gained from Rutherford's lead block experiment?
4. How do α, β, and γ rays differ from each other in their properties?
5. From what part of a radioactive atom do the alpha or beta particles come?
6. Why is $^{35}_{15}P$ likely to be an unstable nucleus?
7. Why is $^{18}_{9}F$ likely to be an unstable nucleus?
8. Would you expect the following nuclei to be stable or unstable: $^{3}_{1}H$, $^{20}_{10}Ne$, $^{58}_{29}Cu$, $^{210}_{83}Bi$? State your reason in each case.
9. What is the relationship between nuclear binding energy and the stability of a nucleus?
10. Write the equation for the emission of an alpha particle from $^{226}_{88}Ra$.
11. Write the equation for the emission of a beta particle from $^{214}_{82}Pb$.
12. Write the equation for successive emissions of an alpha particle and a beta particle from $^{114}_{84}Po$.
13. What is meant by the half-life of a radioactive element?

14. The half-life of Fm-253 is 4.5 d. What fraction of 1 g of Fm would remain after 13.5 d?
15. Describe the path of the accelerated particles in a cyclotron and state what causes them to take this path.
16. Why are neutrons better particles for bombarding atomic nuclei than protons or alpha particles?
17. What can happen when a neutron is fired at the nucleus of an atom?
18. What is meant by the term *transmutation*?
19. What is a fission reaction?
20. What nucleus is left out of the equation:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{147}_{59}\mathrm{Pr} + ? + 3\ ^{1}_{0}\mathrm{n}$$

21. Describe a chain reaction and state how the fission of $^{235}_{92}\mathrm{U}$ can produce a chain reaction.
22. Write notes on a nuclear reactor. Your answer should include descriptions of the parts of the reactor and the main uses of a reactor.
23. In the CANDU system, what happens when the heavy water moderator is released into the dump tank? Why?
24. What is a transuranium element?
25. For what purposes can cobalt-60 be used?
26. What is the purpose of a breeder reactor?
27. What type of nuclear reaction is:

$$^{2}_{1}\mathrm{H} + ^{3}_{1}\mathrm{H} \rightarrow ^{4}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n}$$

28. A one gram sample of wood unearthed from an excavation produced 1.9 beta particles per minute due to the decay of carbon-14. If a one gram sample of new wood produces 15.2 beta particles per minute, what is the age of the old wood?

QUESTIONS TO THINK ABOUT

29. The left-over ore (*tailings*) from uranium processing plants has been used to make cement for the construction of houses. These tailings contain radium (half-life 1620 a) and its daughter product radon (half-life 3.8 d). The radon gas escapes from the cement into the surrounding air. State whether you agree or disagree with the follow-

ing statements, and give your reasons in each case.
   (a) Old tailings do not constitute a health hazard because radon has such a short half-life that it disappears quickly.
   (b) Radon is a noble gas and does not enter into biochemical reactions, so it should not constitute a health hazard.
   (c) In any case, any health hazard could be decreased by using a ventilation system to blow the radon gas outdoors.

30. In light of the fact that used fuel rods from CANDU reactors can be reprocessed to obtain plutonium (an ingredient in nuclear weapons) should Canada continue to sell her reactors to other countries? Do you think that it is possible to ensure that Canadian reactors sold to other countries will be used only for peaceful purposes?
31. Why do environmentalists complain about thermal pollution from nuclear power stations when it is well known that thermal generating stations (often the only alternative source of power) also give off heat into the environment?

APPENDIX I

SI UNITS

In 1960 the General Conference of Weights and Measures adopted the International System of Units. The abbreviation in all languages is SI (for Le Système International d'Unités). Within a few years this system will probably be used around the world.

This system is constructed from seven base units. By various combinations of base units the derived units are obtained.

The base units of most interest to us are:

Physical Quantity	*Unit*	*Symbol*
Length	metre	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin*	K

A metre is defined as 1 650 763.73 wavelengths in vacuum of the orange-red line in the spectrum of krypton-86.

The SI unit of area is the square metre (m^2). The SI unit of volume is the cubic metre (m^3). The litre is now defined as 10^{-3} m^3.

The SI unit of mass is the kilogram, which is defined as the mass of a cylinder of platinum-iridium alloy kept at the International Bureau of Weights and Measures in Paris.

The SI unit of force is the newton (N), which is defined as that force which will give a mass of one kilogram a speed of one metre per second when applied for one second. The SI unit for work and energy is the joule ($1\ J = 1\ N \times 1\ m = 1\ N \cdot m$).

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* The base unit of temperature is the kelvin, but in the everyday world the degree Celsius is used instead.

The SI unit of pressure is the pascal. It is the force of one newton acting over an area of one square metre (1 Pa = 1 N/m^2). Standard atmospheric pressure is 101 325 Pa.

The SI temperature scale is the Kelvin scale. The degree is called a kelvin (K) and the degree sign is omitted in this system. Thus, a temperature is expressed as 273 K, not 273°K.

Fractions and multiples of SI units are expressed by the appropriate prefixes (Table 1).

TABLE 1

PREFIXES FOR FRACTIONS AND MULTIPLES OF SI UNITS

Prefix	*Symbol*	*Factor*	*Prefix*	*Symbol*	*Factor*
exa	E	10^{18}	pico	p	10^{-12}
peta	P	10^{15}	nano	n	10^{-9}
tera	T	10^{12}	micro	μ	10^{-6}
giga	G	10^{9}	milli	m	10^{-3}
mega	M	10^{6}	centi	c	10^{-2}
kilo	k	10^{3}	deci	d	10^{-1}
hecto	h	10^{2}			
deca	da	10^{1}			

Other considerations when using SI units are:

1. Digits are to be grouped in threes about the decimal point without using commas to mark off thousands, millions, etc. E.g., 1 234 567.891 23 and not 1,234,567.89123.
2. There is no period at the end of abbreviations, e.g., write "kg", not "kg.".
3. Units are not pluralized. Thus, a mass of ten kilograms is written as 10 kg, not 10 kgs.
4. The use of product dots is encouraged to avoid ambiguities. For example, ms could mean either "metre-second" or "millisecond". The symbol "m·s" is unambiguous: metre-second.
5. Words and symbols should not be mixed. One may write "kilograms per cubic metre" or "kg/m^3" but not "kilograms/m^3" or "kg per cubic metre", etc.

APPENDIX II

VAPOR PRESSURE OF WATER AT DIFFERENT TEMPERATURES

Temperature (°C)	*Vapor Pressure* (kPa)	*Temperature* (°C)	*Vapor Pressure* (kPa)
0	0.61	26	3.36
5	0.87	27	3.57
10	1.23	28	3.78
15	1.71	29	4.00
16	1.82	30	4.24
17	1.94	35	5.62
18	2.06	40	7.38
19	2.20	45	9.58
20	2.34	50	12.33
21	2.49	60	19.92
22	2.64	70	31.16
23	2.81	80	47.34
24	2.98	90	70.10
25	3.17	100	101.32

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